Effect of the dielectric barrier discharge on the combustion
promotion of ammonia/oxygen/nitrogen premixed gas

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Abstract
The effect of the non-equilibrium plasma superposition on the ammonia / oxygen / nitrogen unburned premixed gas was investigated to improve the laminar burning velocity as the combustion characteristics. When ammonia was used as a fuel, it was necessary to improve the laminar burning velocity of ammonia premixed flame because the combustion characteristics of ammonia were too lower than those of fossil fuel. The plasma-assisted combustion was the one of the methods to improve the combustion characteristics. Especially, the effect of the dielectric barrier discharge (DBD) on the burning velocity as the indicator of combustion quality of ammonia was experimentally investigated in this study. In experiments, a slot burner was used to measure the burning velocity. DBD was superimposed on ammonia / oxygen / nitrogen unburned premixed gas just before it was entered into the flame zone. To understand effects of the condition of the electric power source of DBD, the peak to peak voltage of DBD was varied from 0 kV to 30 kV. The equivalence ratio was varied from 1.0 to 1.2. The results showed that the burning velocities became faster with increasing the peak to peak voltage of DBD, the largest increase of the burning velocity was observed at the stoichiometric condition in all conditions of the DBD power source.

Key words : Renewable energy, Ammonia, Plasma-assisted combustion, Dielectric barrier discharge, Laminar burning velocity, CO₂-free fuel

1. Introduction

Energy consumption in the world has been increased every year. Total energy consumption in the world is supposed to become 1.3-times large value in 2035 compared with that in 2011 (IEA, 2013). That means that the consumption of fossil fuel will be increased with the increase of the primary energy consumption. Although 87% of the primary energy is provided by the combustion of fossil fuels, there are two big problems to be solved to use fossil fuels. First, the emission of CO₂ cannot be avoided as long as we use the hydrocarbon fuel. Second, fossil fuels are supposed to be exhausted in near future. Therefore, it is important to develop the alternative fuel as “CO₂-free” fuel.

Ammonia is focused as one of the alternative fuel which has a feature of “CO₂-free fuel”. Since a big national project for using ammonia as a fuel has started from 2014 in Japan, the number of researches of ammonia as an alternative fuel will increase from now on. Ammonia doesn’t emit CO₂ during the combustion process because it doesn’t have the carbon atoms in its molecular structure. This can be also understood from the overall reaction of ammonia. Ammonia has some advantages: 1) Ammonia can be easily liquefied at 0.85 MPa under the room temperature. 2) The technologies of mass transport and mass storage of ammonia have already been developed. 3) Ammonia is easily generated from hydrogen and nitrogen by the Harbor-Bosch process. Ammonia has the good capacity of hydrogen transport and storage. Its hydrogen mass density is 17.8%, the hydrogen volume density of its liquid is more than 1.5 times as much as liquid hydrogen (Kojima, 2014).

Table 1 shows the flammable ranges of substances (Kojima, 2014). Table 1 shows that risk of explosion substance
of ammonia is low because the flash point of ammonia (132 ℃) and the ignition point (651 ℃) are both higher than hydrogen or fossil fuels. Also, flammable range of ammonia is narrower than that of fossil fuels.

Table 1 The flammable ranges of various substances.

<table>
<thead>
<tr>
<th>Material</th>
<th>Explosion limit (%)</th>
<th>Flash point (℃)</th>
<th>Ignition point (℃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>16 ~ 25</td>
<td>132</td>
<td>651</td>
</tr>
<tr>
<td>Methane</td>
<td>5 ~ 15</td>
<td>-188</td>
<td>537</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4 ~ 74</td>
<td>-157</td>
<td>530</td>
</tr>
<tr>
<td>LPG (propane)</td>
<td>2.1 ~ 9.5</td>
<td>-104</td>
<td>450</td>
</tr>
<tr>
<td>Methanol</td>
<td>6 ~ 36</td>
<td>11</td>
<td>464</td>
</tr>
<tr>
<td>Gasoline</td>
<td>1.4 ~ 7.6</td>
<td>-40</td>
<td>300</td>
</tr>
</tbody>
</table>

To use ammonia as an alternative fuel, one of the major problems is that the low laminar burning velocity of ammonia / air mixture. Takizawa indicated the laminar burning velocity of the ammonia / air premixed gas as 7.2 cm/s (Takizawa, et al., 2008). Ronney showed that the laminar burning velocity of the ammonia / air premixed gas was 8 cm/s (Ronney, 1988). The value of the laminar burning velocity of ammonia was about 20 % compared to the laminar burning velocity of methane which is the lowest value of fossil fuels (Verkamp, et al., 1967). Therefore, to use ammonia as an alternative fuel, it is necessary to obtain the specific condition and/or to develop the effective procedure which can increase the laminar burning velocity of ammonia. In this study, the plasma-assisted combustion was focused as one of the method to improve the combustion qualities.

It is known that the plasma-assisted combustion with using the non-equilibrium plasma can improve the combustion characteristics (Starikovskaia, 2006, Starikovskii, 2005, Bozhenkov, et al., 2003, Kim et al., 2010, Michael and Miles, 2011, Ombrello, et al., 2010, Sasaki and Shinohara, 2012, Starikovskii and Aleksandrov, 2013). Bozhenkov, et al. conducted the shock tube experiment to elucidate the effects of the nanosecond pulsed discharge on combustion. Nanosecond pulse discharge is a non-equilibrium plasma. Non-equilibrium plasma is possible to excite some molecules in the premixed gas without increasing the temperature of the premixed gas. Therefore, it is possible to extract the effects of nanosecond pulsed discharge on the chemical reaction. Results indicated that the ignition delay time of the hydrogen became short by nanosecond pulse discharge (Bozhenkov, et al, 2003). Niemi, et al. succeeded the quantitative measurement of oxygen radicals formed in nanosecond pulse discharge by TALIF (Two Photon Laser Induced Fluorescence). He proved that the consumption of oxygen radicals formed in nanosecond pulse discharge in fuel / air mixture was faster than that in normal air. Therefore, it was shown that fast reactions of fuel and oxygen radicals were led to the combustion process of the plasma-assisted combustion (Niemi, et al., 2005). Zuzeek, et al. elucidated that the exothermic reaction of the ethylene / air mixture and hydrogen / air mixture with the plasma superposition came from the reaction between the fuel and oxygen radicals and hydrogen radicals generated by the plasma superposition (Zuzeek, et al., 2010). Also, there are several studies about the effect of the superposition of the non-equilibrium plasma on the speed of flame propagation. Ombrello, et al. conducted experimental and numerical studies for elucidating the effects of the reaction of ozone and the long life time radical species (O, O2(v) and O2 (1D)) on the flame propagation. Those species were generated by the superposition of dielectric barrier discharge (DBD) to the unburned oxygen. DBD is one of a non-equilibrium plasma that the discharges forms in between the electrodes covered by the dielectric barriers. It is possible to generate spatially uniform discharge because the strength and direction of the electric field are the same in everywhere in the area of electrode. Results showed that the flame propagation velocity of the laminar lifted flame of propane / oxygen / nitrogen gas was increased by ozone (Ombrello, et al., 2010).

As mentioned above, plasma-assisted combustion can be the possible procedure to improve the combustion characteristics of low combustibility fuel such as ammonia. Equation (1) shows that the overall reaction of electron collision when plasma is superimposed to ammonia / oxygen / nitrogen premixed gas.

\[
NH_3 + e \rightarrow 0.5N_2 + 1.5H_2 + e
\] (1)

From Eq. (1), it is considered that hydrogen is generated with the plasma superimposed to ammonia.
Equation (2) to (5) show that the main elementary reactions including electron collision (Kambara, et al., 2013).

\[ \text{NH}_3 + e \leftrightarrow N + H + H_2 + e \]  
\[ H + H + M \leftrightarrow H_2 \]  
\[ N + N \leftrightarrow N_2 \]  
\[ N + 3H \leftrightarrow \text{NH}_3 \]

From Eq. (2) to (5), it can be understood that hydrogen and hydrogen radicals are generated if there is the reaction of electron collision in ammonia / oxygen / nitrogen premixed gas. Since hydrogen and hydrogen radicals are regarded as the promoter of combustion reaction, it is expected to improve the laminar burning velocity of ammonia / oxygen / nitrogen premixed gas by using the plasma assisted combustion. It is also reported that ammonia is decomposed by the non-equilibrium plasma. Kambara, et al. investigated that the effect of non-equilibrium plasma on the Ar / ammonia premixed gas. The results showed that the amount of ammonia was decreased with the increase of the applied voltage, and ammonia was completely decomposed into hydrogen and nitrogen at the applied voltage of 15 kV (Kambara, et al., 2013). Fateev, et al. investigated that the effect of the atmospheric non-equilibrium plasma on Ar / ammonia premixed gas and evaluated for decomposition of ammonia. The results showed that nitrogen, hydrogen and hydrazine were generated. Also, they showed that the amount of hydrazine was correlated to between discharge voltage density and ammonia concentration (Fateev, et al., 2005).

In this study, the DBD superposition on the ammonia / oxygen / nitrogen premixed gas was conducted to clarify the effects of DBD on the ammonia combustion.

2. Material and methods

2.1 Experimental apparatus

Figure 1 shows the schematic illustration of the experimental apparatus. Experimental system was composed with a slot burner and a discharge system. The premixed flame formed on a slot burner is suitable to measure the flame height. In that case, the laminar burning velocity is easy to be calculated. The premixed combustible mixture of ammonia / oxygen / nitrogen was supplied through the sintered metal with pore size of 40 μm, the stainless steel mesh with a size of 1 mm, a ceramic honeycomb with a size of 1 mm and vena contracta.

![Fig. 1 Schematic illustration of experimental apparatus.](image-url)
Figure 2 shows the direct photograph of laminar premixed flame formed on the slot burner and the calculation method of laminar burning velocity. Laminar burning velocity can be calculated by the following equation.

\[ \alpha = \tan^{-1}\left(\frac{X}{H}\right) \]  

(6)

\[ S_u = U_u \sin \alpha \]  

(7)

From Eq. (6), (7), laminar burning velocity was determined by measuring the flame height and flow rate of unburned premixed gas (Mizutani, 1977).

Figure 3 shows the slot burner that have a rectangular exit port of 40 mm × 4 mm. The nozzle of the slot burner was made from glass. This is because the long axis side of the slot burner was used as the dielectric barrier. The burner was provided with two concaves in 10 mm × 36 mm × 2.5 mm, at the position of 8 mm from the burner exit. This concave intends to decrease the distance between the electrodes to generate DBD in low applied voltage. In this study, the gap distance was set to 4 mm and the thickness of dielectric barriers were set to 1 mm. The applied voltage on electrodes is AC sinuous wave. The DBD was generated between the electrodes.
Fig. 3 The direct photograph of glass slot burner in the experiments and its dimensions.

Sine wave AC power supply systems were composed by function generator and high-voltage amplifier. In this study, the voltage was varied from 0 to 40 kV peak to peak and the frequency was varied from 0 to 7000 Hz.

2.2 Experimental conditions and method
2.2.1 Derivation of the averaged laminar burning velocity

Table 2 shows the experimental conditions. It was difficult to form ammonia / air premixed flame on the slot burner because of the low laminar burning velocity of ammonia / air. Therefore, the oxygen-enriched combustion was applied to form the ammonia flame stable. The premixed gas flow rate was set to 6 L/min. The applied voltage was varied at 0 kV, 10 kV, 20 kV, 25 kV, and 30 kV and breakdown voltage. Frequency of the AC power source was set to 7000 Hz. The digital camera (D7000) was used to get shape of the flame from the long axis direction of the slot burner. Exposure time of the photograph and f number of the camera lens were 1/8000 s and 1.2, respectively. The average flame height was calculated by using the area of the flame zone obtained from the direct photograph because the flame shape became wavy with the DBD superposition. The average laminar burning velocity was calculated from the average flame height.
Table 2 Experimental conditions for direct imaging of the flame.

| Frequency of the AC power supply [Hz] | 7000 |
| Flow rate of premixed gas [L/min] | 6 |
| Oxygen concentration [%] | 30 |
| Equivalence ratio : $\phi$ | 1.0, 1.1, 1.2 |
| Applied voltage [kV] | 0, 10, 20, 22 (Breakdown voltage), 25, 30 |
| Exposure time [s] | 1/8000 |

2.2.2 Evaluation of effects of ozone on the laminar burning velocity

The effects of the amount of ozone on the ammonia / oxygen / nitrogen premixed gas were investigated. Table 3 shows the experimental conditions. In this study, oxygen / nitrogen premixed gas was used for evaluating the effect of ozone on the ammonia flame. To keep the flow rate constant, the flow rate of nitrogen was increased in the oxygen / nitrogen premixed gas condition. The applied voltage of DBD was set to 28 kV which was the breakdown voltage in the oxygen / nitrogen premixed gas condition. The frequency was set to 7000 Hz for both conditions. To measure the concentration of ozone, the Kitagawa gas detector tube was used. The measurements of ozone were conducted under unburned conditions. The gas sampling probe of the Kitagawa gas detector was set at the burner exit.

Table 3 Experimental conditions of $O_3$ detection.

| Premixed gas composition | NH$_3$/O$_2$/N$_2$ | O$_2$/N$_2$ |
| Frequency of the AC power supply [Hz] | 7000 |
| Total flow of premixed gas [L/min] | 6 |
| Ammonia flow rate [L/min] | 1.71 |
| $O_2$ flow rate [L/min] | 1.29 |
| $N_2$ flow rate [L/min] | 3.00 |
| Equivalence ratio : $\phi$ | 1.0 |
| Applied voltage [kV] | 28 |
| Shot speed of the single-lens reflex camera [fps] | 8000 |

3. Experimental results and discussion
3.1 Derivation of the averaged laminar burning velocity

Figure 4 (a) ~ (e) shows direct photographs of the flame with the DBD superposition taken from the long axis direction of the slot burner. It is found from Fig. 4 (a) ~ (c) that the deformation of the flame shape (wavy shape) did not appeared under the low applied voltage condition. On the other hand, Fig. 4 (d), (e) showed that the shape of the flame were became wavy shape and the flame height became shorter with increasing applied voltage. It can be understood from Fig. 4 that the DBD superposition affected the flame height, and the flame shape. Flame was deformed to the wavy shape in the DBD superposition condition. DBD has a lot of streamer type discharges which doesn’t appeared at the same place in the same time. Therefore, the effect of DBD superposition on the flame appeared locally and it deformed the flame shape.
Fig. 4 Direct photographs of flames of different equivalence ratios of $\phi = 1.0$, 1.1 and 1.2: (a) w/o, (b) 10 kV, (c) 20 kV, (d) 22 kV, (e) 30 kV.

Figure 5 shows that the relationship between the average laminar burning velocity, equivalence ratio and the applied voltage. Figure 5 showed that the average laminar burning velocities didn’t change with the applied voltage under the breakdown voltage except in the stoichiometric condition. In the stoichiometric condition, it is necessary to investigate the reason why the average laminar burning velocity without DBD was lower than that in the condition of applied voltage 10 kV or 20 kV. Also, Fig. 5 showed that the average laminar burning velocities were increased with increasing the peak to peak voltage of DBD in the conditions of applied voltages higher than 22 kV. Since the applied voltage of 22 kV is the breakdown voltage, it can be thought that the increase of the average laminar burning velocity comes from the effect of the DBD superposition.

Figure 6 shows that the relationship between the increasing rates of the average laminar burning velocities, equivalence ratio and the applied voltage. The increasing rates of the average laminar burning velocities were calculated based on the average laminar burning velocities in the conditions of applied voltages from 0 to 20 kV at each equivalence ratio. Figure 6 showed that the increasing rates of the average laminar burning velocities were higher in low equivalence ratio conditions than those values of high equivalence ratio condition. The maximum increasing rate of the average laminar burning velocity was increased up to 26.1 % when the equivalence ratio was 1.0 and applied voltage was 30 kV. This result indicated that ammonia was decomposed efficiently because the possibility that ammonia molecular could receive energy from the streamer discharge increased with the amount of ammonia in premixed gas per unit volume being lower in the fuel lean condition. These results indicated that the average laminar burning velocities were increased with the DBD superposition increased, and the average laminar burning velocities became faster with increasing the peak to peak DBD voltage. In addition, it was found that the combustion promoting effect of the DBD superposition was high in the stoichiometric condition compared to the fuel rich conditions.
3.2 Evaluation of effects of ozone has on the laminar burning velocity

Figure 7(a) and (b) show that direct photographs of streamer discharges when DBD was superimposed to oxygen / nitrogen premixed gas (a) or ammonia / oxygen / nitrogen premixed gas (b). In Fig. 7(a), streamer discharges with the color of blue-violet was observed. This color can be emission of ozone in streamer discharge because the color of ozone is blue-violet and ozone is generated when the DBD is superimposed to oxygen (Devins, 1956). Also, Fig. 7(b) showed that when DBD was superimposed to the ammonia / oxygen / nitrogen premixed gas, the streamer discharges did not emit the blue-violet color but emit the white color. It can be supposed that the effect of DBD superposition on the gas components was changed whether the ammonia was contained in the premixed gas or not.
To measure the production amount of ozone with the DBD superposition, the amount of ozone was measured on the burner exit by using a Kitagawa gas detector tube. Once the DBD superposition on oxygen/nitrogen premixed gas was applied, ozone was generated 624 ppm. On the contrary, when the DBD superposition on ammonia/oxygen/nitrogen premixed gas was applied, ozone was not generated. Therefore, it is indicated that the factor that increased the average laminar burning velocity did not come from ozone generated by DBD superposition but came from highly reactive radical species and decomposition of ammonia by the highly reactive radical species.

4. Conclusion

In this study, the DBD superposition was applied to ammonia/O$_2$/N$_2$ flame and the effects of DBD superposition to unburned premixed gas on the improvement of laminar burning velocity was investigated. Results obtained in this study are concluded as shown below.

1. The DBD superposition on the premixed gas affected the flame shape. The flame became wavy shape.
2. The average laminar burning velocity doesn’t change without DBD superposed condition. Also, the average laminar burning velocity was increased with DBD superposed condition.
3. The average laminar burning velocity became faster with increasing the peak to peak applied voltage of DBD.
4. The increasing rates of average laminar burning velocity were large under the low equivalence ratio than that of high equivalence ratio. The average laminar burning velocity was increased up to 26.1% under the 1.0 equivalence ratio and 30 kV applied voltage conditions.
5. The reasons that the average laminar burning velocities were increased with DBD superposed condition weren’t the contribution of ozone in the ammonia/oxygen/nitrogen. It was revealed that ozone wasn’t a major factor to increase average laminar burning velocity. The major factor was that ammonia was decomposed by highly reactive radical species generated by the DBD superposition.

References


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