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Citation	Fuel, 281, 118730 <a href="https://doi.org/10.1016/j.fuel.2020.118730">https://doi.org/10.1016/j.fuel.2020.118730</a>
Issue Date	2020-12-01
Doc URL	<a href="http://hdl.handle.net/2115/86349">http://hdl.handle.net/2115/86349</a>
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Type	article (author version)
File Information	Manuscript_clean.pdf



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1 *EGR Gas Composition Effects on Ignition Delays in Diesel Combustion*

2  
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9 **Abstract**

10 This paper presents the effects on ignition delays of a range of exhaust gas compositions  
11 recirculated in the intake air. The ignition delays were measured in a single-cylinder diesel  
12 engine introducing a variety of hydrocarbons, nitrogen oxides (NO<sub>x</sub>), and carbon  
13 monoxide (CO) into the intake gas, and changing the concentrations of these components.  
14 The experimental results show that the ignition delay decreases with the NO<sub>x</sub> addition,  
15 NO<sub>2</sub> promotes the ignition more than NO, and this effect is more pronounced at higher  
16 intake gas temperatures. The ignition delay decreases with HC addition under NO<sub>x</sub> rich  
17 conditions while there is little effect under low NO<sub>x</sub> conditions, and the ignition delay  
18 changes with the kinds of hydrocarbons. The CO has little effect on the ignition delay.  
19 With the aid of chemical reaction analysis, the mechanisms of these changes are  
20 elucidated.

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22 **Keywords:** Ignition Delay, Exhaust Gas Recirculation, Diesel Engine, Nitrogen Oxide

23

24 **Nomenclature:**

25

26  $dQ/d\theta$  The rate of the heat release [J/°CA]

27  $d^2Q/d\theta^2$  Derivative of the rate of the heat release [J/°CA/°CA]

28 EGR Exhaust gas recirculation

29 HCCI Homogeneous charge compression ignition

30 IMEP Indicated mean effective pressure

31 LTC Low temperature combustion

32 LTOR Low temperature oxidation reaction

33 PAHs Polycyclic aromatic hydrocarbons

34  $p_{inj}$  Injection pressure [MPa]

35 TDC Top dead center

36 SOI Start of injection

37  $T_{in}$  Intake air temperature [K]

38  $\tau_{ign}$  Ignition delay [°CA]

39

40

41

## 42 **1. Introduction**

43 To respond to increasingly stringent emission and fuel consumption regulations,

44 combustion improvement strategies have been developed for diesel engines. Exhaust gas

45 recirculation (EGR) is an emission control technology enabling significant nitrogen

46 oxides (NO<sub>x</sub>) reductions, that are achieved due to the decreased flame temperature

47 attributed to the decreased intake oxygen concentration and increased heat capacity.

48 Further, increases in the EGR rate decreases the flame temperature to a level where no

49 soot is formed [1-3], and lengthens the ignition delay while enhancing the homogeneity

50 of the gas mixture [4, 5]. Considering the features of these combustion regime termed  
51 low temperature combustion (LTC), the potential application of EGR has extended  
52 investigations into reductions of soot formation and cooling losses in modern diesel  
53 engines [6, 7]. Also, recent research has payed attention to the effects of fuel properties  
54 in the LTC since they have significant impacts on the ignition delay and mixture formation  
55 that are important factors affecting engine performance and emissions [8-11].

56 As EGR affects the ignition delays of gas oil significantly, the investigations have  
57 been carried out intensively, and have substantiated that the oxygen reduction and  
58 thermodynamic effects due to the high specific-heat capacity of carbon dioxide ( $\text{CO}_2$ ) and  
59 water ( $\text{H}_2\text{O}$ ) lengthen the ignition delays [12-15]. In the LTC regime achieved with a large  
60 amount of EGR, however, the intake gas composition would play a more important role  
61 in the ignition delays, as the concentrations of unburned hydrocarbons and carbon  
62 monoxide ( $\text{CO}$ ) tend to increase in the recirculated intake gas together with the decrease  
63 in the oxygen concentration, and as there is also a non-negligible concentration of  $\text{NO}_x$   
64 that becomes recirculated at high load operation.

65 In spark-ignition engines, it is known that  $\text{NO}_x$  enhances the ignition, leading to  
66 knocking issues [16]. Sjöberg et al. suggested the possibility that such autoignition was  
67 influenced by the presence of unburned or only partially-oxidized hydrocarbons and

68 nitrogen monoxide (NO) in a homogeneous charge compression ignition (HCCI) engine  
69 fueled with gasoline and primary reference fuels [17], and Kawasaki et al. demonstrated  
70 that the ignition was enhanced with either NO and nitrogen dioxide (NO<sub>2</sub>) in a HCCI  
71 engine fueled with natural gas [18]. Chemical kinetic studies considering the presence of  
72 hydrocarbons and NO<sub>x</sub> suggest that the following reaction shows the highest sensitivity  
73 to enhancements in the ignition:



75 suggesting that this reaction shows a strong dependence on the kind of fuels and that it is  
76 important in the low temperature oxidation reaction (LTOR) [19, 20]. This chemical  
77 kinetic mechanism may be important for gas oil which is accompanied by large heat  
78 release during the LTOR. Using a primary reference fuel with octane number 90, the  
79 authors have shown that the ignition of the spray combustion was enhanced by the  
80 entrained gas which consists of the intermediate products during the LTOR [21], but less  
81 study on the effects of intermediate products on the ignition of gas oil have been  
82 implemented as conventional diesel engines primarily have short ignition delays, this is  
83 except for some reports which reported that the ambient gases containing methane (CH<sub>4</sub>)  
84 and propane (C<sub>3</sub>H<sub>8</sub>) have no facilitating influence on the ignition of the diesel spray [22-  
85 25].

86 The present study proposes to investigate the effects of the EGR gas composition on  
87 the ignition delays of diesel combustion in a low temperature combustion regime with  
88 low intake oxygen concentrations, particularly focusing on cases where there is both  
89 hydrocarbons and NO<sub>x</sub>. The ignition delays were measured in a single-cylinder engine  
90 while changing the concentrations of hydrocarbons, CO, and NO<sub>x</sub> as well as the intake  
91 gas temperature. Additional investigation into the effects of the chemical reaction  
92 mechanism on the ignition delays were carried out with the CHEMKIN-PRO software  
93 [26].

94

## 95 **2. Experimental Devices, Setup, and Procedures**

### 96 **2.1 Test Engine and Fuel Used**

97 A four-stroke water-cooled diesel engine (YANMAR, 4TNV98T) was used to measure  
98 the ignition delays. This engine was originally composed of four cylinders, and was  
99 modified to be a single-cylinder engine by detaching the pistons of three of the cylinders.  
100 Table 1 details the specifications of the test engine. The bore and stroke were 98 mm and  
101 110 mm, and the stroke volume was 830 cm<sup>3</sup>. A piston with a toroidal bowl geometry was  
102 used, and the compression ratio was 17.6. The test engine was equipped with a common-  
103 rail fuel injection system. The engine used a G4S injector (DENSO, G4S) equipped with

104 an 8-hole nozzle, nozzle hole diameter 0.125 mm with a spray angle of 155°. A  
105 commercially-available gas oil was used as the test fuel.

## 106 **2.2 Experimental Setup**

107 Figure 1 shows an outline of the experimental setup. The in-cylinder pressure was  
108 measured with a piezoelectric pressure sensor (KISTLER, 6125B) for 180 cycles, and the  
109 electrical charge was introduced via a charge amplifier (KISTLER, 5011B), converted  
110 into a voltage signal, and recorded with a computer via an AD converter (Interface, CBI-  
111 320412). This cycle number recorded was limited by the amount of memory of the AD  
112 converter, but it was enough in cycle number to obtain representative histories of pressure  
113 and heat release rate under the conditions employed in the present study.

114 Unlike the experiments where repetition of measurements is possible, it is difficult for  
115 engine tests to repeat many tests at each operating point due to the many data points  
116 involved, and in engine test, cycle-by-cycle variations in the combustion process may  
117 cause a significant error and deteriorate the accuracy of measurements. In the present  
118 study, to mitigate the effects of the cycle-by-cycle variations, the data obtained in the  
119 experimental conditions where the coefficient of variance of indicated mean effective  
120 pressure were less than 5% were used for the evaluation.

121 The engine employed a low-pressure loop EGR system which contains a diesel

122 oxidation catalyst (DOC) to reduce unburned emissions and a diesel particulate filter  
123 (DPF) to remove soot particles. A 5 kW heater was installed into the channel of the intake  
124 manifold to control the intake air temperature. The EGR rate was controlled by adjusting  
125 the opening positions of two gate valves. One was installed in the EGR channel to control  
126 the EGR rate, another was installed in the exhaust channel to maintain a constant exhaust  
127 gas pressure equal to the intake air pressure.

128 To simulate the EGR gas composition with pure components, pure gases were  
129 introduced into the intake pipe from gas cylinders while controlling the flow rate with  
130 mass flow controllers (KOFLOC, Model 3665 for CO and Model 3660 for the other  
131 gases) which have accuracy better than  $\pm 1.5$  and  $\pm 1.0\%$  of full scale output (FSO). The  
132 flow rates of the pure gases were adjusted to the targeted concentrations at the intake that  
133 are calculated with the flow rate of the intake air. The flow rate of the intake air was  
134 determined with a differential pressure type flowmeter, and the pressure difference was  
135 measured with a digital manometer (Tsukasa Sokken, PE-33-D) which has accuracy  
136 better than  $\pm 0.5\%$  of FSO. Considering these facts, the impact of the measurement error  
137 on the flow rate is negligibly small. Furthermore, the concentrations in the intake gas  
138 were measured with the gas analyzer for verification purposes.

139 The intake NO<sub>2</sub> concentration was changed while introducing NO and O<sub>2</sub> into a heated



140 oxidation catalyst.

141 The concentrations of the intake and exhaust gas components were measured with a  
142 gas analyzer (Best Sokki, BEX-5100D), with the total hydrocarbons (THC) measured  
143 with FID (Flame ionization detector); NO<sub>x</sub> with CLD (Chemiluminescence detector); CO  
144 and CO<sub>2</sub> with NDIR (Non dispersive infrared); oxygen (O<sub>2</sub>) with a dumbbell-type sensor.  
145 More detailed measurements of hydrocarbon species in the exhaust gas were carried out  
146 with a Fourier transform infrared (FTIR) spectrometer (HORIBA, MEXA-4000FT)  
147 which quantifies the concentrations of specified chemical species as detailed in Table 2.  
148 A part of the exhaust gas was collected with a sampling bag, and introduced into the FTIR  
149 spectrometer after diluting the exhaust gas collected with nitrogen (N<sub>2</sub>) to an appropriate  
150 concentration.

### 151 **2.3 Definitions of the Ignition and Start of Injection**

152 The definitions of the ignition and start of injection are shown in Fig.2. The ignition  
153 timing was determined as the derivative of the heat release rate  $d^2Q/d\theta^2$  where it exceeds  
154  $5 \text{ J/}^\circ\text{CA/}^\circ\text{CA}$ , and the fuel injection timing was adjusted to fix the ignition timing at -  
155  $3^\circ\text{CA ATDC}$ . The fuel injection timing was determined as the timing of the drop in the  
156 fuel pressure measured with the G4S injector.

157

### 158 **3. Results and Discussion**

#### 159 **3.1 Nitrogen Oxide Addition under Real EGR Conditions**

##### 160 **3.1.1 Experimental Conditions**

161 The experimental conditions are detailed in Table 3. The injection quantity was fixed  
162 at 20 mm<sup>3</sup>/cycle. With this fuel quantity, the indicated mean effective pressure (IMEP)  
163 was around 0.25 MPa. A naturally aspirated operation was implemented without any  
164 boosting, while the oxygen concentration was reduced to 7% with the EGR to ensure low  
165 temperature combustion. The intake air temperature was changed to examine the  
166 dependence of the ignition delay on the in-cylinder gas temperature.

167 Prior to the ignition delay measurements, the composition of the intake gas was  
168 measured. As a result, the concentrations of CO, CO<sub>2</sub>, and NO<sub>x</sub> were 4%, 7%, and 0 ppm,  
169 and those of the hydrocarbons are as shown in Fig.3. The unknown hydrocarbons which  
170 are the difference between the THC measured with the FID (BEX-5100D) and the  
171 hydrocarbons measured with the FTIR spectrometer (MEXA-4000FT) were  
172 approximately half. One major reason for this discrepancy is that the detectable species  
173 of the FTIR spectrometer are limited as listed in Table 2. And the FTIR spectroscopy was  
174 carried out after the gas was collected with a sampling bag at room temperature so that  
175 high boiling point components could not be detected, while the BEX-5100D gas analyzer

176 sucked the gas in via a hot hose maintained at the temperature of 191°C. Except for  
177 unknown species, the highest concentration of hydrocarbons was CH<sub>4</sub>, followed by C<sub>2</sub>H<sub>4</sub>,  
178 and C<sub>6</sub>H<sub>6</sub>. Small amounts of C<sub>3</sub>H<sub>6</sub>, 1,3-C<sub>4</sub>H<sub>6</sub> and iso-C<sub>4</sub>H<sub>8</sub> were also detected.

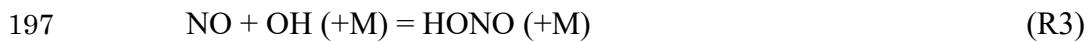
179 In this section, NO<sub>x</sub> which was not present in the intake gas was supplied from gas  
180 cylinders together with the EGR while changing the intake air temperature  $T_{in}$ . The intake  
181 NO<sub>x</sub> concentration changed more widely than can be anticipated in practical diesel  
182 engines, to more fully understand details of the dependence on the experimental  
183 parameters. The addition of the gases to the intake flow had no direct impact on the EGR  
184 rate set to maintain the constant oxygen concentration due to the very low concentrations.

### 185 **3.1.2 Effects of Nitrogen Oxide Addition on Ignition**

186 Figure 4 shows the changes of the ignition delays with the NO<sub>x</sub> concentrations. The  
187 open symbols are the case where pure NO was introduced into the intake gas, while the  
188 closed symbols are for where a NO and NO<sub>2</sub> mixture produced from NO via the heated  
189 oxidation catalyst is introduced into the intake air. The volume fractions of NO and NO<sub>2</sub>  
190 are detailed in Table 4. Approximately half of NO was converted into NO<sub>2</sub> via the  
191 oxidation catalyst.

192 The ignition delay decreased with increasing intake NO concentration, and it  
193 decreased significantly with lower concentrations of NO at the higher intake temperature

194  $T_{in}$ . At the lower temperature, reactions R2 and R3 have an inhibiting impact on the  
195 ignition vis-a-vis reaction R1, as follows [20, 27]:



198 Where R is an alkyl radical. With increasing temperature, reaction R1 becomes more  
199 important, and the dissociation of HONO exceeds its production (R3 is reversed),  
200 enhancing the ignition.

201 The intake  $NO_2$  has the stronger impact on acceleration of the ignition. A possible  
202 explanation is that  $NO_2$  produces reactive radicals in the  $C_1$ - $C_2$  chemistry as follows [16]:



204 Where  $R'$  is a small alkyl radical. As the intake gas consisted of small hydrocarbons (see  
205 Fig.3), this reaction enhanced the oxidation reaction of the in-cylinder gas during the  
206 compression stroke, and the ignition of the spray combustion was promoted while  
207 entraining the intermediate products into the spray.

208 Figure 5 shows the profiles of the in-cylinder pressure and heat release rate  $dQ/d\theta$ .  
209 The arrows indicating the fuel injection timings were retarded with increases in the NO  
210 concentration, to adjust the ignition timing to be at  $-3^\circ CA$  ATDC. The heat release before  
211 the fuel injection can be seen at the NO concentration of 670 ppm, suggesting that

212 hydrocarbons contained in the in-cylinder gas ignited with the aid of the NO reactions.  
213 With the NO concentrations less than 370 ppm, there appeared to be a small heat release  
214 before the main heat release. This is a low temperature oxidation reaction (LTOR) of the  
215 gas oil as evidenced by the fact that the timing of the heat release is changed with the start  
216 of injection (SOI). To compare the LTOR, the heat release rate  $dQ/d\theta$  arranged with the  
217 crank angle after the SOI is shown in Fig.6. Beginning from  $3^\circ\text{CA}$  after SOI, there is a  
218 small heat release due to the LTOR. This heat release increased with increases in the NO,  
219 suggesting that the intermediate products of the in-cylinder gas facilitated the LTOR.

## 220 **3.2 Nitrogen Oxide and Hydrocarbon Additions under $\text{N}_2$ -dilution Conditions**

### 221 **3.2.1 Experimental Conditions**

222 The intake gas composition was changed by introducing pure gases from the gas  
223 cylinders without use of EGR. The gas compositions investigated for this are detailed in  
224 Table 5. The recent paper elucidated that much polycyclic aromatic hydrocarbons (PAHs)  
225 are formed in the LTC regime [28], and thus it would be interesting to examine the effects  
226 of the PAHs on the ignition. The FTIR spectrometer employed in the present study,  
227 however, is not able to detect the PAHs, so that the investigation did not cover the effects  
228 of the PAHs on ignition. There is a paper showing that much HCHO is formed and affects  
229 ignition delays in the LTC [29], but low concentration of HCHO in the order of tens of

230 ppm was recirculated into the intake according to the FTIR measurement, and HCHO was  
231 not introduced in the intake in the present study. The oxygen concentration was set at 11%  
232 which is higher than that in the above section, as operation failed due to misfiring at lower  
233 oxygen concentrations. In the above section, the passage in the exhaust pipe was narrowed  
234 with a valve to recirculate the large amount of the exhaust gas into the intake, causing the  
235 increase in the exhaust gas pressure, and in the amount of hot residual gas in the  
236 combustion chamber. This might increase the in-cylinder temperature, and shorten the  
237 ignition delay. On the other hand, the exhaust valve was fully opened in this section, and  
238 less residual gas was remained in the combustion chamber.

239 The CO, NO, and hydrocarbons were introduced on a one-by-one basis to examine  
240 their impact on the ignition. To examine the combined effects of NO and hydrocarbons,  
241 the CH<sub>4</sub> concentration was fixed at 5000 ppmC, and the hydrocarbon species were  
242 changed while increasing the concentrations up to 5000 ppmC. These conditions were  
243 determined referring to Fig.3, increasing the concentrations to achieve extreme conditions.  
244 The intake air temperature  $T_{in}$  was maintained at 125°C, with other conditions the same  
245 as in Table 3.

### 246 **3.2.2 Effects of Nitrogen Oxide and Hydrocarbon Addition on Ignition**

247 Figure 7 shows the ignition delays  $\tau_{ign}$  with the different intake CO concentrations.

248 The CO concentration had a very small impact on the ignition delay. Figure 8 shows the  
249 ignition delays  $\tau_{\text{ign}}$  with the various intake hydrocarbon species and concentrations. There  
250 is no significant change in the ignition delays with the addition of the hydrocarbons.

251 Figure 9 shows the ignition delays  $\tau_{\text{ign}}$  with the different intake NO concentrations.  
252 The increase in NO decreased the ignition delays, suggesting that NO entrained into the  
253 spray enhanced the ignition. The NO concentrations here are rather higher than those  
254 under actual EGR conditions, and it is notable that the ignition delay decreases with lower  
255 NO concentrations at the higher intake gas temperatures  $T_{\text{in}}$  (see Fig.4).

256 The profiles of the in-cylinder pressure and heat release rate  $dQ/d\theta$  are shown in Fig.10.  
257 Similar to Fig.5, there was a small heat release due to the LTOR between the SOI and the  
258 main combustion which was promoted with the increase in NO.

259 Figure 11 shows the effects of the hydrocarbon species on the ignition delays  $\tau_{\text{ign}}$ .  
260 Compared to the case with only NO, the ignition delays  $\tau_{\text{ign}}$  were decreased with the  
261 additions of the other hydrocarbons. This result indicates that the NO and hydrocarbons  
262 of the in-cylinder gas reacted and yielded intermediate products that enhance the ignition  
263 of the diesel spray. The impact of the  $\text{C}_2\text{H}_4$  and  $\text{C}_3\text{H}_6$  additions were equivalent and the  
264 strongest, followed by those of the  $\text{C}_3\text{H}_8$  addition. The addition of  $\text{CH}_4$  also decreased the  
265 ignition delay but to a smaller degree. The results here were reproducible, and similar

266 tendencies were obtained under the other intake air temperature conditions tested here.

### 267 **3.2.3 Chemical Kinetic Analysis of the Effects of Nitrogen Oxide and Hydrocarbon**

#### 268 **Additions**

269 The ignition enhancement effects of NO and hydrocarbon addition were analyzed with  
270 chemical kinetic calculations. The software used was CHEMKIN-PRO selecting the  
271 single-zone IC HCCI Engine model which predicts chemical reactions during a  
272 compression and expansion stroke [26]. These calculations were carried out to simulate  
273 the chemical reaction of the in-cylinder gas without fuel injections, focusing on the  
274 concentration of the OH radical which is known to be the key species in the development  
275 of ignition. The development of the reaction model of hydrocarbons and nitrogen oxide  
276 species is in progress [30, 31], but the authors chosen the model proposed by Anderlohr  
277 et al. [20] since the good agreements on the validations with the experiments in an HCCI  
278 engine where the pressure and temperature conditions are relevant to the present study,  
279 and the model has been widely utilized in the recent research of internal combustion  
280 engines [32, 33].

281 The calculation conditions are equivalent to the engine tests in section 3.2, except for  
282 the initial temperature which was adjusted to the calculated temperature close to the TDC  
283 (Top dead center) for the engine tests. The concentrations of NO and CH<sub>4</sub> were fixed at



284 100 ppm and 5000 ppmC. The hydrocarbon species of CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>8</sub> were  
285 added to the NO and CH<sub>4</sub> mixture on a one-by-one basis while maintain the  
286 concentrations of 5000 ppmC. Note that no gas oil component was fed in the calculation  
287 to examine the ignition promotion effects of the NO and hydrocarbon addition.

288 Figure 12 shows the profiles of the temperature and the OH radical, for the mixture of  
289 CH<sub>4</sub> (5000 ppmC) and C<sub>2</sub>H<sub>4</sub> (5000 ppmC). In this calculation, no high temperature  
290 oxidation reaction took place due to the very lean mixture, and the impact on the chemical  
291 reactions on the temperature rise was limited in analogy with the experiments shown in  
292 the above sections. With the addition of NO, the OH concentration became 500 times that  
293 without the addition of NO at the TDC as can be seen in this figure. The effects of the gas  
294 composition on the OH concentrations are compared in Fig.13, where four different  
295 hydrocarbons at 5000 ppmC are mixed with CH<sub>4</sub> (5000 ppmC) and NO (100 ppm). The  
296 highest OH concentration was achieved with the mixture of C<sub>3</sub>H<sub>6</sub>, followed by that of  
297 C<sub>2</sub>H<sub>4</sub>. The OH concentrations of C<sub>3</sub>H<sub>8</sub> and CH<sub>4</sub> were lower than those of C<sub>3</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub>.  
298 The order of the OH concentrations was analogous with that of the ignition delay  
299 measured in the engine tests, except for the opposite trend between C<sub>3</sub>H<sub>8</sub> and CH<sub>4</sub>.

300 To develop an understanding of the chemical reactions that predominantly produced  
301 the OH radical, the rate of production was analyzed. Figure 14 shows the major rates of

302 production with respect to the OH radical at the TDC. Regardless of the hydrocarbon  
303 species, the OH production was governed with the R1 reaction. The OH production via  
304 the R1 reaction was highest with the addition of C<sub>3</sub>H<sub>6</sub>, followed by that of C<sub>2</sub>H<sub>4</sub>. The rates  
305 of OH production of C<sub>3</sub>H<sub>8</sub> and CH<sub>4</sub> were lower than those of C<sub>3</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub>. Note that  
306 the range of the horizontal axis in C<sub>3</sub>H<sub>6</sub> is larger than that in the others. At the TDC, the  
307 HONO dissociation in R3 as well as the CH<sub>3</sub>OO dissociation was pronounced. The OH  
308 radical was predominantly consumed by the reactions with CH<sub>4</sub> and the other added  
309 hydrocarbons. From this result, it may be summarized that the R1 reaction is most  
310 important in the OH production.

311 The rate of production was analyzed with respect to HO<sub>2</sub>. The major rates of HO<sub>2</sub>  
312 production are shown in Fig.15. Note that the range of the horizontal axis in C<sub>3</sub>H<sub>6</sub> is larger  
313 than that in the others. The reactions relating to the HO<sub>2</sub> production with C<sub>3</sub>H<sub>8</sub> and CH<sub>4</sub>  
314 were similar, except for the fact that the intermediate product C<sub>3</sub>H<sub>6</sub>OOH of C<sub>3</sub>H<sub>8</sub> leads to  
315 the higher rate of production than CH<sub>4</sub>. With C<sub>3</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub>, the reaction between the  
316 formyl radical CHO and oxygen O<sub>2</sub> has the highest rate of production. The primary attack  
317 on C<sub>2</sub>H<sub>4</sub> is by addition of the O radical, and the primary products of this reaction are CH<sub>3</sub>  
318 and CHO radicals [34]. With respect to C<sub>3</sub>H<sub>6</sub>, it has been suggested that the O addition is  
319 the dominant decay route through an intermediate complex, and the primary products of

320 this reaction are  $C_2H_5$  and  $CHO$  radicals [34]. Thus, it may be suggested that the  $CHO$   
321 radical production with  $C_3H_6$  and  $C_2H_4$  promotes the  $HO_2$  production, although  $C_2H_5$  and  
322  $C_2H_4OOH$  also have non-negligible impacts on the rate of the  $HO_2$  production.

323

#### 324 **4. Conclusions**

325 To investigate the effects of EGR gas composition on the ignition delays in low  
326 temperature diesel combustion, the ignition delays were measured in a single-cylinder  
327 engine while introducing hydrocarbons and nitrogen oxides. The conclusions may be  
328 summarized as follows:

- 329 1. The ignition delay of the diesel combustion is decreased with introduced nitrogen  
330 oxide ( $NO$ ) present in the intake, and its effect is more pronounced with higher intake  
331 temperatures.
- 332 2. The ignition promotion effects with nitrogen dioxide ( $NO_2$ ) are more pronounced than  
333 those with  $NO$ .
- 334 3. Introducing carbon monoxide ( $CO$ ) and hydrocarbons ( $CH_4$ ,  $C_2H_4$ ,  $C_3H_6$  and  $C_3H_8$ )  
335 in the intake has little effect on the ignition delay.
- 336 4. Compared to feeding only  $NO$ , simultaneous feeding of  $NO$  and hydrocarbons  
337 achieves a shorter ignition delay of the diesel combustion. The hydrocarbons

338 producing more hydroperoxyl radicals ( $\text{HO}_2$ ) tend to decrease the ignition delay as  
339 they enhance the  $\text{NO} + \text{HO}_2 = \text{NO}_2 + \text{OH}$  reaction.

340

341 Small amounts of  $\text{NO}_x$  are recirculated under EGR conditions, and the effects on the  
342 ignition are notable with the recirculated hydrocarbons at higher intake temperatures.

343

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Table 1 Specifications of the test engine

Type of engine	4TNV98T (Yanmar)
Bore x stroke [mm]	98 x 110
Displacement volume [cm <sup>3</sup> ]	830
Compression ratio [-]	17.6
Type of injector	G4S (DENSO)
Nozzle hole diameter [mm]	0.125
Included spray angle [°]	155
Number of nozzles	8

Table 2 Gaseous species determined with the FTIR spectrometer

CO	CO <sub>2</sub>	NO	NO <sub>2</sub>	N <sub>2</sub> O
H <sub>2</sub> O	NH <sub>3</sub>	SO <sub>2</sub>	HCHO	CH <sub>3</sub> CHO
CH <sub>3</sub> OH	C <sub>3</sub> H <sub>6</sub> O	MTBE	HCOOH	CH <sub>4</sub>
C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>	1,3-C <sub>4</sub> H <sub>6</sub>	iso-C <sub>4</sub> H <sub>8</sub>
C <sub>6</sub> H <sub>6</sub>	C <sub>7</sub> H <sub>8</sub>			

Table 3 Experimental conditions

Engine rotation speed [rpm]	1000
IMEP [MPa]	0.25
Intake air	Naturally aspirated
Intake air temperature, $T_{in}$ [°C]	100, 125, 150
Injection pressure [MPa]	86
Injection quantity [mm <sup>3</sup> /cycle]	20
Intake oxygen concentration [%]	7
Intake NO <sub>x</sub> concentration [ppm]	0 - 1200



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Table 4 Fractions of NO and NO<sub>2</sub> in the intake gas, measured with the FTIR spectrometer

$T_{in} = 100^{\circ}\text{C}$		$T_{in} = 125^{\circ}\text{C}$		$T_{in} = 150^{\circ}\text{C}$	
NO [ppm]	NO <sub>2</sub> [ppm]	NO [ppm]	NO <sub>2</sub> [ppm]	NO [ppm]	NO <sub>2</sub> [ppm]
110	120	50	60	0	0
230	180	110	120	0	15
320	260	180	130	60	70
410	350	230	170	-	-

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Table 5 Intake gas composition as the experimental variable

	O <sub>2</sub> [%]	N <sub>2</sub>	CO [%]	NO [ppm]	CH <sub>4</sub> [ppmC]	C <sub>2</sub> H <sub>4</sub> [ppmC]	C <sub>3</sub> H <sub>6</sub> [ppmC]	C <sub>3</sub> H <sub>8</sub> [ppmC]
CO	11	balance	0 – 4	-	-	-	-	-
NO			0 – 470	-	-	-	-	
NO+CH <sub>4</sub>			0 – 200	10000	-	-	-	
NO+C <sub>2</sub> H <sub>4</sub>			0 – 200	5000	5000	-	-	
NO+C <sub>3</sub> H <sub>6</sub>				5000	-	5000	-	
NO+C <sub>3</sub> H <sub>8</sub>				5000	-	-	5000	

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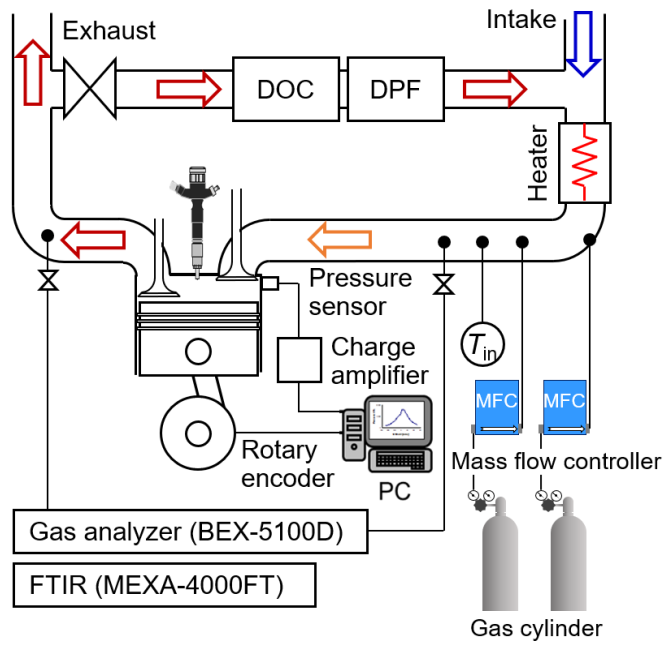


Fig.1 Outline of the experimental setup

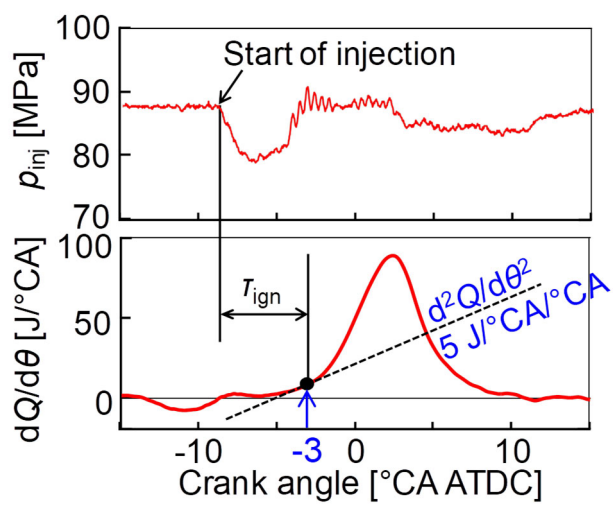


Fig.2 Definition of the ignition set at  $-3^{\circ}\text{CA ATDC}$  and the ignition delay  $\tau_{\text{ign}}$

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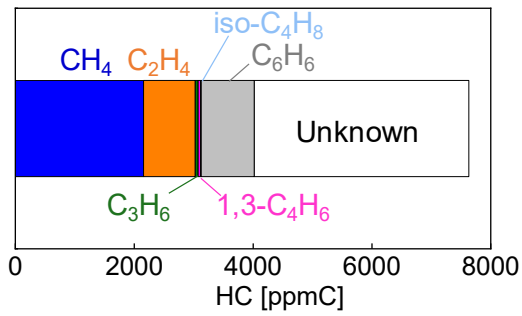


Fig.3 Measured intake hydrocarbon species ( $T_{in} = 125^{\circ}\text{C}$ )

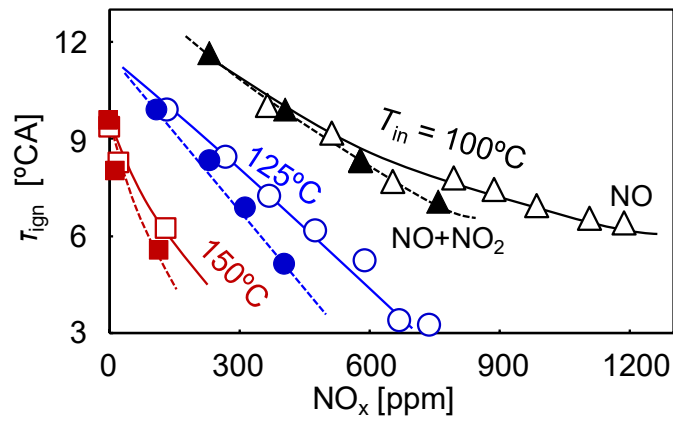


Fig.4 Effect of NO and NO<sub>2</sub> introduced in the intake gas vs the ignition delay  $\tau_{ign}$  (w/EGR, open symbols: NO addition, closed symbols: NO + NO<sub>2</sub> addition)

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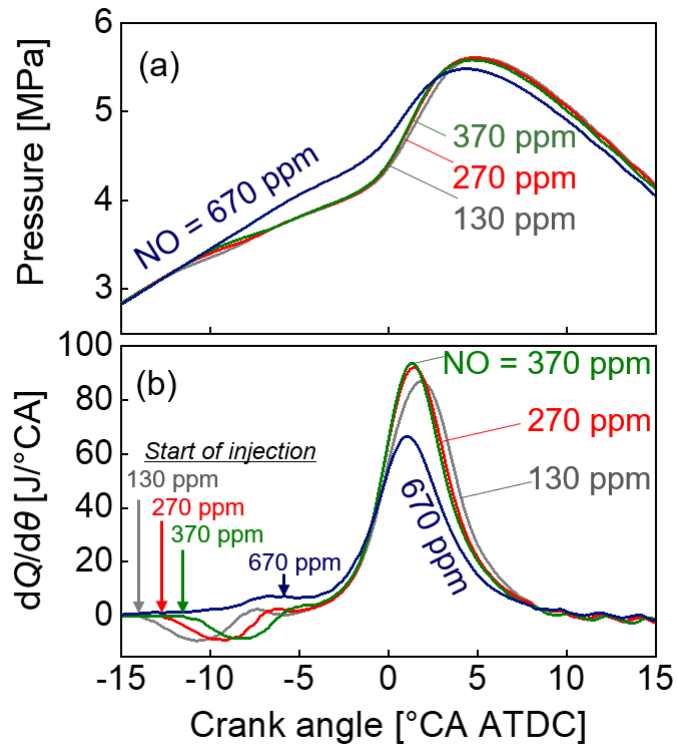


Fig.5 Profiles of in-cylinder pressure and heat release rate  $dQ/d\theta$ , changed with the NO concentration ( $T_{in} = 125^\circ\text{C}$ , w/EGR)

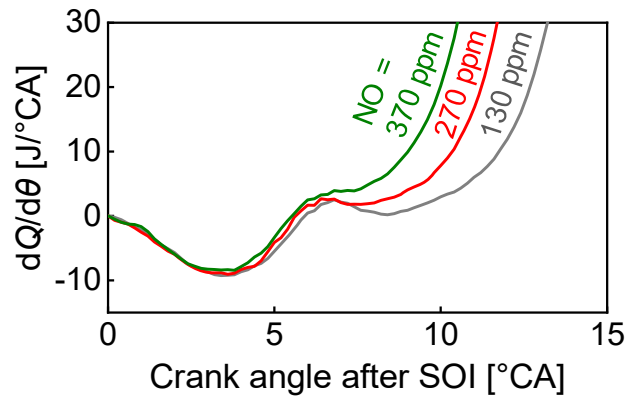


Fig.6 Profiles of heat release rate  $dQ/d\theta$ , arranged against the crank angle after the start of injection (SOI) ( $T_{in} = 125^\circ\text{C}$ , w/EGR)

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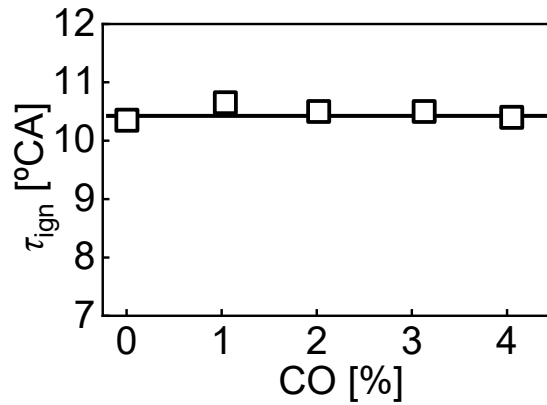


Fig.7 Ignition delays  $\tau_{ign}$  vs changes in the intake CO concentration ( $T_{in} = 125^{\circ}\text{C}$ , NO = 0 ppm)

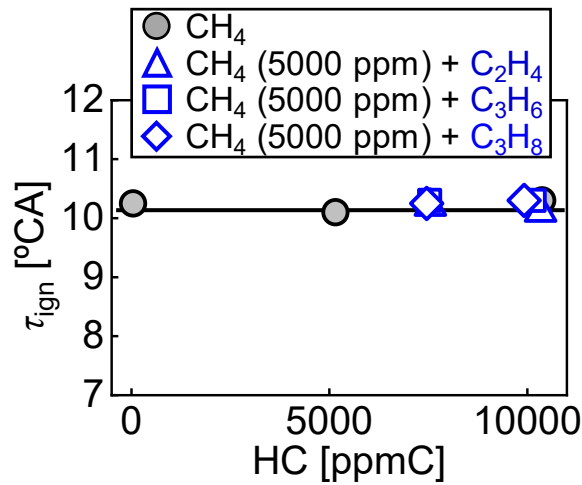


Fig.8 Ignition delays  $\tau_{ign}$  vs changes of the intake hydrocarbon species and concentrations ( $T_{in} = 125^{\circ}\text{C}$ , NO = 0 ppm)

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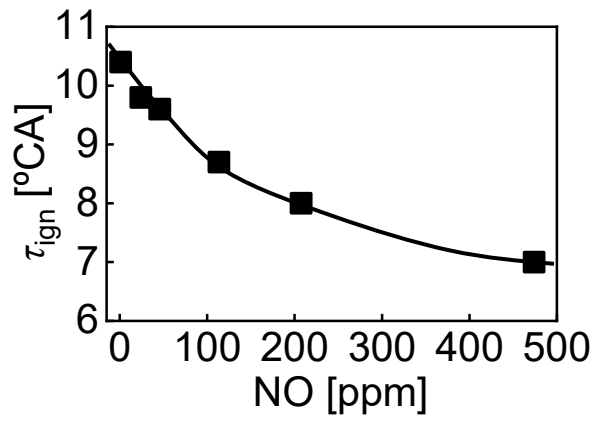


Fig.9 Ignition delays  $\tau_{ign}$  vs changes of the intake NO concentration ( $T_{in} = 125^{\circ}\text{C}$ , HC = 0 ppmC)

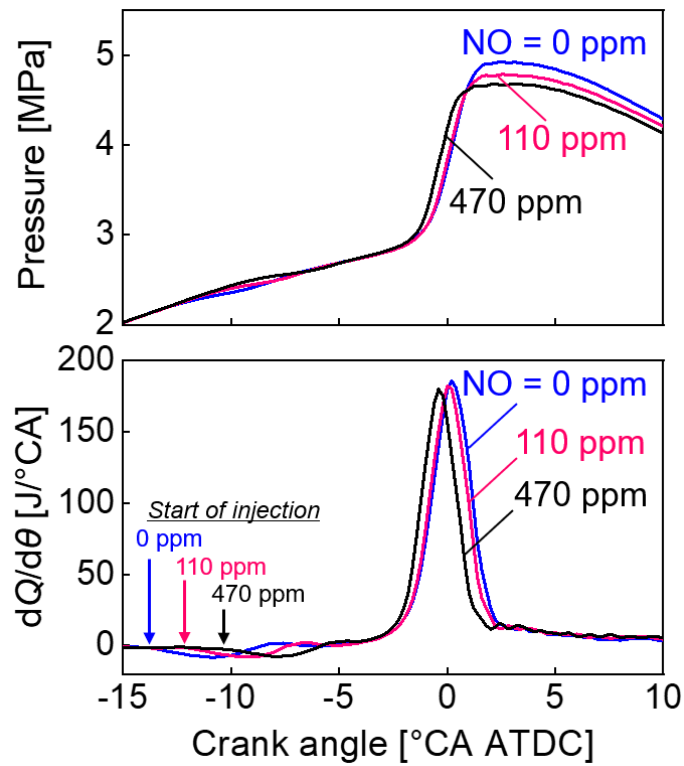


Fig.10 Profiles of the in-cylinder pressure and heat release rate  $dQ/d\theta$ , changed with the NO concentration ( $T_{in} = 125^{\circ}\text{C}$ , HC = 0 ppmC)

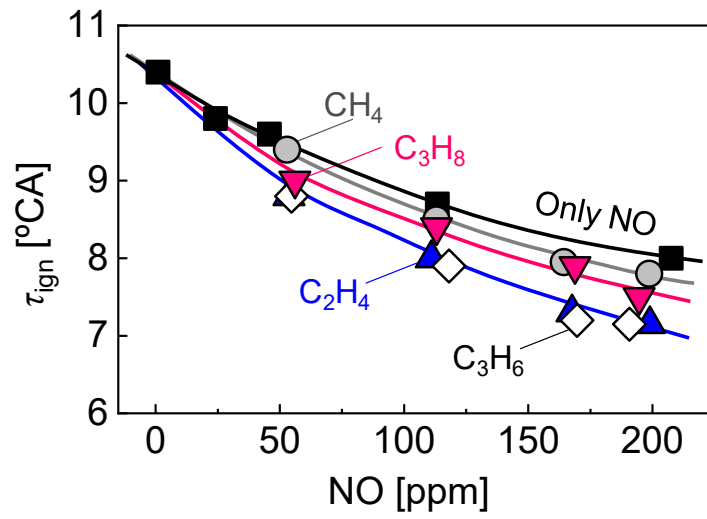


Fig.11 Effects of hydrocarbon species and NO concentration on the ignition delay  $\tau_{ign}$   
 ( $T_{in} = 125^{\circ}\text{C}$ , HC = 10000 ppmC)

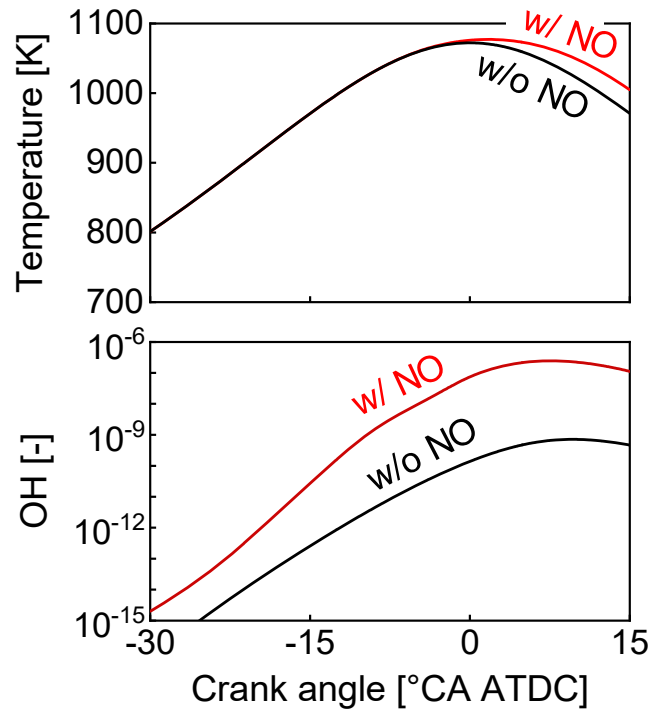


Fig.12 Calculated profiles of the in-cylinder mean temperature and OH concentration  
 ( $\text{CH}_4 = 5000 \text{ ppmC}$ ,  $\text{C}_2\text{H}_4 = 5000 \text{ ppmC}$ ,  $\text{NO} = 100 \text{ ppm}$ )

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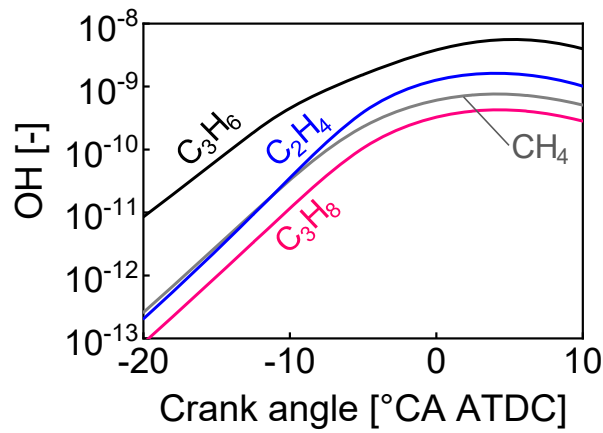


Fig.13 Plot of calculated OH concentrations for the tested hydrocarbon species  
(HC = 10000 ppmC, NO = 100 ppm)



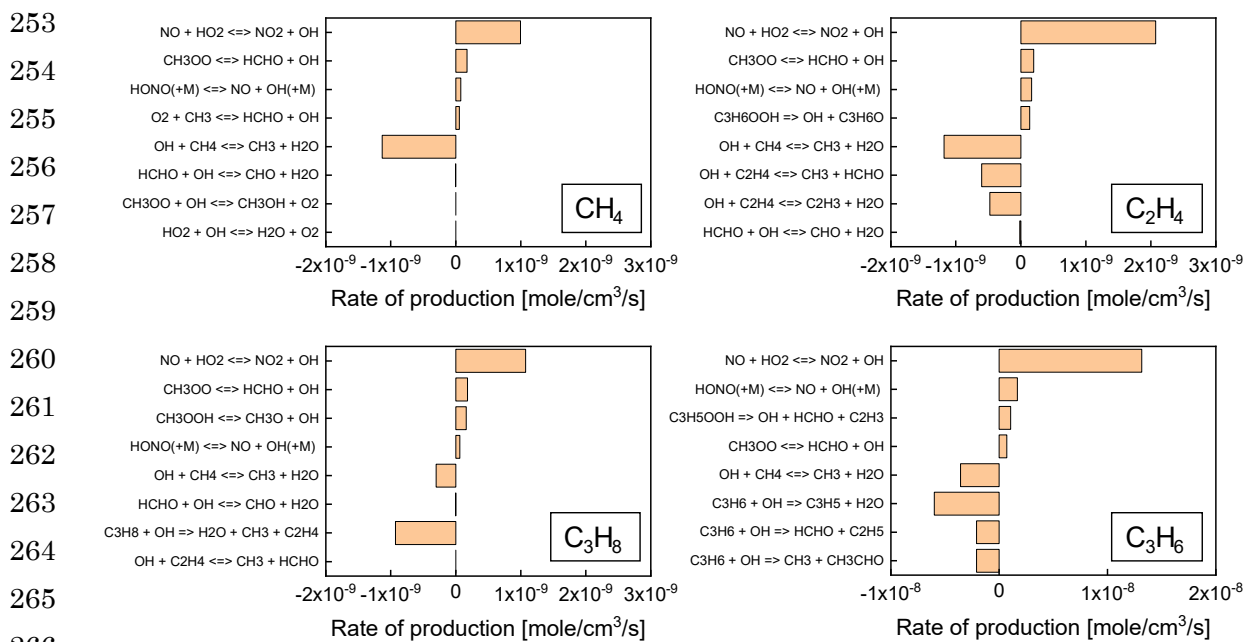


Fig.14 Major OH production rates and their chemical equations for the tested hydrocarbon species (HC = 10000 ppmC, NO = 100 ppm)

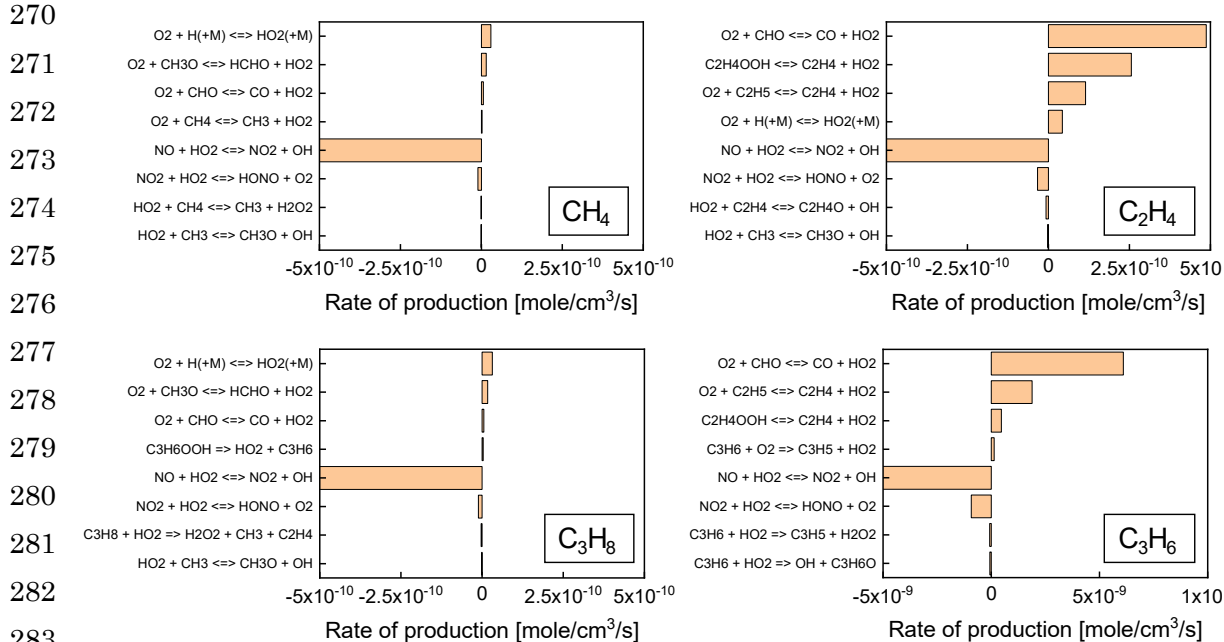


Fig.15 Major HO<sub>2</sub> production rates and their chemical equations for the tested hydrocarbon species (HC = 10000 ppmC, NO = 100 ppm)