Influence of Gas Humidity and Gas Flow Rate on Ozone Production and Ethylene Decomposition Using Dielectric Barrier Discharge

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Abstract—An influence of relative humidity and gas flow rate on O3 production and ethylene decomposition using dielectric barrier discharge is evaluated. The removal of C2H4 is also investigated in the presence of manganese dioxide (MnO2). In the present experiment, N2 and O2 gas mixture is fed into the DBD reactor with a mixing rate of N2: O2 = 8:2 at 5 or 10 L/min gas flow rate. C2H4 gas is diluted by N2 to 8 ppm. The relative humidity of the gas is adjusted by bubbling gas through water at 0 and 80%RH. The experimental result shows that the O3 concentration and yield with bubbling are lower than without bubbling and it is almost independent of gas flow rate. The concentration of C2H4 without bubbling is lower than that with bubbling. With bubbling, the concentration of C2H4 with catalyst is higher than that without catalyst.

II. METHODOLOGY

Fig. 1 shows the schematic diagrams of the DBD reactor. The reactor consists of a resinous box. 12 parallel electrodes are placed in the box. The electrode consists of a wire covered by alumina as a dielectric barrier. The outer diameter and thickness of the dielectric barrier are 1.0 mm and 0.25 mm, respectively. The wire in the electrodes are connected to a high voltage power supply and the ground terminal. Six electrode pairs are set in line perpendicular to the gas flow. The gap and distance between the electrode pairs are 0.33 mm and 2.17 mm, respectively. The sinusoidal high voltage is supplied to the reactor at the frequency of 33 kHz. Fig. 2 shows the photographs of the DBD reactor with and without discharges. When the high voltage is applied to the high voltage electrode, discharge occurs only in the shorter gap between electrodes. The electrode structure enables a large gas flow rate with the cooling effect.

Fig. 3 shows the schematic diagram of the experimental setup. In the present experiment, C2H4 is diluted by 8ppm with 20% O2 and N2 balance, and is fed into the DBD reactor at a gas flow rate of 5 L/min and 10 L/min. The MnO2 catalyst (WAKO System MD-7) is employed to investigate decomposition of ethylene and put in a cylinder (28 mm in inner diameter and 150 mm in height). The catalyst has pellet (3 mm diameter and 7 mm in length). The volume of the catalyst set into the catalytic reactor is 92×10^-3 L. Relative humidity of the gas is adjusted to 80%RH, 22×10^3 ppm in H2O concentration at 25°C, by bubbling the gas into the water in the bubbling vessel. Without bubbling, the water molecular is not contained in the gas. The gas temperature is fixed at 25°C and the temperature and relative humidity is measured using a thermo-hygrometer (TENMARS TM-305). The O3 concentration of the exhaust gas is measured using an O3 monitor (Ebara EG-2001B). The C2H4 concentration is lower than that with bubbling. With bubbling, the concentration of C2H4 with catalyst is higher than that without catalyst.
where $U (J)$ is the consumed energy in the DBD reactor per a cycle, $v (V)$ is the applied voltage to the DBD reactor and $q (C)$ is the accumulated charge on the capacitor.

The input energy density $w (J/L)$ is determined using the consumed energy as follows:

\[ w = \frac{60 \cdot U \cdot f}{Q} \]  \hspace{1cm} (2)

where $f (33 \text{ kHz})$ and $Q (L/min)$ are the frequency of the applied voltage and the gas flow rate, respectively. The energy efficiency $\eta_{O3} (\text{g/kWh})$, which is determined as $O_3$ production per input energy density, is obtained using

\[ \eta_{O3} = \frac{60 \cdot Q \cdot [O_3] \cdot M_{O3}}{n \cdot U \cdot f} \]  \hspace{1cm} (3)

where $[O_3]$ is the $O_3$ concentration (ppm) in the gas mixture after treatment, $M_{O3}$ is the $O_3$ molecular mass (g/mol) and $n$ is the mass volume per mol (L/mol).

### III. RESULTS AND DISCUSSION

#### A. Characteristics of Discharges

Fig. 4 shows the waveforms of the applied voltage to the reactor, the discharge current and accumulated charge on the capacitor without bubbling. The applied voltage is 6.5 kVpp. The numerous micro-discharges occur in every half cycle. Fig. 5 shows $V-Q$ Lissajous diagram at 6.5 kVpp applied voltage with and without bubbling. $V-Q$ Lissajous is independent of relative humidity. The permittivity of the dielectric barrier is determined to be 9.0 from $V-Q$ Lissajous which is obtained by dividing the capacitance by the volume of the dielectric barriers [17]. Fig. 6 shows the...

![Fig. 1. The schematic diagrams of (a) the cross section and (b) electrode arrangement of the DBD reactor.](image1)

![Fig. 2. The photographs of the DBD reactor. (a) without discharge (b) with discharge.](image2)

![Fig. 3. The schematic diagram of the experimental setup.](image3)

![Fig. 4. Waveforms of the applied voltage, the discharge current and accumulated charge on the capacitor.](image4)

![Fig. 5. V-Q Lissajous diagram at 6.5 kVpp applied voltage at relative humidity.](image5)
consumed energy and input energy density into the DBD reactor per one cycle of applied voltage as a function of applied voltage with and without bubbling. The consumed energy and the input energy density increase with increasing the applied voltage and are almost independent of the humidity.

Fig. 7 shows the consumed energy and input energy density as a function of applied voltage at the gas flow rate of 5 and 10 L/min. The consumed energy in the case of 5 L/min is higher than that of 10 L/min. Fig. 8 shows the temperature distribution chart of DBD reactor taken by a thermal imaging camera (FLIR TG165K) at continuous operation time of 5 min without bubbling. The highest temperature in the reactor is observed on the surface of the electrode, and is 27.2, 50.0 and 99.0°C in the case of applied voltage of 5.2, 7.2 and 8.3 kVpp, respectively. In the experiment, the temperature of exhaust gas is almost same as the inlet gas, 25°C, for every experimental condition. Fig. 9 shows the electrode temperature as a function of continuous operation time for two gas flow rates, 5 and 10 L/min. The electrode temperature in the case of 5 L/min is higher than that of 10 L/min at the same applied voltage. The onset voltage is estimated from $V-Q$ Lissajous and is 0.66 and 0.47 at the gas flow rate of 5 L/min and 10 L/min, respectively. Since the mean free path increases with increasing the temperature according to Boyle Charles law, the discharge onset voltage decreases [18]. The gas temperature at vicinity of the electrode surface is heated by the electrode. Therefore, the input energy density which is proportional to the consumed energy per a pulse increases with decreasing the gas flow rate.

B. $O_3$ production

Fig. 10 shows the $O_3$ concentration and yield as a function of input energy density with and without bubbling. The $O_3$ concentration increases with increasing input energy density and is saturated when the input energy density is higher than 143 J/L. The $O_3$ yield decreases with increasing input energy density. The $O_3$ concentration and yield with bubbling are lower than that without bubbling. Fig. 11 shows the $O_3$ concentration as a function of continuous operation time with and without bubbling for various applied voltages. The DBD operation is started at time of 0 min. The $O_3$ concentration increases until 1 minute and then decreases with increasing the operation time. Increase in gas temperature could decrease $O_3$ concentration by increasing decomposition reaction of $O_3$ [19]. In non-thermal plasma generated by DBD, atomic oxygen is produced through the direct electron impact process through the following reactions;

![Fig. 6. Consumed energy and input energy density as a function of applied voltage with and without bubbling.](image)

![Fig. 7. Consumed energy and input energy density as a function of applied voltages at gas flow rate of 5 and 10 L/min.](image)

![Fig. 8. Temperature distribution chart of DBD reactor taken by a thermal imaging camera at gas flow rate of 5L/min.](image)

![Fig. 9. The electrode temperature as a function of continuous operation time.](image)
\[ e + O_2 \rightarrow O + O + e \]
\[ k_1 = \exp\left(-7.9-16.9/(E/N)\right) \text{ cm}^3/\text{s} \quad \text{(R1)}, \]
\[ O + O_2 + M \rightarrow O_3 + M \]
\[ k_2 = 6.2 \times 10^{-34} \times (300/T)^2 \text{ cm}^6/\text{s} \quad \text{(R2)}, \]

where \( E/N \) means the reduced electric field and \( M \) is the third body and \( T \) is the gas temperature [20].

When the \( O_3 \) concentration or gas temperature is high, \( O_3 \) reacts with \( O \) and it returns to \( O_2 \) [21];
\[ O + O_3 \rightarrow 2O_2 \]
\[ k_3 = 1.8 \times 10^{-11} \exp(-2300/T)^2 \text{ cm}^3/\text{s} \quad \text{(R3)}. \]

When the gas contains \( H_2O \) molecule, \( O \) radical and \( O_3 \) react with \( H_2O \) and hydroxyl radical (OH) as following reaction:
\[ H_2O + O \rightarrow 2OH \]
\[ k_4 = 2.2 \times 10^{-10} \text{ cm}^3/\text{s} \quad \text{(R4)}, \]
\[ OH + O \rightarrow O_2 + H \]
\[ k_5 = 2.4 \times 10^{-11} \text{ cm}^3/\text{s} \quad \text{(R5)}, \]
\[ OH + O_3 \rightarrow HO_2 + O_2 \]
\[ k_6 = 1.7 \times 10^{-12} \text{ cm}^3/\text{s} \quad \text{(R6)}. \]

The values of \( k_4, k_5 \) and \( k_6 \) are calculated with 300 K of temperature [19], [22]. Therefore, the \( O_3 \) concentration decreases [20].

Fig. 12 shows the \( O_3 \) concentration and yield as a function of input energy density at gas flow rate of 10 L/min without bubbling. In comparison with \( O_3 \) concentration and yield without bubbling (0%RH) in Fig. 10, the \( O_3 \) concentration and yield are almost independent of gas flow rate. As shown in Fig. 12, the \( O_3 \) concentration is lower than 400 ppm without bubbling, the amount of \( O \) consumed in R3 increases with increasing \( O_3 \) concentration and gas temperature [21]. When the \( O_3 \) concentration is in order of \( 10^2 \) ppm in the case of a cylindrical DBD reactor [23], \( O_3 \) concentration linearly increases with increasing input energy density. The almost inlet gas is passed through the gap without discharge occurs in the cylindrical DBD reactor. On the other hands, assuming that the gas flow rate is proportional to the cross sectional area for gas, the only one seventh of the total inlet gas could pass through the gap with discharge because the cross section of the area between electrodes without discharges is approximately 7 times wider than that with discharge. When the exhaust \( O_3 \) concentration is 400ppm, the local \( O_3 \) concentration in the discharge area is obtained by multiplying the exhaust \( O_3 \) concentration by 7 and estimated to be approximately 2800ppm. When the \( O_3 \) concentration is high, the \( O_3 \)
production is limited by O$_3$ decomposition by O as shown in R3. Furthermore, the increase in gas temperature enhances the O$_3$ decomposition. Therefore, O$_3$ yield decreases as a function of input energy density.

Fig. 13 shows the O$_3$ concentration as a function of input energy density with and without MnO$_2$ catalyst. The O$_3$ concentration with the catalyst is lower than without catalyst because the catalyst decomposes O$_3$ to oxygen molecules and atomic oxygen species on the catalyst surface [6].

C. C$_2$H$_4$ decompositions

Fig. 14 shows the C$_2$H$_4$ concentration as a function of input energy density with and without MnO$_2$ catalyst. The concentration of C$_2$H$_4$ without bubbling is lower than that with bubbling. With bubbling, the concentration of C$_2$H$_4$ with catalyst is not lower than that without catalyst. When O$_3$ is not present in the inlet gas into the cylinder contains the catalyst, the C$_2$H$_4$ concentration does not change. Therefore, the C$_2$H$_4$ is not absorbed to the catalyst. [6]. It has been reported that the oxidation activity of a certain kind of catalysts is enhanced with O$_3$ by active species such as the peroxide species and the atomic oxygen species formed on their surface by the decomposition of O$_3$ [24]. Therefore, the amount of active species increases with increasing O$_3$ concentration and the active species on the catalyst surface improves the C$_2$H$_4$ decomposition [24]. O$_3$ decomposition by the catalysts could be disturbed by the adsorption of H$_2$O.

When the gas includes C$_2$H$_4$, the O radicals or O$_3$ react with C$_2$H$_4$ as follows [7], [25];

\[
\text{O + C}_2\text{H}_4 \rightarrow \text{CHO} + \text{CH}_3, \\
k_7 = 3.45 \times 10^{-18} \times T^{2.08} \text{ cm}^3/\text{s} \quad (R7),
\]

\[
\text{O + C}_2\text{H}_4 \rightarrow \text{CH}_2\text{CHO} + \text{H}, \\
k_8 = 2.0 \times 10^{-18} \times T^{2.08} \text{ cm}^3/\text{s} \quad (R8),
\]

\[
\text{O}_3 + \text{C}_2\text{H}_4 \rightarrow \text{products} \\
k_9 = 1.2 \times 10^{-14} \times \exp (-2630/7) \text{ cm}^3/\text{s} \quad (R9).
\]

The rate constants $k_7$, $k_8$ and $k_9$ are obtained as $4.9 \times 10^{-13}$, $2.8 \times 10^{-13}$, and $1.9 \times 10^{-18} \text{ cm}^3/\text{s}$ under the assumption of $T = 300 \text{ K}$. OH radicals produced by R4 also react with C$_2$H$_4$:

\[
\text{OH} + \text{C}_2\text{H}_4 \rightarrow \text{products} \\
k_{10} = 8.0 \times 10^{-12} \text{ cm}^3/\text{s} \quad (R10).
\]

The rate constant of C$_2$H$_4$ oxidation by O$_3$ is much lower than those by O and OH radicals. Since the life-time of O and OH radicals are several ten μs to hundred μs and several ten μs, respectively, these reactions occur at the vicinity of the discharge channel between the pair of the electrodes. One seventh of the total gas passes through the discharge regions due to the ratio of the cross-sectional area. Therefore, the reaction between C$_2$H$_4$ and O$_3$ as shown in R9 mainly contributes to C$_2$H$_4$ decomposition. However, as shown in Fig. 14, the concentration of C$_2$H$_4$ with the MnO$_2$ catalyst is higher than without MnO$_2$ when the gas includes H$_2$O molecule. It is assumed that the C$_2$H$_4$ decomposition on the catalyst surface decreases since O radicals formed on their surface is consumed by the reaction with H$_2$O molecules [26].

IV. CONCLUSIONS

The influence of the humidity and gas flow rate on O$_3$ production and C$_2$H$_4$ decomposition is investigated. The consumed energy and the electrode temperature in the case of 5 L/min are higher than that of 10 L/min at the same applied voltage. Since the mean free path increases with increasing the temperature, the discharge onset voltage decreases. The O$_3$ concentration and yield with bubbling are lower than without bubbling because O radicals and O$_3$ react with OH radicals and H$_2$O molecules. The O$_3$ concentration is lower than 400 ppm without bubbling because O$_3$ destruction by R3 occurs and it causes the decline of O$_3$ yield as a function of input energy density. The concentration of C$_2$H$_4$ without bubbling is lower than that with bubbling because the amount of active species increases with increasing O$_3$ concentration and the active species on the catalyst surface improves the C$_2$H$_4$ decomposition. With bubbling, the concentration of C$_2$H$_4$ with catalyst is not lower than that without catalyst because the C$_2$H$_4$ decomposition on the catalyst surface decreases since O radicals formed on their surface is consumed by the reaction with H$_2$O molecules.

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REFERENCES


