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# Fundamental Studies on the Chemical Changes and Its Combustion Properties of Hydrocarbon Compounds by Ozone Injection

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Additional information is available at the end of the chapter

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## 1. Introduction

The prevention of global warming caused by increasing of CO<sub>2</sub> has been high interest to the public and grows environmental awareness, and also effective use of fossil fuel especially for a vehicle with internal combustion engine, such as an automobile, a ship and an aircraft, has been developed in several research field. Hydrogen for fuel cell, bio-diesel fuel (BDF), dimethyl ether (DME) and ethanol as alternative energy source for vehicle has been widely studied (S. Verhelst&T. Wallner, 2009, M.Y. Kim et al., 2008, B. Kegl, 2011, T.M.I. Mahlia et al., 2012) and some of them have begun to exist at the market in the recent decade. However, these new energy sources may take a long time until reaching at a real general use because of high investment not only for improving an infrastructure but retrofitting a system of vehicle.

Effects of ozone addition on combustion of fuels were reported as original research works. Combustion of natural gas with ozone was studied, and reduction of concentration of CO and C<sub>n</sub>H<sub>m</sub> by ozone injection was observed (M. Wilk&A. Magdziarz, 2010). Ozone injection to internal compression engine is effective to decrease in the emission rate of NO, CO and CH and an improvement of cetane number and fuel efficiency (T. Tachibana et al., 1997). Also there are patent applications covering the invention developed by the effect of ozone injection (Imagineering Inc.: JP 19-113570(A), Sun chemical Co., Ltd.: JP 7-301160, Nissan Motor Co., Ltd.: JP 15-113570(A)). Although the results of ozone injection were often reported, the mechanism of the phenomenon is still unclear. Discharge system for generating ozone was usually introduced before or directly in a cylinder, and then before expansion stroke the excited oxygen species including ozone reacts on hydrocarbon compounds, such as petrol and light diesel oil. Previous reports are chiefly focused on the

phenomena/effects and are not mentioned. We focused on the measurement of reaction products and investigated chemical changes among vapourised hydrocarbon compounds and activated dry air or oxygen including ozone by exposing discharge in this paper.

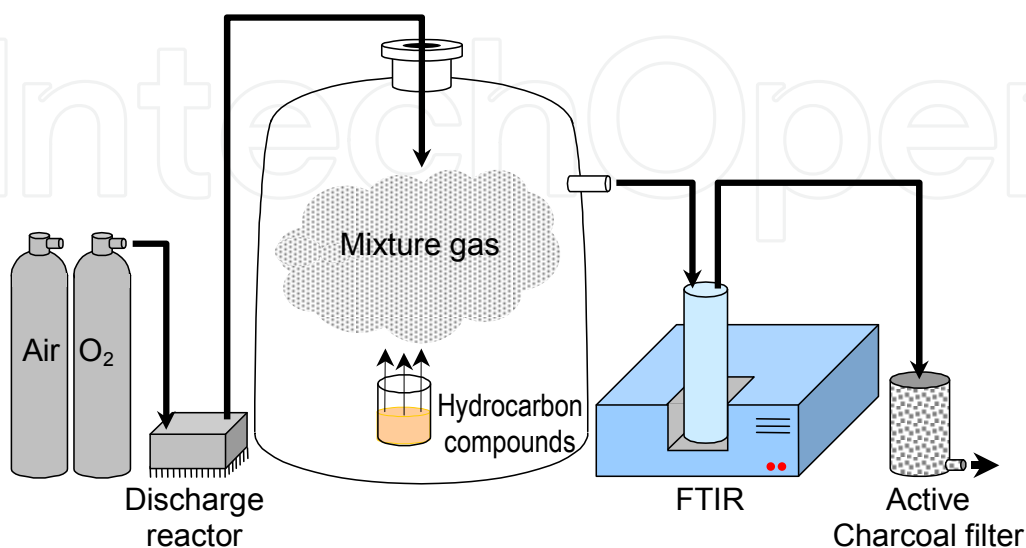
## 2. Material and method

### 2.1. Discharge reactor

Discharge was generated on the surface of a grid pattern discharge element (size: 85mm × 40mm, grid size: 5mm with 1mm in width of electrode) placed in the discharge reactor. The element was designed for generating surface discharge, and the discharge voltage was generated by high AC voltage power supply (Logy Electric Co., LHV-13AC) and varying from 8.0kV to 13.0kV (with approx. 9kHz~11kHz in frequency). Ozone concentration was measured as a standard of active oxygen species and was generated between 0.62g/m<sup>3</sup> to 8.8g/m<sup>3</sup> by dry air or pure oxygen.

### 2.2. Reactor vessel and hydrocarbon compounds

Petrol and light diesel oil were used for reaction with dry air or oxygen exposed to discharge. We used commercially available petrol and light diesel oil in the test, and the octane number of petrol and the cetane number of light diesel oil are among 90 to 92 and among 53 to 55 respectively. Hydrocarbon compounds as typified by petrol and light diesel oil consist of a lot of chemical substances. Isooctane (2,2,4-trimethylpentane, C<sub>8</sub>H<sub>18</sub>), which are one of the components of petrol and light diesel oil, are also applied as reacting substance of the test. These hydrocarbon compounds were vapourized in the reactor vessel (Figure 1), and air or oxygen exposed to discharge was injected through inlet to investigate chemical reaction between active species and vapourised hydrocarbon compounds. The condition of the entire experiment was not controlled and was carried out under an atmospheric pressure and temperature around 23 degrees Celsius.



**Figure 1.** A schematic of the experimental apparatus

### 2.3. Analysis of the mixture gas

A composition of the mixture gas of dry air exposed to discharge and vapourised hydrocarbon compounds was detected by Fourier transform infrared spectroscopy (FTIR, Shimadzu corp., FTIR-8900) and gas chromatography mass spectroscopy analysis (GC-MS, Shimadzu corp., GCMS-QP2010). Twenty-two meters reflective long-path distance gas cell (Pike Technologies inc., Permanently Aligned Gas Cell 162-2530) was installed to the FTIR for detecting the detail of the gas. Wavenumber of the mixture gas was measured between  $4000\text{cm}^{-1}$  to  $1000\text{cm}^{-1}$  and the FTIR spectra of the mixture gas were accumulated to 40 times.

Temperature of the vapourizing chamber of GC (gas chromatography) was set up from 30 to 250 degrees Celsius with increasing 10 degrees Celsius a minute, and entire measurement time was 24 minutes. Column flow stayed constant on 2.43mL a minute and column pressure was kept 97.9kPa. Mass-to-charge ratio in MS (mass spectrometry) was detected from 35 to 250m/z.

### 3. FTIR analysis

First of all of the investigations, dry air exposed to discharge and hydrocarbon compounds was mixed in the transparent bell jar (approximately 18L). Fifty mL of commercially available petrol (octan number 90 ~ 92) was poured into the beaker, and it was placed in the centre of the bell jar. Flow rate of the injected gas to the bell jar was consistently kept on 12L/min. The vapourized hydrocarbon compounds became clouded immediately after injecting dry air exposed to the discharge, and it grew into a dense fume increasingly (Figure 2). It was suggested that active species in the gas decomposed a part of structure of hydrocarbon compounds and water molecules were generated. Thus the generation of cloudy mixture gas was probably caused by saturated water vapour.



**Figure 2.** A picture of the bell jar with discharge (left) and without discharge (right).

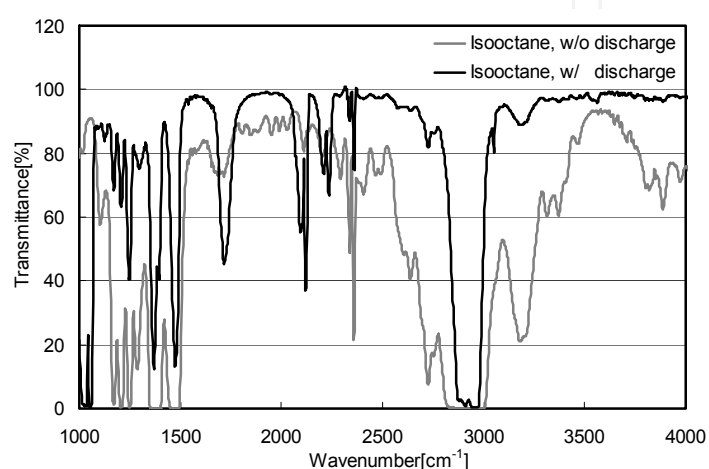
Isooctane (2,2,4-trimethylpentane,  $C_8H_{18}$ ) as elemental substances of petrol was mixed with dry air through the discharge chamber. Ozone concentration was adopted as a measure of several parameters and was kept at  $2.7\text{g/m}^3$  in the tests. FTIR spectra of the mixture gases were indicated in Figure 3. The peak at  $1725\text{cm}^{-1}$  was remarkably detected at FTIR spectra. It was supposed to be a reaction product, which were generated from hydrocarbon compound and active species in the discharged dry air. Relatively-sharp feature near  $1058\text{cm}^{-1}$  and  $2120\text{cm}^{-1}$  of the FTIR spectra was due to extra ozone. Also  $\text{CO}_2$  near  $2360\text{cm}^{-1}$  and  $\text{N}_2\text{O}$  near  $2237\text{cm}^{-1}$  were detected. Broad features of hydrocarbon compounds around  $3000\text{cm}^{-1}$  particularly decreased after injecting discharged dry air. These disappearing or decreasing spectra such as around  $3000\text{cm}^{-1}$  were changed into other chemical structure. However,  $\text{H}_2\text{O}$  was not observed in the spectra because it might be much weaker than other spectra. It was clearly found that the injection of discharged dry air caused partial chemical changes of isooctane from the FTIR spectra analysis.

We analysed the spectra of  $1725\text{cm}^{-1}$  prominently figured in both FTIR spectra as reaction product. Oxidative products of hydrocarbon compounds were mainly searched and some candidates, which had strong peak near  $1725\text{cm}^{-1}$ , were found such as heptanal ( $C_7H_{14}\text{O}$ ), 2-hexanone ( $C_7H_{14}\text{O}$ ), acetone ( $C_3H_6\text{O}$ ), octanal ( $C_8H_{16}\text{O}$ ), trans-cyclohexane ( $C_8H_{16}\text{O}_2$ ) and dodecanal ( $C_{12}H_{24}\text{O}$ ). FTIR spectra of octanal that was one of these hydrocarbon oxide/dioxide compounds were indicated in Figure 4. Ozone was possibly major element of generating oxidative products of hydrocarbon compounds because a lifetime of other active oxygen species, which were for instance oxygen atom, singlet oxygen molecule and hydroxide, was very shorter than it.

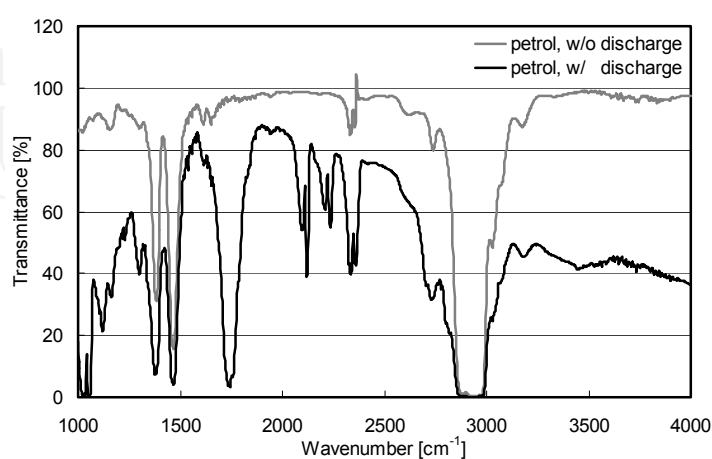
Typical FTIR spectra of the mixture gas consisting of vapourized petrol and dry air exposed to the discharge were indicated in Figure 4. Almost same spectra of Isooctane (2,2,4-trimethylpentane) (Figure 3) at around  $1725\text{cm}^{-1}$  were also detected as the reaction product although these spectra were not observed before injecting dry air passed through the discharge reactor. The production rate of reaction products was gradually saturated with increasing ozone concentration (Figure 5). The production rate of the newly detected spectra and the decreasing peak of hydrocarbon compounds were strongly dependent on the concentration of ozone in the discharged dry air. Typical peaks of ozone gas were observed at  $1058\text{cm}^{-1}$  and  $2120\text{cm}^{-1}$  as extra ozone, which did not react to hydrocarbon compounds. The peaks of reaction products and the extra ozone gas were detected in the case that the thinnest  $0.62\text{g/m}^3$  of ozone was injected in this investigation. FTIR spectra above  $3200\text{cm}^{-1}$  tend to indicate lower % of transmittance. Shorter wavelength of infrared light has tendency to be scattered about small particles in the long-path distance gas cell such as water molecule obtained in the reaction between ozone and hydrocarbon compound.

The spectra of vapourised light diesel oil blended with ozone were similar to other FTIR spectra (Figure 6). The peaks of reaction products at around  $1725\text{cm}^{-1}$  were also found. The production rate of the reaction product near  $1725\text{cm}^{-1}$  was less than the case of petrol because petrol indicated higher evaporation rate due to lower specific gravity in comparison with light diesel oil.

Ozone is one of the essential active gases for chemically changing the composition of vapourized hydrocarbon compounds. It was supposed that ozone decomposed CH band of hydrocarbon compounds partially and ozonised hydrocarbon compounds were produced as these reaction products at  $1725\text{cm}^{-1}$ . In conclusion, it was found that the reaction products, which were also generated by the thinnest ozone concentration in the test, were made by the injected ozone and the hydrocarbon compounds. These ozonised hydrocarbon compounds might be directly/indirectly contributed toward the improvement more efficient combustion of the internal combustion engine.

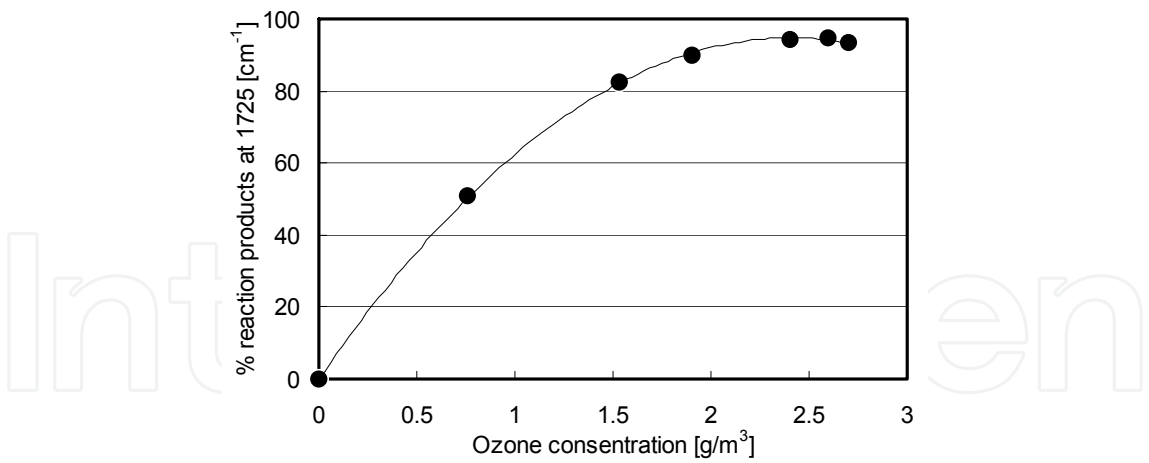


**Figure 3.** Typical FTIR spectra of the mixture gas blended isooctane (2,2,4-trimethylpentane,  $\text{C}_8\text{H}_{18}$ ) and dry air exposed to discharge

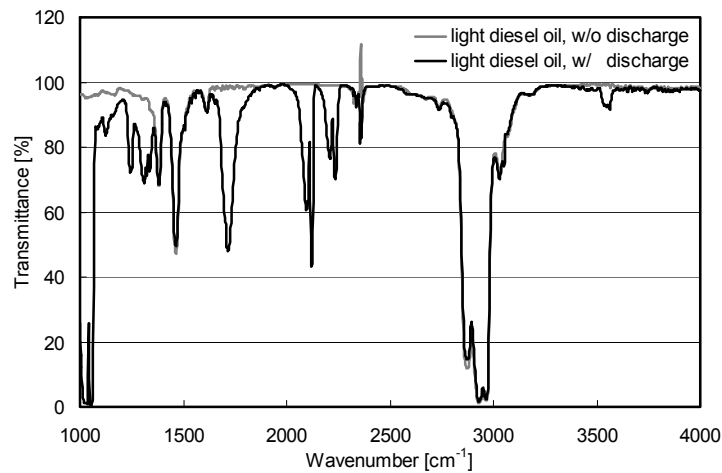


**Figure 4.** Typical FTIR spectra of the mixture gas blended petrol and dry air exposed to discharge





**Figure 5.** Generation rate of reaction products near 1725cm<sup>-1</sup> of FTIR spectra



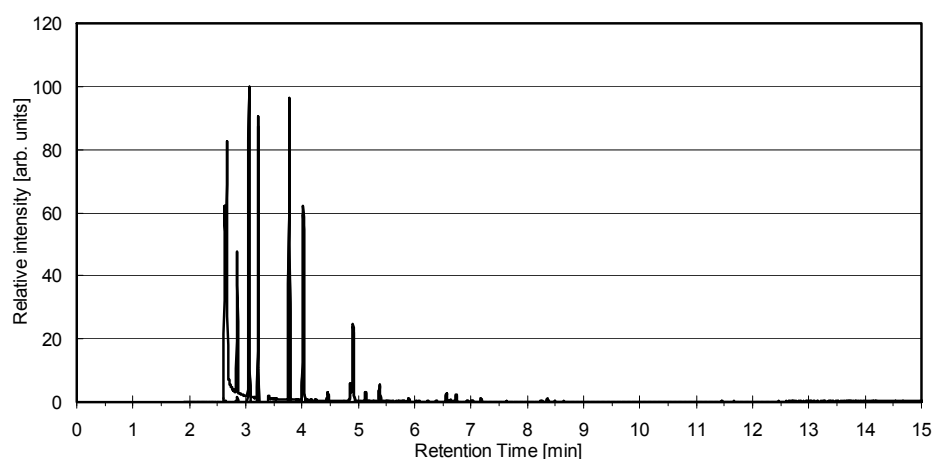
**Figure 6.** Typical FTIR spectra of the mixture gas blended light diesel oil and dry air exposed to discharge.

**4. GC-MS analysis**

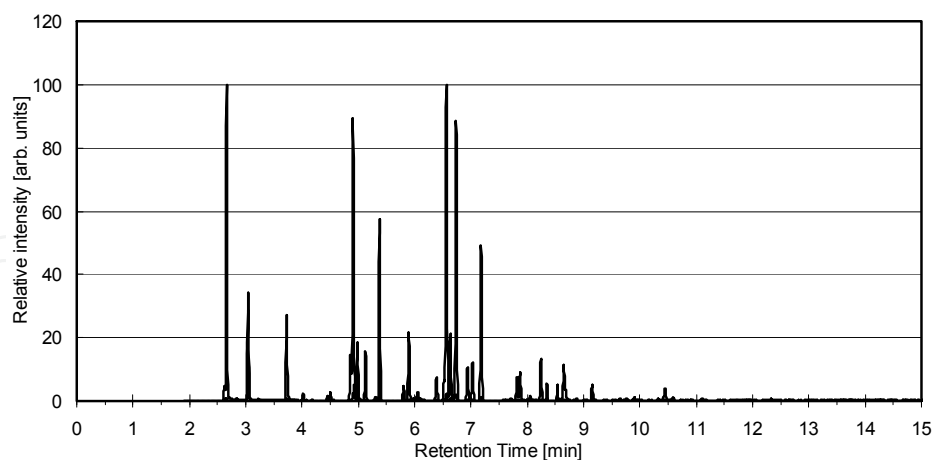
The details of reaction products, especially to search the composition of the strong peak detected near 1725cm<sup>-1</sup> by FTIR, were analysed by GC-MS. Petrol vapourised at room temperature (23 degrees Celsius) was injected to inlet of the GC-MS and its retention time data of GC were indicated in Figure 7. Also, vapourised petrol was blended in the closed container with oxygen passed through the discharge reactor. The mixture gas was introduced to the GC-MS directly and its spectra were indicated in Figure 8. Spectral lines of GC-MS were identified by spectral library and chemical substances were mainly indicated in Table 1. Chemical substances were searched when relative intensity obtained more than 5 arbitrary units. Shaded cells in column of “without Ozone” in Table 1 indicated chemically changed substances after ozone injection. Also, shaded cells in column of “with Ozone” of Table 1 indicated newly produced mainly oxidative products of hydrocarbon compounds by ozone injection.

It was found that after ozone injection hydrocarbon compounds were combined with oxygen atom or oxygen molecule. Vapourised petrol was comprised of approximately 300 kinds of hydrocarbon compounds, and several compounds with a high amount rate were detected from the vapourised petrol by GC-MS such as butane ( $C_4H_{10}$ ) pentane ( $C_5H_{12}$ ) and hexane ( $C_6H_{14}$ ) (Table 1; without ozone). In the case after ozone injection, several reactive products were detected such as acetaldehyde ( $C_2H_4O$ ), heptanal ( $C_7H_{14}O$ ), 2-Hexanone ( $C_6H_{12}O$ ) and octanal ( $C_8H_{16}O$ ) (Table 1; with ozone).

Number of carbon atom after ozone injection had tendency to be higher than the vapourised petrol without ozone treatment. It was expected that decomposed hydrocarbon compounds recombined themselves after that ozone decomposed CH band partially.



**Figure 7.** Typical retention time data of petrol without ozone.

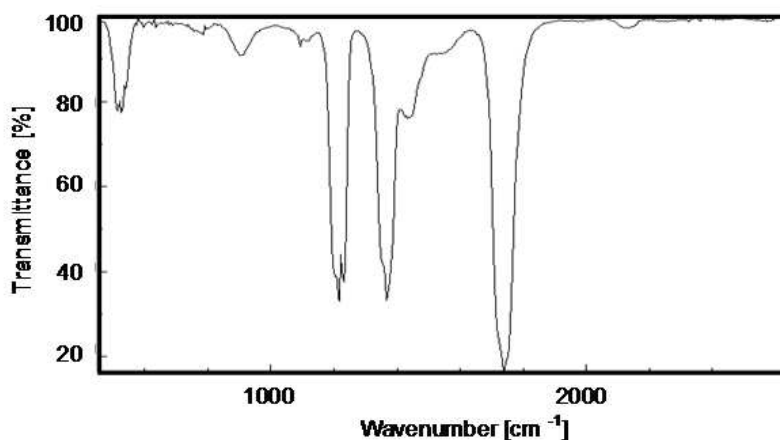


**Figure 8.** Typical retention time data of petrol with ozone.

The FTIR spectra of the reaction products, which were detected hydrocarbon compounds combined with oxygen atom or molecule, were searched by scientific database of The National Institute of Standards and Technology (NIST Standard Reference Database). It was found that many of reaction products had FTIR spectra near  $1725\text{cm}^{-1}$  such as acetaldehyde ( $C_2H_4O$ ), acetone ( $C_3H_6O$ ), heptanal ( $C_7H_{14}O$ ), octanal ( $C_8H_{16}O$ ) and dodecanal ( $C_{12}H_{24}O$ ).



(Table 1). As an example of them, FTIR spectra of Acetone ( $C_3H_6O$ ) and octanal ( $C_8H_{16}O$ ) were indicated in Figure 9 and Figure 10, respectively.



**Figure 9.** FTIR spectra of acetone ( $C_3H_6O$ ), which is one of the oxidative products of hydrocarbon compounds (NIST Standard Reference Database).

without Ozone					with Ozone				
Ret. time	chemical formula	chemical substance	similarity	M.W.	Ret. time	chemical formula	chemical substance	similarity	M.W.
					2.66	$C_3H_2O_2$	Propiolic acid	98	70
					3.04	$C_2H_4O$	Acetaldehyde	99	44
3.06	$C_4H_{10}$	Isobutane	97	58					
3.22	$C_4H_{10}$	Butane	97	58					
					3.72	$C_3H_6O$	Acetone	97	58
3.77	$C_5H_{12}$	Butane, 2-methyl-	97	72					
4.02	$C_5H_{12}$	Pentane	98	72					
4.46	$C_6H_{14}$	Butane, 2,2-dimethyl-	96	86					
4.86	$C_6H_{14}$	Butane, 2,3-dimethyl-	94	86	4.86	$C_6H_{14}$	Butane, 2,3-dimethyl-	96	86
4.9	$C_6H_{14}$	Pentane, 2-methyl-	94	86	4.9	$C_6H_{14}$	Pentane, 2-methyl-	95	86
					4.99	$C_4H_8O$	2-Butanone	97	72
5.13	$C_6H_{14}$	Pentane, 3-methyl-	98	98	5.13	$C_6H_{14}$	Pentane, 3-methyl-	98	86
					5.13	$C_6H_{14}$	Pentane, 3-methyl-	98	86
5.38	$C_6H_{14}$	Hexane	98	86	5.38	$C_6H_{14}$	Hexane	98	86
					5.8	$C_7H_{16}$	Pentane, 2,2-dimethyl-	96	100
					5.89	$C_6H_{12}$	Cyclopentane, methyl-	93	84
					5.98	$C_5H_{10}O$	Butanal, 3-methyl-	95	86
					6.06	$C_5H_{10}O$	2-Pentanone	83	86
					6.39	$C_7H_{16}$	Pentane, 3,3-dimethyl-	93	100
6.57	$C_7H_{16}$	Heptane, 3-methyl-	92	114	6.57	$C_7H_{16}$	Heptane, 3-methyl-	93	100
					6.64	$C_7H_{16}$	Pentane, 2,3-dimethyl-	96	100
6.74	$C_7H_{16}$	Hexane, 3-methyl-	95	100	6.74	$C_7H_{16}$	Hexane, 3-methyl-	96	100
					6.94	$C_{10}H_{20}$	1-Octane, 3-ethyl-	91	140
					7.03	$C_8H_{18}$	Hexane, 2,2-dimethyl-	95	114
					7.18	$C_7H_{16}$	Hexane, 3-methyl-	94	100

without Ozone					with Ozone				
Ret. time	chemical formula	chemical substance	similarity	M.W.	Ret. time	chemical formula	chemical substance	similarity	M.W.
					7.82	C <sub>8</sub> H <sub>18</sub>	Hexane, 2,5-dimethyl-	95	114
					7.87	C <sub>8</sub> H <sub>18</sub>	Hexane, 2,4-dimethyl-	95	114
					8.24	C <sub>8</sub> H <sub>18</sub>	Pentane, 2,3,4-trimethyl-	98	114
					8.35	C <sub>7</sub> H <sub>8</sub>	Toluen	98	92
					8.54	C <sub>8</sub> H <sub>16</sub>	Heptane, 4-methyl-	96	114
					8.65	C <sub>8</sub> H <sub>18</sub>	Heptane, 3-methyl-	93	114
					8.83	C <sub>8</sub> H <sub>16</sub>	Cyclohexane, 1,3-dimethyl-, trans-	93	112
					8.87	C <sub>9</sub> H <sub>20</sub>	Hexane, 2,2,5-trimethyl-	90	128
					9.01	C <sub>8</sub> H <sub>16</sub>	Cyclopentane, 1-ethyl-3-methyl, trans-	94	112
					9.05	C <sub>8</sub> H <sub>16</sub>	Cyclopentane, 1-ethyl-3-methyl, trans-	94	112
					9.15	C <sub>8</sub> H <sub>18</sub>	Hexane, 2,4-dimethyl-	93	114
					9.38	C <sub>8</sub> H <sub>16</sub>	Cylohexane, 1,4-dimethyl-, cis-	93	112
					9.53	C <sub>9</sub> H <sub>20</sub>	Hexane, 2,3,5-trimethyl-	86	128
					9.65	C <sub>8</sub> H <sub>18</sub>	Heptane, 2,4,6-trimethyl-	90	142
					9.73	C <sub>6</sub> HO <sub>2</sub>	2,3-dioxabicyclo[2,2,1]heptane, 1-methyl-	82	114
					9.76	C <sub>11</sub> H <sub>24</sub>	Octane, 2,3,3-triethyl-	88	156
					9.9	C <sub>9</sub> H <sub>20</sub>	heptane, 2,5-dimethyl-	93	128
					9.98	C <sub>7</sub> H <sub>14</sub> O	Heptanal	82	114
					10	C <sub>5</sub> H <sub>10</sub> O	Butanal, 3-methyl-	78	86
					10.3	C <sub>12</sub> H <sub>26</sub>	Octane, 4,5-diethyl-	87	170
					10.4	C <sub>8</sub> H <sub>10</sub>	o-Xylene	94	106
					10.4	C <sub>12</sub> H <sub>18</sub>	Benzene, (3,3-dimethylbutyl)-	80	162
					10.5	C <sub>7</sub> H <sub>12</sub> O	2-Hexanone, 4-methyl-	83	114
					10.6	C <sub>9</sub> H <sub>20</sub>	Octane, 3-methyl-	93	128
					10.8	C <sub>8</sub> H <sub>16</sub> O	Octanal	83	128
					11.1	C <sub>12</sub> H <sub>26</sub> O	1-Octanol, 2-butyl-	89	186
					11.2	C <sub>7</sub> H <sub>6</sub> O	Heptanal	82	114
					11.4	C <sub>17</sub> H <sub>28</sub>	5-Tetradecane, (Z)-	82	196
					11.5	C <sub>9</sub> H <sub>12</sub>	Benzene, (1-methylethyl)-	83	120
					11.6	C <sub>12</sub> H <sub>26</sub> O	1-Decanol, 2-ethyl-	87	186
					11.7	C <sub>8</sub> H <sub>16</sub> O	Octanal	83	128
					11.8	C <sub>9</sub> H <sub>20</sub> O	1-Pentanol, 4-methyl-2-propyl-	85	144
					11.9	C <sub>7</sub> H <sub>6</sub> O	Benzaldehyde	78	106
					11.9	C <sub>10</sub> H <sub>20</sub> O	isooctane,(ethyenyloxy)-	81	156
					12	C <sub>11</sub> H <sub>17</sub> N	n-Butylbenzylamine	79	163
					12.2	C <sub>9</sub> H <sub>12</sub>	Benzene, 1-ethyl-3-methyl-	93	120
					12.3	C <sub>8</sub> H <sub>16</sub> O	Octanal	74	128
					12.3	C <sub>12</sub> H <sub>26</sub> O	1-Decanol, 2-ethyl-	76	186
					12.3	C <sub>9</sub> H <sub>12</sub>	Benzene, 1,3,5-trimethyl-	85	120
					12.5	C <sub>12</sub> H <sub>24</sub>	1-Decanol, 3,4-dimethyl-	87	168
					12.7	C <sub>8</sub> H <sub>16</sub> O	Octanal	86	128
					13	C <sub>10</sub> H <sub>20</sub> O	isooctane,(ethyenyloxy)-	84	156
					13.1	C <sub>8</sub> H <sub>16</sub> O	Octanal	79	128
					13.1	C <sub>8</sub> H <sub>16</sub> O	Octanal	75	128
					13.4	C <sub>9</sub> H <sub>12</sub>	Benzene	92	120
					13.4	C <sub>12</sub> H <sub>24</sub> O	Decanal	78	156
					13.5	C <sub>10</sub> H <sub>22</sub> O	1-Octanol, 2,7-dimetyl-	78	158
					13.6	C <sub>24</sub> H <sub>48</sub> O <sub>2</sub>	Hexanoic acid, octadecy ester	75	368
					13.7	C <sub>8</sub> H <sub>16</sub> O	Octanal	74	128
					14	C <sub>12</sub> H <sub>24</sub> O	Dodecanal	79	184
					14	C <sub>10</sub> H <sub>20</sub> O	Decanal	80	156
					14.1	C <sub>10</sub> H <sub>20</sub> O	Decanal	78	156

without Ozone					with Ozone				
Ret. time	chemical formula	chemical substance	simi-larity	M.W.	Ret. time	chemical formula	chemical substance	simi-larity	M.W.
					14.2	C <sub>11</sub> H <sub>22</sub> O	Undecanal	80	170
					14.5	C <sub>9</sub> H <sub>18</sub> O	Nonanal	85	142
					14.7	C <sub>12</sub> H <sub>24</sub> O	Dodecanal	77	184
					16.1	C <sub>10</sub> H <sub>20</sub> O	Decanal	87	156

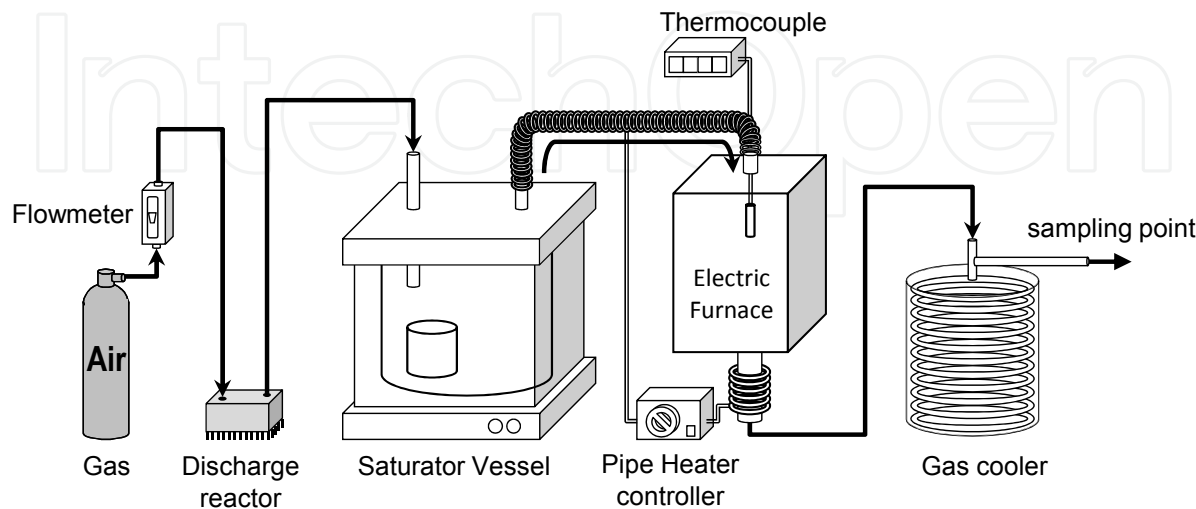
**Table 1.** List of chemical substances detected by GC-MS with and without ozone.

## 5. Combustion properties of n-Octane by ozone

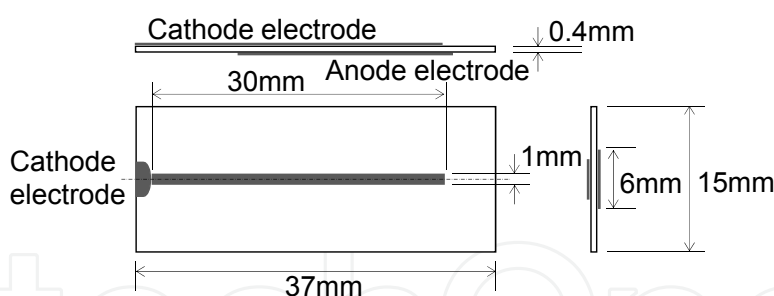
### 5.1. Reactor and analysis

Vapour-phase combustion reactions of n-octane with ozone are tested in a flow reactor indicated in Figure 10. Flow reactor mainly consists of discharge reactor to make ozonized air, saturator vessel to vaporise n-octane, electric furnace to combust vaporised n-octane and measure combustion temperature. Sampling point is located at the end of the flow reactor to analyse combustion reactions properties in the electric furnace. Ozone in gaseous form is generated by discharge reactor, which has four surface discharge chips indicated in Figure 11. Dry air is a source of ozone generation at discharge reactor and ozone concentration is maintained at 6.4g/m<sup>3</sup> in the test.

Carbon dioxide, carbon monoxide, oxygen and nitrogen in the exhaust gas, which is generated in the vapour-phase combustion reactions of n-octane, are analysed by gas chromatography with thermal conductivity detector (GC-TCD). Organic compounds in a gas at sampling point are analysed by gas chromatography with flame ionization detector (GC-FID). GC column with 4.0mm~6.0mm radius and 2.0m~6.0m length is made out of copper or stainless. GC column has packing materials for measuring gases in exhaust gas; Porapak-QS is used for analysing carbon dioxide, and MS-5A is used for analysing nitrogen, oxygen and carbon monoxide.



**Figure 10.** A schematic diagram of flow reactor system.



**Figure 11.** A schematic diagram of a surface discharge chip in discharge reactor.

## 5.2. Inversion rate of n-octane

Dry air or ozonized dry air is mixed to n-octane in saturator vessel and the gas mixture is combusted in the electric furnace varied from 200 to 800 degrees C for an hour. Combustion product gases are trapped and then analysed by GC-FID with diethyl ether as internal standard substance. Inversion rate of n-octane in vapour-phase combustion reactions is evaluated from n-octane concentration in exhaust gases. Concentration of n-octane is estimated by calibration curve, which determine the ratio of peak area and mass ratio of n-octane to that of the internal standard (diethyl ether) obtained from gas chromatogram. Furthermore, concentration of other main combustion product gases, such as nitrogen, oxygen, carbon dioxide and carbon monoxide, are analysed by GC-TCD as mentioned above and are appropriately quantified using calibration curve of peak area from gas chromatogram against known concentration.

Inversion rate of n-octane is derived from equation (1) that relates to the vapour pressure of n-octane (Antoine equation (2)) and the amount of n-octane (equation (3)).

$$I_r = 1 - \frac{C_o}{C_i} \quad (1)$$

$I_r$ : inversion rate of n-octane [%]

$C_o$ : concentration of unreacted n-octane in liquid reaction product [mol]

$C_i$ : initial concentration of n-octane [mol]

$$\text{Log}P = A - \frac{B}{T + C} \quad (2)$$

$P$ : vapour pressure [mmHg]

$A$ : 6.924 (as Antoine constant of n-octane)

$B$ : 11355.126 (as Antoine constant of n-octane)

$C$ : 209.517 (as Antoine constant of n-octane)

$T$ : temperature

$$F_{n-octane} = \frac{P_{n-octane} F_{air}}{P_{air}} \quad (3)$$

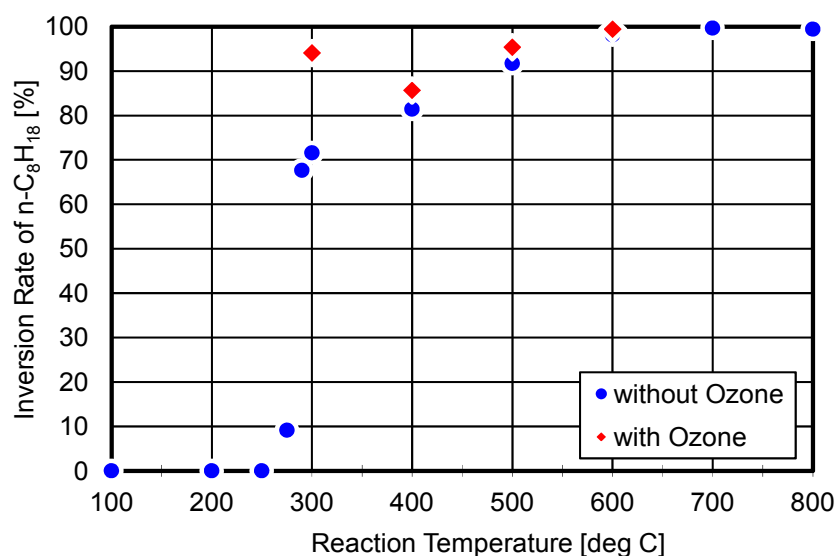
$F_{n\text{-octane}}$ : flow rate of n-octane [ml/min]

$P_{n\text{-octane}}$ : vapour pressure of n-octane [atm]

$F_{\text{air}}$ : flow rate of air [ml/min]

$P_{\text{air}}$ : vapour pressure of air [atm]

Inversion rate of n-octane in vapour-phase combustion against reaction temperature between 100 and 800 degree C is indicated in Figure 12. In comparison with dry air (without ozone), inversion rate tends to be higher when ozone is injected to saturator vessel. Especially, the rate indicates approximately 20% higher than without ozone around 300 degrees C of reaction temperature. Ozone gas is possible to react to n-octane in lower reaction temperature. Inversion rate of n-octane become similar in high temperature because it is suggested that half-life period of ozone tends to be shorter and then ozone becomes easily to decompose.

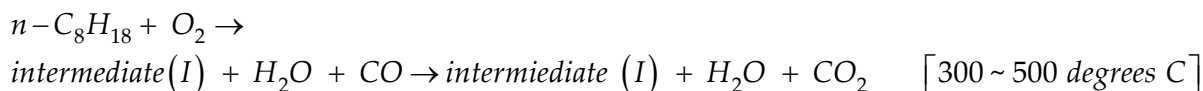


**Figure 12.** Relationship between reaction temperature and inversion rate of n-octane in vapour-phase combustion

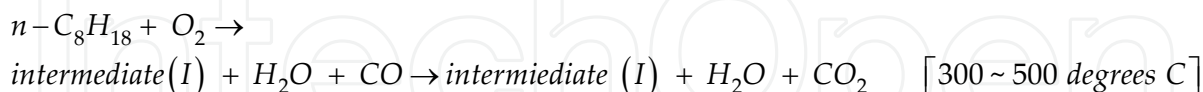
### 5.3. Concentration of combustion product gases

On vapour-phase combustion reactions of n-octane with/without ozone, concentration of carbon dioxide and carbon monoxide is measured. Relationship between product gas concentration and reaction temperature is indicated in Figure 13. When with/without ozone flow into saturation vessel, concentration of carbon monoxide that is produced at the time of incomplete combustion gradually increases until 600 degrees C. Then concentration of carbon monoxide rapidly decreases in 700 degrees C of reaction temperature, and simultaneously, carbon dioxide increases very quickly in the case of combustion with dry air. Furthermore, in combustion with ozone-rich air, concentration of carbon dioxide indicates rapidly higher in 600 degrees C. It is supposed that n-octane with ozone combustion almost achieve complete combustion in 100 degrees lower than without ozone combustion. As a result, it is suggested that combustion reactions with/without ozone indicate a same reactions and proceed simultaneously with different reactions below.

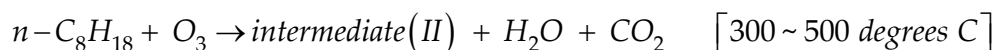
## Combustion reactions of n-octane without ozone



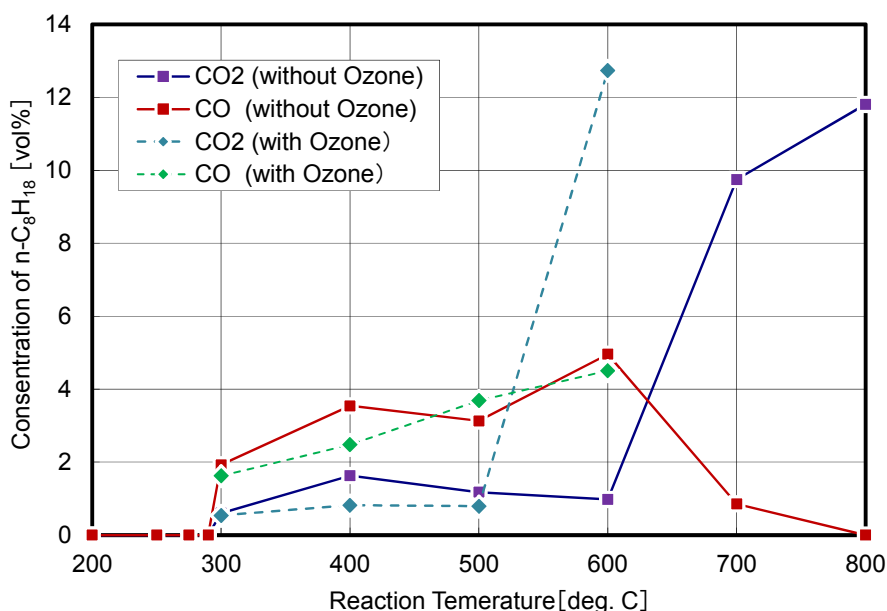
## Combustion reactions of n-octane with ozone



## Combustion reactions of n-octane with ozone



Intermediate (I) and (II) in chemical equation indicate reaction products in combustion with/without ozone respectively. Combustibility of intermediate (II) is possibly higher than intermediate (I) and carbon dioxide directly generate by complete combustion. Therefore, concentration of carbon monoxide against reaction temperature indicates a similar tendency regardless of ozone injection. Furthermore, it is found that the intermediate product is obtained by GC-FID when mixture gas of n-octane and ozone or dry air is combusted. In addition, the intermediate product is NOT detected under the condition of only mixing vapour n-octane and ozone or dry air.



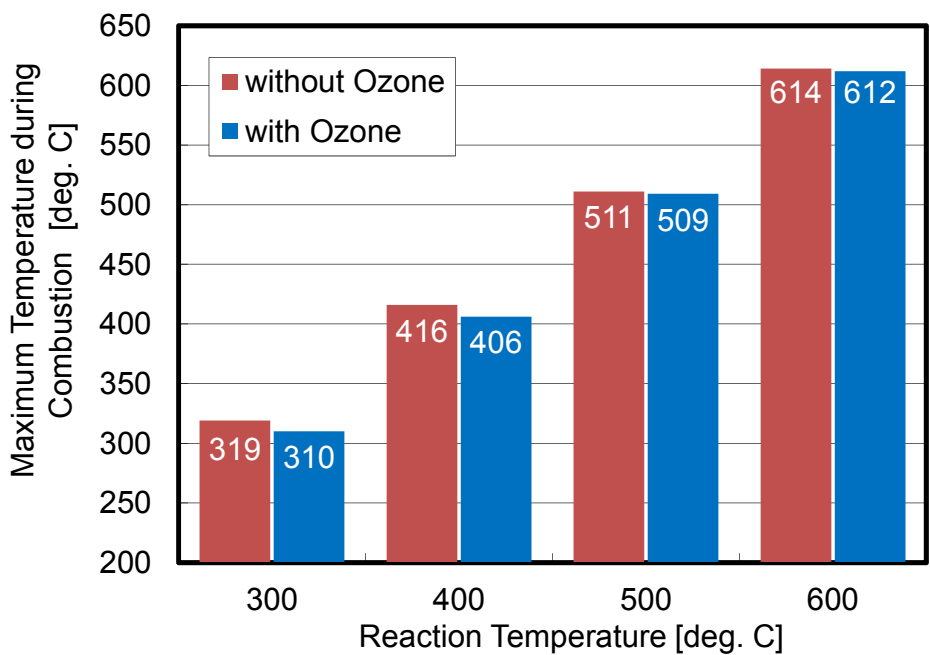
**Figure 13.** Relationship between product gas concentration and reaction temperature

#### 5.4. Combustion heat

On vapour-phase combustion reactions of n-octane with/without ozone, maximum combustion heat in electric furnace is measured when reaction temperature is from 300 to

600 degrees C (Figure 14). Combustion heat with ozone indicates around 10 degrees C lower on each reaction temperatures compared with dry air (without ozone). One of the reasons of low combustion heat is possibly intermediate products caused by ozone.

Besides, the time to even out the combustion heat of electric furnace takes approximately 10 minutes in the case of ozone injection, although combustion heat without ozone takes more than 30 minutes. Ozone injection may contribute stable combustion because the time to even out the temperature of electric furnace also becomes shorter than without ozone.



**Figure 14.** Relationship between maximum combustion heat and reaction temperature

## 6. Conclusion

FTIR spectra of vaporised hydrocarbon compounds (commercially available petrol and light diesel oil) mixed with discharged dry air were analysed for investigating intake stroke. Reaction products were found after ozone injection at around  $1725\text{cm}^{-1}$  of FTIR spectra, and generation rate of it was strongly related to ozone concentration. Furthermore, it was found that thin ozone ( $0.76\text{g/m}^3$ ) contributed to the generation of the reaction products, and ozone unused for the reaction was detected as extra at around  $1058\text{cm}^{-1}$  and  $2120\text{cm}^{-1}$ . Hydrocarbon combined with oxygen atom or molecule was detected by GC-MS and many of these reaction products had the FTIR spectra near  $1725\text{cm}^{-1}$ . Extra ozone logically decomposed in the cylinder under the condition of the high pressure and high temperature. It was supposed that hydrocarbon was progressively ozonised in the cylinder, and these reaction products contributed to an efficient combustion.



It was found that the inversion rate indicates approximately 20% higher than without ozone especially in low temperature around 300 degrees C of reaction temperature. Furthermore, it is supposed that n-octane with ozone combustion almost achieve complete combustion in 100 degrees lower in comparison with air combustion. One of the reasons of high combustibility is possibly intermediate product obtained by combustion of mixture gas of n-octane and ozone.

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