Effects of oxygen concentration on the radiative characteristics of ammonia/N\textsubscript{2}/O\textsubscript{2} laminar premixed flame

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Abstract
Ammonia is regarded as one of the possible alternative fuels for industrial furnaces because of its high transportability and storability. In the industrial furnaces, it is important to understand the radiative characteristics of flame. However, the knowledge of the radiative characteristics of ammonia flame is extremely limited. In this study, the radiative heat flux and the radiation spectra from the ammonia flame were measured to understand the radiative characteristics of ammonia flame. A slot burner was used for stabilizing the laminar ammonia/N\textsubscript{2}/O\textsubscript{2} premixed flame. The concentration of O\textsubscript{2} in the oxidizer and equivalence ratio were varied for increasing the flame temperature. The results showed that radiative heat flux of ammonia was lower than that of methane/air premixed flame in all condition of that has the same net heating values per unit time. Ammonia/N\textsubscript{2}/O\textsubscript{2} premixed flame doesn’t have any intensity in the spectra band of CO\textsubscript{2} absorption. In addition, oxygen-enriched ammonia/N\textsubscript{2}/O\textsubscript{2} premixed flame showed higher intensity than that of methane/air premixed flame in the spectra band of H\textsubscript{2}O at around 2.7 μm band.

Key words: Ammonia, alternative fuel, Radiative heat flux, Spectrum, Premixed flame

1. Introduction
The increase of world energy consumption caused by the population growth brings the concerns of the depression of fossil fuel and the global warming. Renewable energies have been attracted as the potential way to wipe out those concerns, however those renewable energies have the fluctuation of electricity supply rate. In addition, since some power plants of renewable energies used to be placed in the suburb, we need to deliver the electricity from the area of power plants to the consumption area. In these days, the procedure, so called “energy carrier”, is considered to achieve the delivery of the electricity. In the “energy carrier” concept, the electricity is converted to the chemical species. Hydrogen has the possibility of the energy carrier (Kojima, 2014), (Sakata and Sasakura, 2014), because it has already been applied as a fuel in the gas turbine (Kawasaki Heavy Industries, Co. Ltd., 2014), (Hitachi Co. Ltd., 2011), (Enel Co. Ltd., 2010). To use the hydrogen as an energy carrier, the investigation for transporting hydrogen was conducted empirically (Kamiya, 2006), (Chiyoda Co. Ltd, 2015), (Okada and Yasui, 2012). However, hydrogen has some issues in transportation and storage, because its physical properties and combustion characteristics require a huge investment/cost for developing infrastructure as the energy carrier (Jensen, et al., 2007), (Zamfirescu, Dincer, 2008), (Kojima, 2014).

Ammonia is thought to be the other realistic species of the energy carrier because the infrastructures for the delivery of ammonia already exist and a lot of investment is not required (Zamfirescu, Dincer, 2008, Kojima, 2014). To apply the ammonia as a fuel, the basic combustion characteristics have been investigated so far. Duynslaeghera et al. (2010), (2012). Those studies indicated that ammonia has a narrow flammable range and low burning velocity. In these days, Takeishi et al. (2014) reported the experimental study of the enhancement of combustion characteristics of ammonia by applying the oxygen-enriched combustion. They indicated that the ammonia fuel can make a stable laminar flame when the oxygen concentration becomes larger than 27%. The laminar burning velocity increases up to similar level of hydrocarbon fuels.

Ammonia is expected to be applied for various equipment, including gas turbine, industrial furnace, boiler, and so on. We focus the industrial furnace and boiler as use of ammonia fuel. Heat transfer in industrial furnaces and boilers consists mainly of the radiative heat transfer between burned gases, furnace wall and heating objects, and convective heat transfer.
transfer from burned gases. In large-scale furnaces (e.g.; soaking pit, heating furnace for steel), it is known that the amount of radiative heat transfer occupies over 80% of the total amount of heat transfer in the furnace. From the viewpoint of utilizing ammonia as a fuel, the basic knowledge about radiative heat transfer is important in the industrial furnace.

Radiation from flames is roughly classified into radiation from luminous flame and from nonluminous flames. Radiation from ammonia flame is classified into the latter one because ammonia flame does not emit any soot. As well known, radiation from H\textsubscript{2}O, CO\textsubscript{2}, CO and NO\textsubscript{x}, occupies most of radiative heat transfer in the nonluminous flames. Whereas a lot of experimental studies and theoretical studies about radiation from nonluminous flame of hydrocarbon fuels have been conducted so far, the basic knowledge about the radiation from the flames of ammonia was extremely limited. Ammonia does not emit CO\textsubscript{2} and CO but produce large amounts of H\textsubscript{2}O and NO\textsubscript{x} because of its molecular structure. In addition, unburned ammonia could be remained in the burned gas. Because of the above-mentioned differences, the basic radiation characteristics of ammonia flame have not been cleared yet. The aim of this study is thus to understand radiative characteristics of ammonia flame by comparing the difference of radiative heat flux and spectra with the methane flame that have been widely used as fuel in industrial furnace and boiler. In addition, we investigated the effects of oxygen-enriched conditions on the radiative heat transfer of ammonia flame in order to enhance the radiative heat flux from ammonia flame. Oxygen-enriched condition means that the oxygen concentration in oxidizer is higher than that of conventional condition. Andersson and his co-workers and other research group demonstrated that flame temperature and radiative heat flux from hydrocarbon flame were increased when oxygen concentration in oxidizer increases (Andersson and Johnsson, 2007), (Andersson et al., 2008), (Ditaranto and Oppelt, 2011). Therefore, the oxygen-enriched combustion is expected to increase radiative heat flux from ammonia flame by increasing flame temperature.

2. Experimental set-up

A schematic illustration of the burner and the supply lines of fuel, and oxidizer is shown in Fig. 1. Laminar premixed flame was stabilized on the slot-burner. The slot burner has a rectangular outlet of 8 mm in width and of 40 mm in depth. A honeycomb and a fine grid of metal wire placed in the settling chamber upstream of the nozzle were used to make the uniform flow field. Premixed gases pass through stainless sintered metal filter (60 μm in diameter), and stainless wire gauze (1 mm square mesh), and ceramic honeycomb (1 mm square passage) before combustion. The flame on the burner does not have the longitudinal distribution (Seo, et al., 2006). Mass flow controllers (SEC-N100, HORIBA STEC) were used to control flow rates of fuel and oxidizer. Fuel and oxidizer flow to a static mixer at the upstream of the burner and are mixed uniformly. Premixed fuel and oxidizer supplied to the burner through a flame trap intends to prevent the flashback. At downstream of the burner, flame stack and exhaust treatment equipment can absorb unburned ammonia. In this study, measurements of radiative heat flux and infrared spectra are conducted. The following explains experimental setup.

![Fig. 1: The burner and the supply lines of fuel, and oxidizer.](image1)

![Fig. 2: Direct photograph of the exit of slot burner (a), Ammonia/N\textsubscript{2}/O\textsubscript{2} laminar premixed flame on the slot burner (b).](image2)
2.1 Measurement of radiative heat flux

The schematic diagram of experimental set up for the measurement of radiative heat flux was shown in Fig. 3 (a). Radiative heat flux sensor (CAPTHERM for radiant heat flux, Captec Enterprise) was used as a detector. It has a black body paint coated sensor head of 12 mm in diameter. In order to eliminate the heat convection from the flame and to measure whole radiative heat flux, the sensor is placed at 300 mm away from the burner in horizontal direction and 30 mm in height above the burner exit. A black body paint coated cover was attached in front of the sensor, when the background noise was measured.

A water chiller (Cool Ace CCA-1111, EYELA) was connected to the sensor to keep the inner temperature of the sensor stable. A data logger (midi LOGGER GL220, GRAPHTEC) was used to record output signal from the sensor. A black body paint coated cover was attached in front of the sensor, when the background noise was measured. A background wall was set in 100 mm away from the burner in the horizontal direction. The size of the wall was 1000 mm \( \times \) 1000 mm and it can cover with the whole field of view of the sensor. The wall surface was coated with black body paint (THI-1B, TASCO JAPAN) of 0.94 emissivity in order to avoid reflections. Results are corrected by using the measurement signal from background. The radiative heat flux was sampled with the sampling rate of 10 Hz. The averaged values of 500 samples were used for every experimental condition. In addition, those results were corrected by using the average value of background.

To describe the radiative heat flux, the followings assumption was applied on the results obtained by the above-mentioned measurements. Here, \( q_t \), the integrated radiation intensity from flame and the background wall to the sensor, represents the summation of:

\[
q_t = q_f + q_w
\]

where \( q_t \) is the summation of \( q_f \), \( q_w \) and the emissivity of the flame and combustion gases at a certain wavelength \( \varepsilon_\lambda \). The second term of right hand side of Eq. 1 needs to consider the absorption of radiation by the flame in the area of sight of the sensor. The \( \varepsilon_b \), indicates the emissivity of the background wall. The function \( R_{\lambda T} \) is obtained from a certain temperature \( T \) (K) and a wavelength from \( \lambda \) to \( \lambda + d\lambda \). The integrated value of \( R_{\lambda T} \) for all wavelength (0 to \( \infty \)) becomes Stefan-Boltzmann’s law (Eq. (2)).

\[
\int_{0}^{\infty} R_{\lambda T} \, d\lambda = \sigma T^4
\]

\( \sigma \) is Stefan-Boltzmann constant. \( T_g \) and \( T_s \) are the temperatures of burned gas and wall, respectively. From the viewpoint of simplification, the reflected radiation form the wall is ignored, because the temperature of the wall \( T_s \) was about 300 K. This temperature is quite low compared with the temperature of burned gas \( T_g \). This is because that the temperature of the wall is almost same as the temperature of ambient gases. As a result, Eq. (1) becomes the following (Eq. (3)).

\[
q_t = \int_{0}^{\infty} \varepsilon_\lambda R_{\lambda T_g} \, d\lambda
\]

Eq. (3) means total radiation can be treated as the radiation from flame and burned gases. In the following section, we use \( q \) instead of \( q_t \). The value of \( q \) indicates the measured value and that is a part of total radiation flux \( q_t \).
2.2 Measurement of infrared spectra

The experimental apparatus used in the study is shown in Fig. 3 (b). Infrared spectra is measured with a FTIR spectrometer (FT-IR Rocket 2.5 – 12 μm, ARCoptix S.A.) with optical fiber (Polycrystalline IR-Fibers, art photonics) NA of the fiber is 0.28, the core diameter is 900 μm, the cladding diameter is 1000 μm and the length is 1 m. The spectrometer can disperse infrared light in wavelength 2.5 – 12 μm. The optical fiber made by AgCl0.25Br0.75 can transparent across a broad spectral range from 2.5 to 12 μm. The combustion of hydrocarbon forms carbon dioxide and water vapor. The radiation from the burned gases is dominated by these two species. It is known that there are significant bands of 1.38, 2.7 and 6.3 μm for H2O and 2.7, 4.3 and 15 μm for CO2 (Grosshandler, 1980). Coppalle and Vervish reports that the small scale flame in atmospheric pressure radiates the bands of 2.7 and 6.3 μm bands for H2O and 2.7, 4.3 μm for CO2 (Coppalle and Vervish, 1983). Ammonia flame forms NOx and NH3 (Duynslaegher, et al, 2012) and those gases has a significant bands of 2.7, 5.3 μm for NO, 4.5, 7.8 μm for N2O, 3, 6, 9 μm for NH3 (Kunitomo, et al, 1974). Those bands of radiation are included in the measurement range of FTIR spectrometer. The FTIR spectrometer with the optical fiber is calibrated by 1273 K black body furnace (BBZ5-30W1000, JAPAN SENSOR CORPORATION) and intensities of the bands can be compared. The procedure for measurement of radiative heat flux is to sample and average 30 values from the sensor at a sampling rate of 1 Hz.

3. Results and discussion

In this study, the total radiation intensity and the spectra from the ammonia flame were measured to understand the radiative characteristics of ammonia flame. Equivalence ratio $\phi$ was varied from 0.8 to 1.4 in each O2 concentration condition. Conditions of O2 concentration in the oxidizer is defined as the following.

$$\Omega = \frac{Q_{O_2}}{Q_{O_2} + Q_{N_2}}$$  \hspace{1cm} (4)

$Q_{O_2}$ is the total content of oxygen in the oxidizer. $Q_{N_2}$ is the total content of nitrogen in the oxidizer. The some different conditions of O2 concentration in the oxidizer ($\Omega = 0.33 \sim 0.38$) were applied for increasing the flame temperature and radiation. Moreover, the total radiation intensity and the spectra from the methane flame ($\phi = 0.8 \sim 1.4$, $\Omega = 0.21$) were measured as the reference condition. The conditions of methane flame were set to be same lower heating value of ammonia flame. Experiment condition is shown as Table 1.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>$m$ (NL/min)</th>
<th>$\Omega$</th>
<th>$\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>2.00</td>
<td>0.21</td>
<td>0.8~1.4</td>
</tr>
<tr>
<td>NH3</td>
<td>4.97</td>
<td>0.33~0.38</td>
<td>0.8~1.4</td>
</tr>
</tbody>
</table>

Fig. 3: Schematic illustration of the experimental apparatus for measurement of radiative heat flux (a), for measurement of infrared spectra (b).
3.1 Radiative characteristics of ammonia/N$_2$/O$_2$ laminar premixed flame

Figure 4 shows comparison of radiative heat flux between ammonia flame ($\phi = 1.0$, $\Omega = 0.33$) and methane flame ($\phi = 1.0$, $\Omega = 0.21$). $q_{r1}$ indicates the value of methane flame. Each measured values plotted in Fig. 4 are normalized by using $q_{r1}$. The adiabatic flame temperature of oxygen-enriched ammonia flame (2459 K) is higher than methane flame (2232 K). However, radiative heat flux from ammonia flame is about 30% weaker than that of methane flame as shown in Fig. 4. The difference between radiative heat flux from ammonia flame and methane flame is clear, even though the relative value is influenced by wavelength sensitivity of the radiative heat flux sensor.

Figure 5 shows comparison of spectra between ammonia flame ($\phi = 1.0$, $\Omega = 0.33$) and methane flame ($\phi = 1.0$, $\Omega = 0.21$). Each values plotted in Fig. 5 are normalized by maximum intensity of spectra measured in methane flame (4.378 $\mu$m). Spectra from ammonia flame show a peak value around 2.7 $\mu$m (H$_2$O band). It can be considered that radiation from H$_2$O is dominant in radiative heat flux in ammonia flame. On the other hand, it is also found from Fig. 5 that the radiation spectra of NOx and unburned NH$_3$ are small. Spectra measured in methane flame have two peaks around 2.7 $\mu$m (H$_2$O and CO$_2$ band) and 4.3 $\mu$m (CO$_2$ band). This result agrees with well-known knowledge that dominant gases in radiative heat flux in methane flame are H$_2$O and CO$_2$. Moreover, the shape of spectra from methane flame indicated same as other work done by Sato et al. (Sato T. et al., 1968). Ammonia flame has only H$_2$O band spectra of 2.7 $\mu$m. The intensity of this spectra band in the ammonia flame shows higher intensity than that in methane flame. On the other hand, spectra band around 4.3 $\mu$m in ammonia flame did not appeared because CO$_2$ does not emitted from the burned gas of ammonia flame. In addition, the difference of intensity of spectra band around 4.3 $\mu$m between ammonia flame and methane flame is larger than the difference of intensity of spectra band around 2.7 $\mu$m as shown in Fig. 5. This is the reason why the total radiation heat flux in ammonia flame is lower than that in methane flame.

3.2 Effects of oxygen concentration on the radiative characteristics

Figure 6 shows the relationship between the radiative heat flux and equivalence ratio. The legends in Fig. 6 indicate the conditions of different O$_2$ concentration. Every value shown in Fig. 6 is normalized by $q_{r1}$. The radiative heat flux from ammonia flame and O$_2$ concentration in the oxidizer $\Omega$ has positive correlation. The radiative heat flux from ammonia flame increases about 3 ~ 10% compared with increasing O$_2$ concentration from $\Omega = 0.33$ to $\Omega = 0.38$. However, that from ammonia flame in all equivalence ratio condition ($\phi = 0.8 ~ 1.4$) is lower than that from methane flame, because CO$_2$ does not emitted from the burned gas of ammonia flame regardless of equivalence condition. The changes of radiative heat flux from ammonia flame are smaller than that of methane flame when $\phi$ is varied as shown in Fig. 6.
4. Conclusions

Measurements of radiative heat flux and spectra from ammonia/N\textsubscript{2}/O\textsubscript{2} premixed flame and methane/N\textsubscript{2}/O\textsubscript{2} premixed flame were experimentally conducted to determine the radiative characteristics of ammonia/N\textsubscript{2}/O\textsubscript{2} laminar premixed flame and the effects of oxygen concentration on the radiative characteristics. The results can be summarized as follows:

1. Radiative heat flux from ammonia/N\textsubscript{2}/O\textsubscript{2} premixed flame ($\phi = 0.8 \sim 1.4, \Omega = 0.33 \sim 0.38$) is about 30% weaker than that of methane/N\textsubscript{2}/O\textsubscript{2} premixed flame ($\phi = 1.0, \Omega = 0.21$).
2. Spectra measured in ammonia flame show a peak value around 2.7 $\mu$m (H\textsubscript{2}O band). On the other hand, spectra band around 4.3 $\mu$m in ammonia flame is very low compared with those spectra obtained in methane flame.
3. The radiative heat flux from ammonia flame increases about 3 ~ 10% compared with increasing O\textsubscript{2} concentration from $\Omega = 0.33$ to $\Omega = 0.38$.

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6. References


