

Experimental Study on Gases Produced from Polymers Burning with Water Mist: Influence of droplet size of spray

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Abstract. Water spray extinguishing system, whose water spray volume per unit time is generally larger than water mist fire suppression system, has been used in underground parking lot in Japan. With the application of water mist, fires can be controlled and/or extinguished by cooling effect and oxygen diluted by evaporation of water. Recently, few researches have been studied on toxic gases generated from combustion of polymeric materials with water spray. The purpose of this study is to determine the produced toxic gases with the influence of water mist size distribution discharged from two kinds of nozzles on natural or thermoplastic polymer burning in bench scale experiment. The concentration of toxic gases and temperature at several points inside test chamber were measured. The results of this study showed that water mist in the range of 100-1000 μm in diameter significantly influenced on the effectiveness of fire extinguishment. Furthermore, the concentration of asphyxiant gases especially CO were associated with water droplet diameter less than 270 μm on the combustion of natural polymer. Some toxic gases from synthetic polymers burning with water mist of droplet diameter exceeding 135 μm were produced due to the combustion state and types of solid fuel.

1. Introduction

These days, water mist fire suppression system (WMFSS) is considered as the alternative instead of bubble extinguishing system, inert gas extinguishing system and halogenated extinguishing system. In addition, water mist system has generally been used as a clean fire suppression system in underground parking garages in Japan [1-2]. Fires can be reduced in size or extinguished with dominant physical mechanism of water mist droplets, wetting and cooling fuel surface and displacing oxygen due to evaporation of water mist [3-4]. In order to enhance the fire suppression efficiency of WMFSS, various factors, for instance water droplet size and distribution, water flux density, spray flow rate, water droplet velocity and the operating pressure, have been studied [5]. On the other hand, a few studies have been concerned about toxic gases generated from combustion of solid fuel with water spray. The effects of toxic gases produced during water mist discharging are mainly concerned for incapacitation, injury, and death during fires [6]. Previously, Hietaniemi et al. researched on the burning characteristics and the yields of produced toxic gases with and without the suppression of water spray on polypropylene (PP) and nylon-6,6 conducted in control-ventilated cone calorimeter [7]. The results indicated that the yields of carbon monoxide (CO) and hydrogen cyanide (HCN) produced from the combustion of polymers with water spray discharge was twice compared to the combustion without it. Consequently, the comparison analysis under the condition between

with and without water spray was demonstrated that the suppression of water spray could cause significant variations of fire toxic gas production.

The purpose of this study is to determine the effectiveness of water mist for fire extinguishment and the generation of toxic gases with the different size distributions of water droplets discharged on natural and thermoplastic polymeric materials burning. The results of the concentration of produced toxic gases, flame-out time, burning characteristics and temperature from combustibles with the application of water mist in small-scale experiment were investigated in this paper.

2. Experimental methods

2.1 Test apparatus set-up

The experiments were conducted as small-scale test in Fire Research and Test Laboratory, Centre for Fire Science and Technology at Tokyo University of Science in Japan. Figure 1 shows the schematic of 0.70 m (w) x 0.70 m (d) x 0.92 m (h) stainless-steel box chamber connected to spraying device and experimental apparatus. In the combustion chamber, two openings in the size of 0.19 m (w) x 0.09 m (h) were provided at the top and bottom parts of stainless-steel walls to allow supply fresh air and exhaust smoke. The opening at the upper part of the chamber was kept opened during the experiment. Test samples were located at the centre of the combustion chamber below the position of single-fluid nozzle. Spraying height from the nozzle to the surface of polymers burning can be adjusted with a lab jack installed under the test sample. Internal temperatures were measured by K-thermocouples at 10 positions installed in the combustion chamber. Fire extinguishing process of each test sample was observed with video cameras located in the front, side and back of the combustion chamber. Concentrations of CO and CO₂ were measured by Nondispersive infrared (NDIR) gas analyzer and concentration of O₂ was measured by magnetic oxygen analyzer with sampling rate for 1.0 L/min. Gases concentrations with low-molecular weight such as NO, NO₂, SO₂, HCl, HF, formaldehyde and acrolein were measured by Fourier transform infrared (FTIR) gas analyzer with sampling rate for 4.0 L/min. Two spray nozzles were used in this experiment from *Ikeuchi* company, which were the nozzle models of “7KB” (Hereafter, nozzle A) and “J” (Hereafter, nozzle B). In this experiment, the solid test samples were timber, polypropylene (PP) and polyethylene (PE) with the nominal size of 0.02 m × 0.02 m × 0.12 m arranged as a crib using 10 sticks with 3 layers.

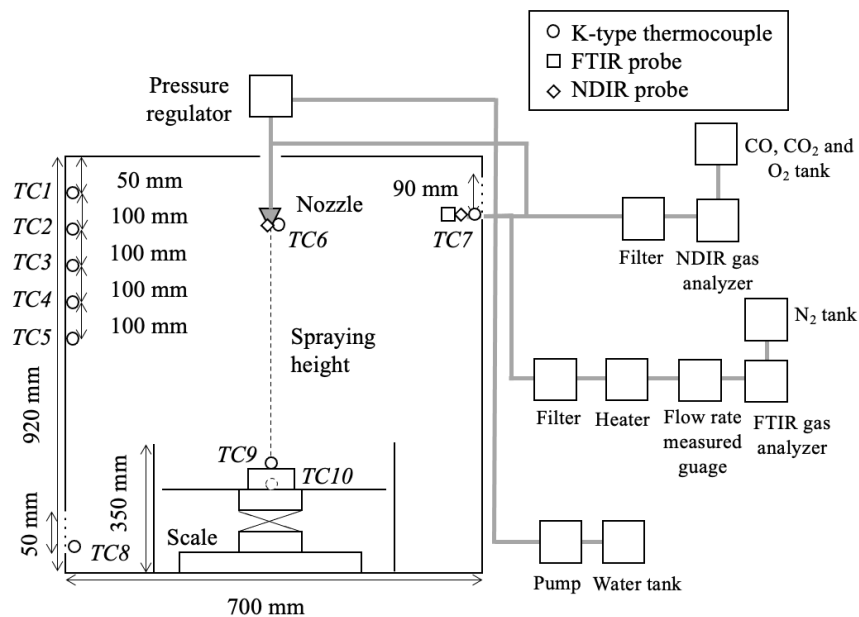


Figure 1. A schematic view of combustion chamber connected to test apparatus.

In the experiment, each test sample was ignited with the flames on flammable gel including methanol as ignition accelerator. Water mist was discharged at a certain time when the combustion of polymers was sustained at approximate 2.0-8.0 kW. Water mist spraying was shut off when the combustion was completely extinguished. If the combustion could not be extinguished within 15 minutes, the external water was supplied to the burning polymers until the combustion was completely extinguished. In this experiment, each test sample was repeated twice with water mist nozzle A and nozzle B. The produced toxic gas concentration and temperature measurement were turned off at 30 minutes after the combustion was completely extinguished to determine the remaining gas concentration and temperature.

2.2 Water mist characteristics

The specified water flux density discharged from the nozzle was regulated with the experiment conducted by *National Research Institute of Fire and Disaster* in Japan with the range of water flux density were 1.20 to 2.30 L/m²·min, and the distance between the nozzle and the fuel surface from 1.0 to 2.6 m [8-10]. The size distribution of water mist droplets was characterized by catching droplets on a coated plate surface with oil [11]. The spraying height from the nozzle to the surface of the solid fuel was fixed at 0.20 m in nozzle A and 0.25 m in nozzle B. The working pressure was 1.0 MPa, operating in low pressure water mist systems. Water droplet was discharged horizontally projected area was equal to 0.01431 m². The size distribution of water droplets discharged by nozzles A and B were described in term of cumulative distribution function and frequency distribution chart as shown in Figures 2. In this study, the total number of water mist droplets from nozzle A and nozzle B were 3,379 and 2,289 droplets, respectively.

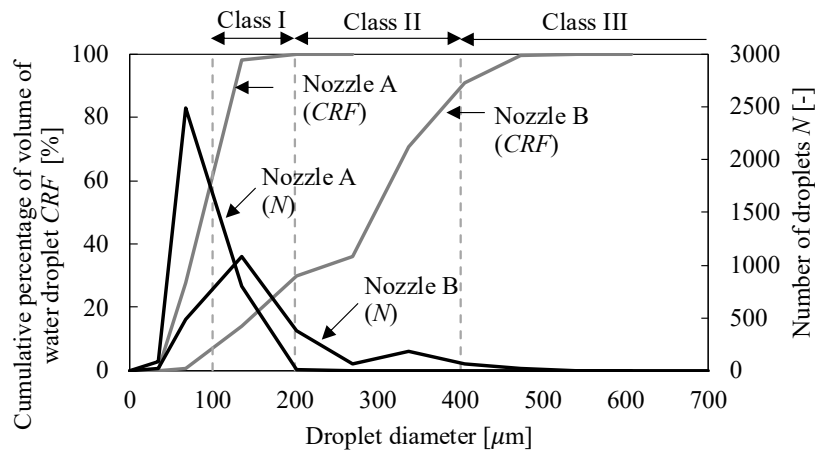


Figure 2. Cumulative percentage of volume and number of droplets as a function of droplet diameter classified in 3 classes according to NFPA 750

The distributions of droplets discharged from both nozzles were characterized and represented by mean diameter because this value was considered as the main factor to analyze the fire extinguishment efficiency. The configurations of water mist droplet produced from the nozzles were assumed as uniformly semispherical particle with finely dispersed spray. In this study two types of mean diameter calculations due to their size distribution of number and volume were examined: Arithmetic mean diameter and Sauter mean diameter. *Arithmetic mean diameter* or average mean diameter of water mist droplets was calculated considering the total number of water droplet diameters N using the following Equation (1):

$$D_{10} = \frac{\sum n_i d_i}{N} \tag{1}$$

Also, another mean diameter calculated by volume and surface area ratio as a representative droplet known as *Sauter mean diameter* or surface moment mean diameter was calculated by Equation (2):

$$D_{32} = \frac{D_v^3}{D_s^2} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \quad (2)$$

where D_{10} is Arithmetic mean diameter [μm] and D_{32} is Sauter mean diameter [μm]. Also, d_i is the diameter of the water droplet, n_i is the number of the water droplet measured in the experiment [μm] and N was the number of particle count in total. Sauter mean diameter is calculated from the ratio of volumetric diameter of droplet (D_v) to surface area mean diameter of droplet (D_s) in unit of μm [12].

Table 1. The characteristics of nozzles.

Nozzle characteristics	Nozzle A	Nozzle B
Operating pressure [MPa]	1.0	1.0
Spraying height [m]	20.0	25.0
Spray flow rate [g/s]	0.388	0.396
Water flux density [$\text{L}/\text{m}^2\text{min}$]	1.625	1.619
Number of droplets	3,379	2,289
Average mean diameter, D_{10} [μm]	82.8	160.4
Sauter mean diameter, D_{32} [μm]	106.2	262.7

The results of water droplet diameter were confirmed that more than 99% of particle sizes discharged from both nozzles were in the range of 100 to 1000 μm . Owing to the fact that the chemical reaction of water mist on solid fuel combustion and the production of toxic gas would be focused on this study, Sauter mean diameter that considering identical total surface and volume of water mist droplets was used as a representative mean diameter. The mean droplet diameters of water spraying on a horizontally projected area with nozzles A and B were 106.2 and 262.7 μm , respectively. According to National Fire Protection Association (NFPA) 750, water mist droplet sizes are subdivided into 3 classes; class I is defined as water droplets in the range of 100-200 μm , class II in the range of 200-400 μm , and class III in the range of 400-1000 μm [13]. In this study, water droplets produced from nozzle A were classified in class II, and from nozzle B were classified in class III as shown in Table 1. The droplet size distributions were observed significantly different in two cases. In case of water mist discharged from nozzle A, water droplets were uniformly dispersed with the diameter less than 270 μm of water droplets. On the other hand, the diameter size distribution of water droplets discharged by nozzle B was in the range of 33.75-540 μm in total number of water droplets. Furthermore, water mist droplets discharged from nozzle B was in a wide range of distribution compared to water mist from nozzle A.

3. Experimental results

The results of heat release rate (HRR) calculated by mass loss rate and combustion heat of test sample before water mist activated are shown in Figure 3. It can be observed that HRR between timber and thermoplastic polymers were significantly different. HRR of the timber burning increased rapidly in short time. Water mist was discharged when it reached a peak of 6.0-8.0 kW at approximately 100 s. For PP and PE, water mist was activated when HRR of thermoplastic polymers burning stayed unchanged due to the results of their mass loss rate. When the combustion of thermoplastic polymers was sustained, water mist was discharged at 300 s and 400 s after the ignition in the combustion of PP and PE, respectively. In all cases, the flammable gel was burned out by visual observation, and then water mist was discharged to test sample.

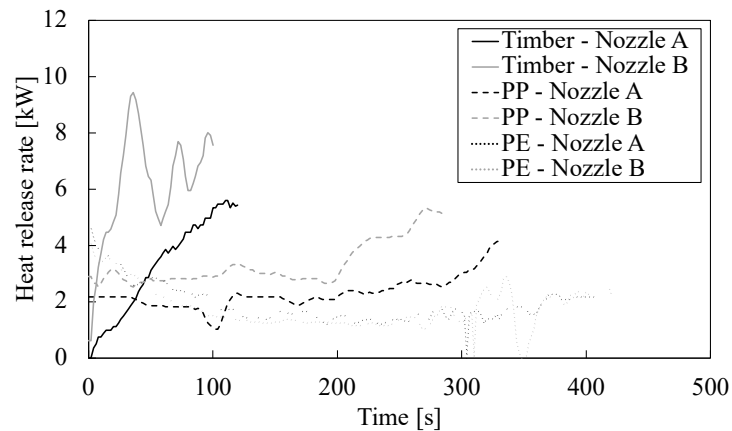


Figure 3. Heat release rate before water mist sprayed on timber, PP and PE burning.

Table 2. Time to extinguishing polymers burning.

Test sample	Heat release rate [kW]	Fire extinguishing time [s]	
		Nozzle A	Nozzle B
Timber	6.0-8.0	191	18
Polypropylene (PP)	~5.0	26	3
Polyethylene (PE)	2.0	External extinguished	3

3.1 Influence of the water mist on extinguishment of natural polymer burning

Timber combustion scenarios with water mist from nozzles A and B were shown in Figure 4. The figure depicts those two periods were distinguished before and after water spray activation time: free burning period and water mist discharged period. At the free burning period of timber, it can be physically observed that surface of the wood crib was gradually change to black. It can be observed that fire extinguishing time for the combustion of timber with water discharge by nozzle A was longer than the application of water mist from nozzle B in water mist discharged period. With the water suppression by nozzle A that produce small size of water droplets, the size of flame gradually reduced, and it took 191 s to completely extinguished timber burning. As a result, it can be indicated that small size of water mist droplets which is less than 405 μm discharged by nozzle A could cool down the hot environment nearby the flame by gradually reducing generated heat by combustion reaction.

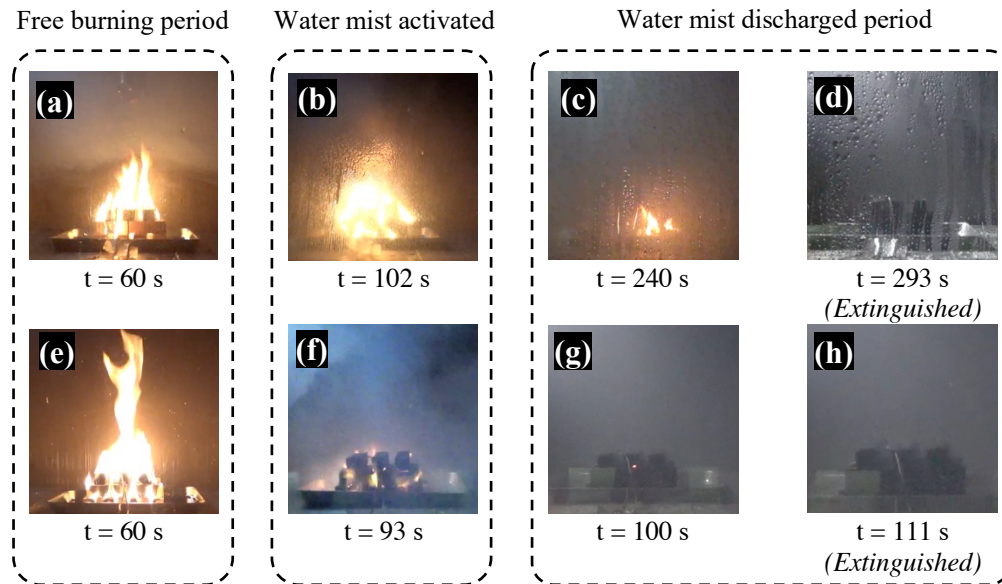


Figure 4. Timber combustion scenarios with the application of water mist from nozzle A at (a)-(d) and nozzle B at (e)-(h).

Temperatures were measured by thermocouple tree at the corner of the combustion chamber between TC4 and TC5 were significantly different, and temperature at TC5 remained constant as shown in Figure 5. The result confirmed that the horizontal boundary plane between a smoke layer and an air layer stayed stable at a period of time and the height of smoke layer in this experiment was approximate 400 mm from the ceiling before water mist activated. Also, compared to the application of water mist produced by nozzle A, it should be noted that timber burning with water application from nozzle B that discharge the size of water droplets quite larger than with nozzle A and suddenly suppressed by cooling effects of water mist within 18 s. As a result, the temperature on the surface of solid fuel could be directly cool down.

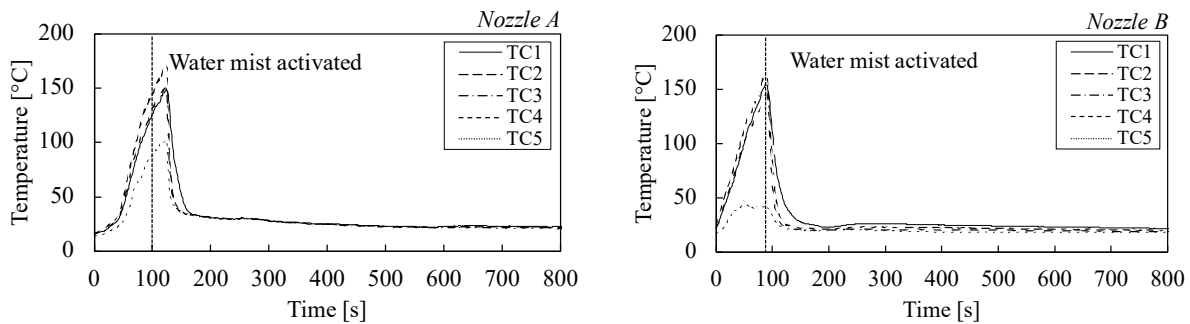


Figure 5. Temperature measured at 5 positions inside chamber in the case of timber burning (left: nozzle A, right: nozzle B).

3.2 Influence of the water mist on extinguishment of thermoplastic polymer burning

In this experiment, the effect of water sprays on extinguishing burning PP and PE with two different droplet size distribution was determined. It was noticed that the combustion of both thermoplastic polymers was observed as the similar process. After ignition of the flammable gel on PP and PE samples, the surface of test sample was gradually melted into the liquid phase during the combustion process. The combustion state

of PP with the application of water mist from nozzle A and nozzle B was shown in Figure 6. The suppression by water spray from nozzle A after 300 s, and slowly extinguished at 326 s. The combustion of PP could be completely extinguished in within 3 seconds with water mist sprayed by nozzle B as shown in Figure 6 (h).

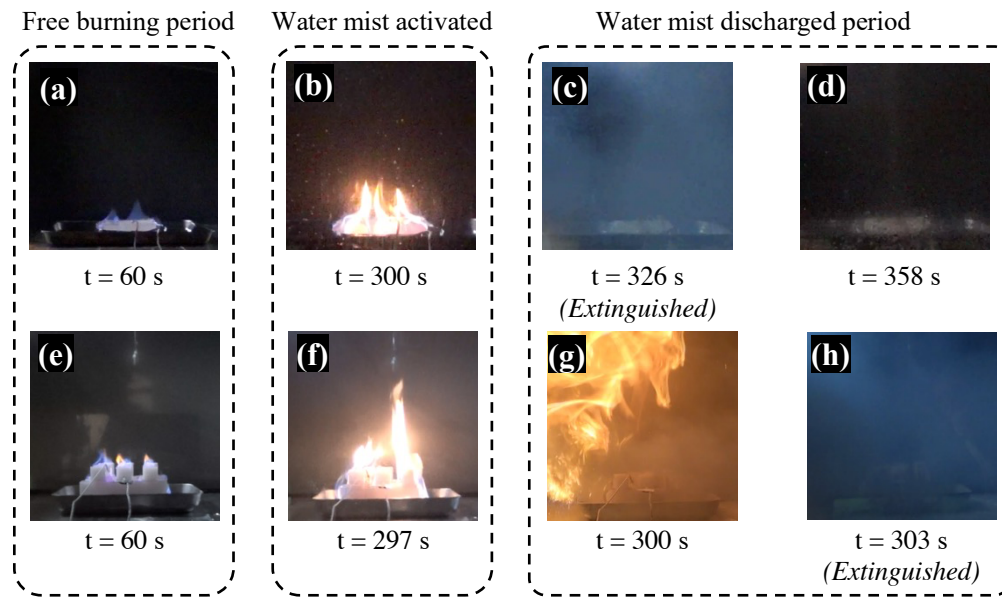


Figure 6. PP combustion scenarios with the application of water mist produced from nozzle A at (a)-(d) and nozzle B at (e)-(h).

It is important to note that a huge size of flame appeared suddenly as observed in Figure 6 (g) in the case of the suppression with large size of water mist droplets by nozzle B on PP combustion. The experimental results show the temperatures by PP burning with water spray from nozzle B, water droplet diameter in the range of $33.75\text{-}540\ \mu\text{m}$, rapidly increased due to boil-over phenomenon. This phenomenon occurred due to vapor explosion [14-15]. The height of smoke layer in the experiment of PP burning could be confirmed with the result of temperature at TC5 as shown in Figure 7. Also, the graphs illustrate the temperature inside the chamber reached to the peak at $140\ ^\circ\text{C}$ as soon as water mist was discharged from nozzle. It can be observed that the temperatures inside the test chamber rapidly rise after water spray using nozzle B, resulting in large size of flame.

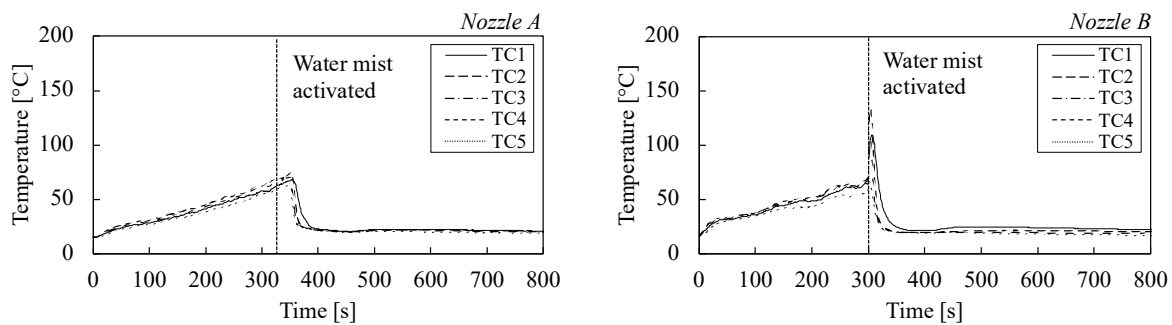


Figure 7. Temperature measured at 5 positions inside chamber in the case of PP burning (left: nozzle A, right: nozzle B).

3.3 Influence of the water mist on toxic gases generation from polymers burning

Figure 8 illustrates the relationship between toxic gas concentration produced from the combustion of timber over the time. In free burning period of timber combustion, the concentration of CO increased and reached to the peak during at initial stage due to the combustion of flammable gel. The combustion rate of polymers after the flammable gel completely evaporated was depended upon combustion heat of the polymer. In water mist discharged period, temperature in water application of nozzle B was abruptly declined. In timber, CO concentration with water discharged by nozzle B on the timber burning abruptly decreased, but kept stable and gradually reduced by nozzle A. Also, the increasing concentrations of formaldehyde and acrolein was detected after the water mist activation in both cases.

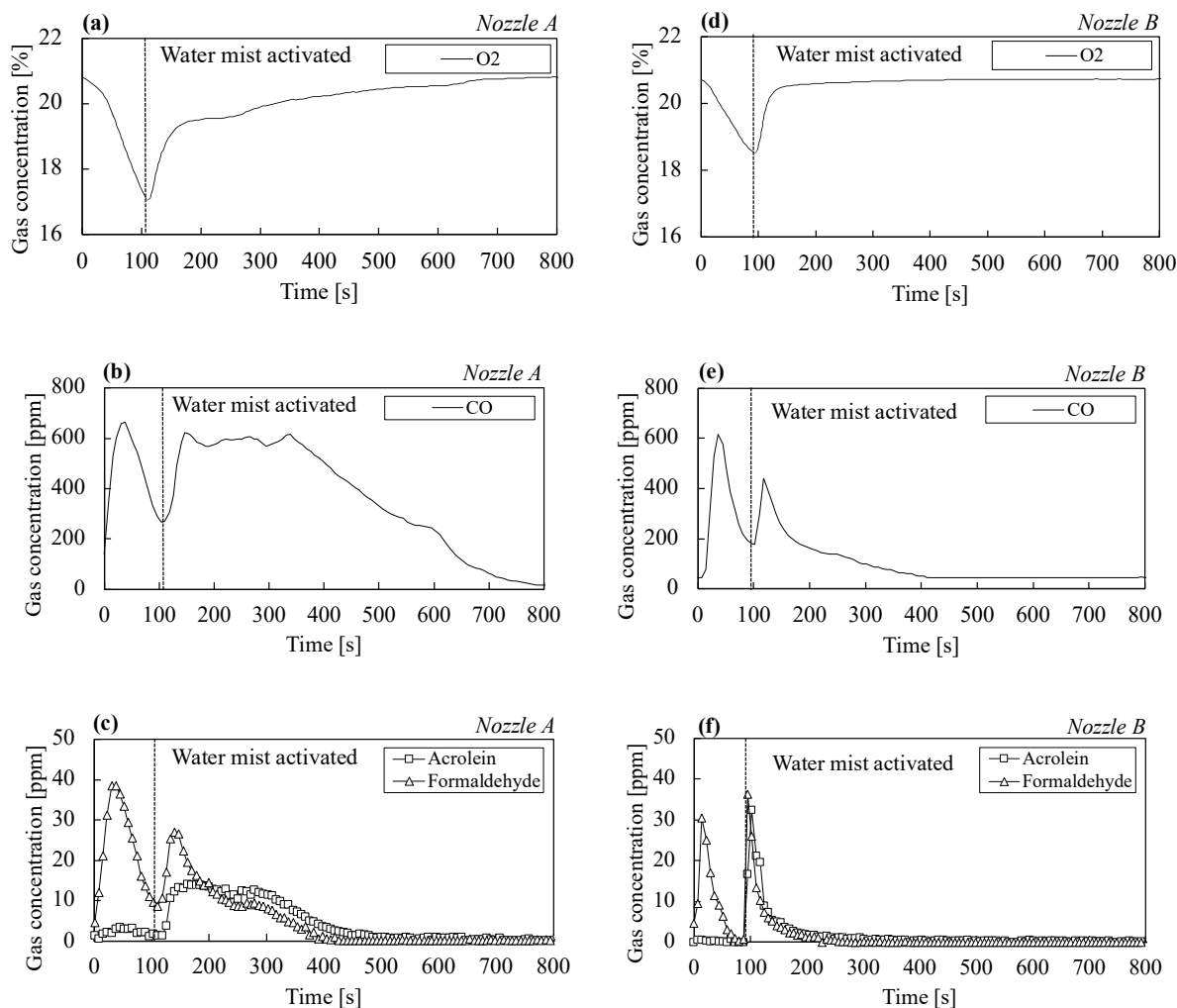


Figure 8. The concentration of O₂, CO, acrolein and formaldehyde measured by magnetic oxygen analyzer, NDIR and FTIR gas analyzers produced from timber burning with water sprayed from nozzle A at (a)-(c) and nozzle B at (d)-(f).

Figures 9(b), 9(c), 9(e) and 9(f) show the concentrations of CO, NO₂ and acrolein produced from PP combustion with influence of water mist. As illustrated in Figure 9(e), the concentration of CO immediately rose and almost reached to 146 ppm in the case of the application of nozzle B in water mist discharged period. On the other hand, the water spraying on the combustion of synthetic polymers with the application

of small size of water droplets from nozzle A was not significantly influence on the generation of CO concentration as shown in Figure 9(b).

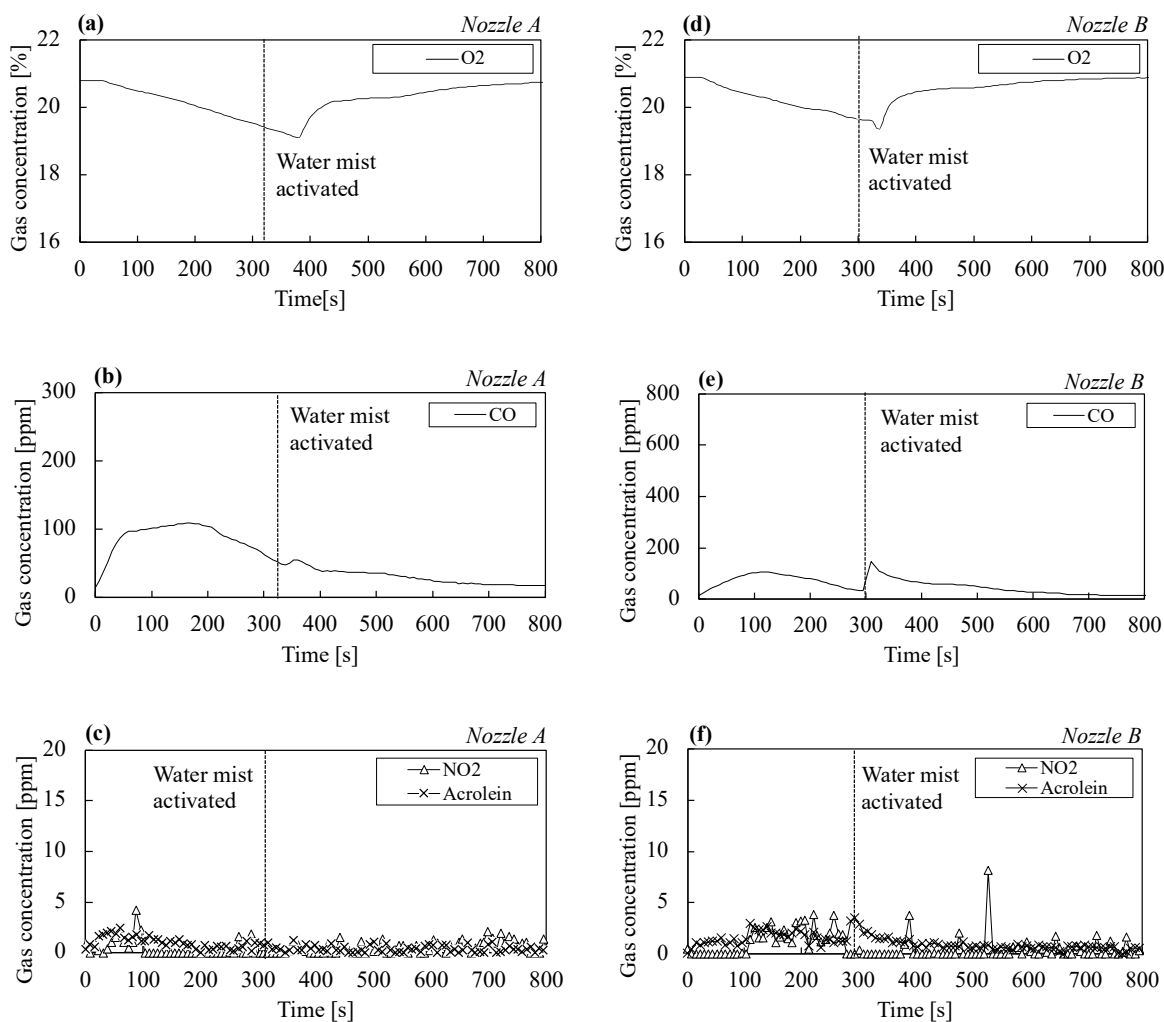


Figure 9. The concentration of O₂, CO, acrolein and formaldehyde measured by magnetic oxygen analyzer, NDIR and FTIR gas analyzers produced from PP burning with water sprayed from nozzle A at (a)-(c) and nozzle B at (d)-(f).

The concentrations of CO, NO, HCN, NO₂ and acrolein produced from PE combustion with water spray are illustrated in Figures 10(b), 10(c), 10(e) and 10(f). It is important to note that HCN and acrolein concentrations immediately increased and reached to the peak at 18.5 and 18.7 ppm, respectively, with the application of water mist by nozzle B as shown in Figure 10(f). On the other hand, the experimental result show that small size of water droplets, which mean droplet diameters were approximate 106.2 μm , was not significantly affected to the concentration of toxic gas produced by the combustion of both PE and PP as observed in Figure 10(c) and 10(c). Also, it could be confirmed by the result of NO₂ concentration that thermal NO_x reaction occurred with high temperature during the combustion of PE.

The experimental results of the water mist suppression on PE burning by nozzle B were clearly shown that at 200 s after water mist sprayed on the sample PE, the NO concentration was slowly reduced as demonstrated in Figure 10(e). After that, the concentrations of HCN and NO₂ often increased at approximately 2 ppm for a period as shown in Figure 10(f).

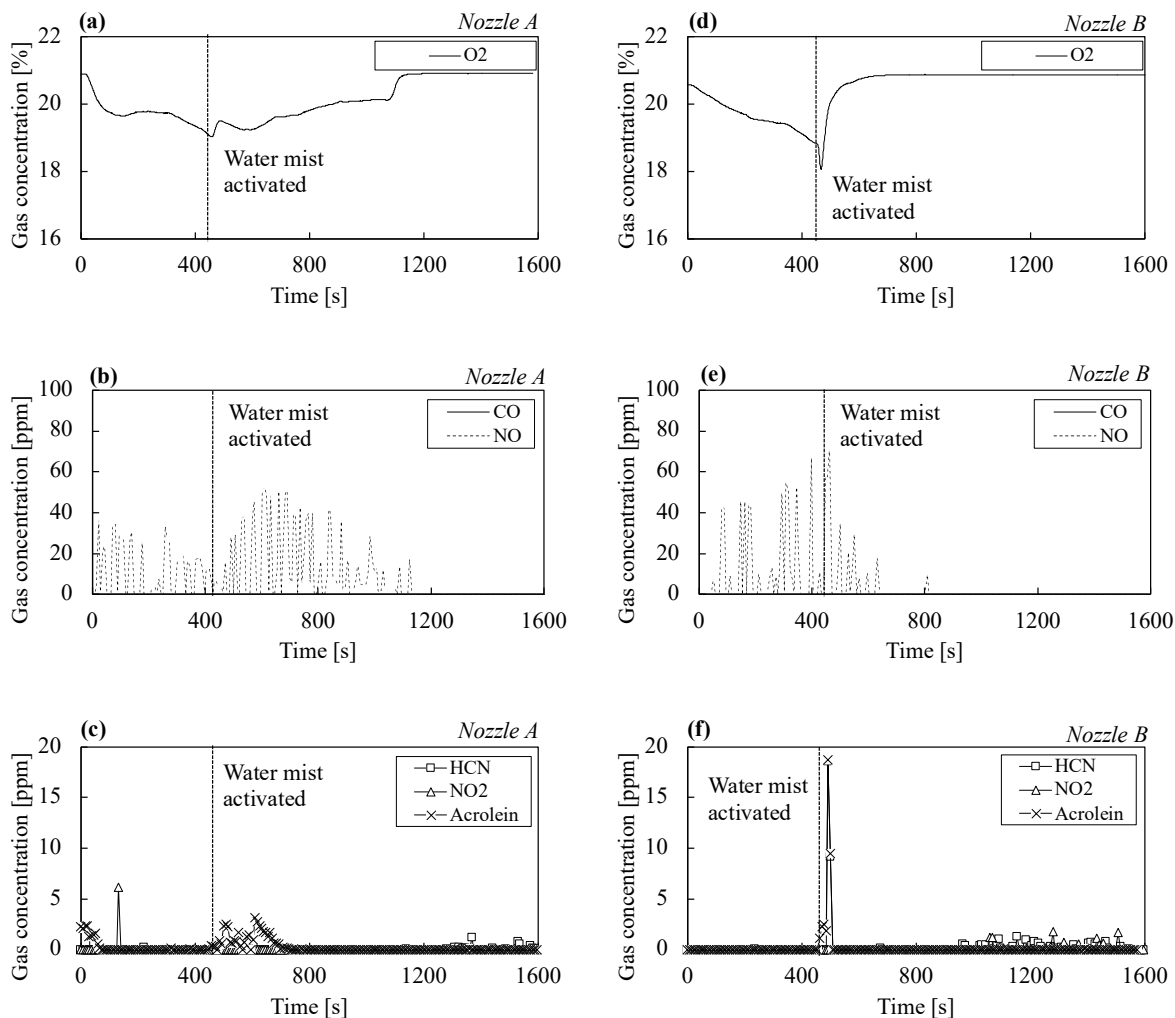


Figure 10. The concentration of O₂, CO, acrolein and formaldehyde measured by magnetic oxygen analyzer, NDIR and FTIR gas analyzers produced from PE burning with water sprayed from nozzle A at (a)-(c) and nozzle B at (d)-(f).

The concentrations of O₂ produced from PE combustion measured by magnetic oxygen analyzer were demonstrated in Figures 8(a) and 8(d). The results of O₂ concentration in the combustion of polymers show the declined tendency after the ignition. However, the concentration immediately increased to 21 percentage after the water mist was activated by nozzle B because of the evaporation of water mist in order to displace the oxygen in the atmosphere. Consequently, the combustion of PE was completely extinguished within 3 s as described in Table 2. Interestingly, water fire suppression of burning PE by nozzle A shown in 10(d) should be remarked. It is noted that with small droplets size less than 270 μm of water mist discharged by nozzle A was not completely extinguished over a short time. Figure 10(a) shows that O₂ concentration

gradually increased due to entrained air by PE burning and remained unchanged at 1100 s. As the result, external extinguished by water was utilized to completely suppress the combustion of PE.

4. Discussion

In this study, the influences of water mist droplets size in the range of 100 to 1000 μm on natural and synthetic polymers burning in bench-scale tests were experimentally investigated. The ventilation in this experiment was determined as fuel-controlled considered by the consistency of the horizontal boundary plane between a smoke layer and an air layer before the suppression of water. Consequently, the smoke layer was constant at 450 mm from the ceiling of the chamber and unable to descend to the test sample. It could be confirmed by the results of temperature that the sufficient supply of oxygen in the atmosphere in air layer would sustain in the combustion process of solid fuel. The results of the experiments shows that the droplet sizes of water mist had significantly influenced the time to extinguishing burning polymers by the physical mechanisms of cooling effect and oxygen dilution. The evaporation of water mist could remove the heat released from the burning polymers. In addition, water mist could reduce the oxidation process between entrained O_2 and by the application of the small water droplets that were evaporated around the combustion zone of the flame and on the surface of test samples burning. As a result, the flame could be limited or extinguished by the application of water mist. As water mist droplets, which has mean diameter equalled to 106.2 μm from nozzle A, was discharged to PE burning, PE was continued to burn with the smaller flame size. At some points of the water mist discharged period, it could be observed that water mist could not sufficiently reach to the top surface of PE by buoyancy force of plume generated by the combustion. Hence, the size of flame was sustained and cannot be completely extinguished. However, the fire suppression process was rapidly completed with the application of water mist that has mean droplet size approximate 262.7 μm from nozzle B. The results indicated that the combustible polymer burning could be extinguished by the physical mechanism of water mist fire suppression using nozzle B.

To understand the influence of water mist droplet size and distribution on the polymeric materials burning, the concentrations of toxic gases were compared between free burning period and water mist discharged period. The results in water discharged period demonstrated that the toxic gases concentrations especially CO concentration were related to water droplets size discharged on natural polymers burning due to water gas reaction. Therefore, the relatively high concentration of CO accumulated inside the chamber for a long time with small size of water mist droplets. Also, the experimental results were confirmed that the water mist droplet size classified in class III instantly increased the concentration of HCN and acrolein produced from the combustion of thermoplastic polymers especially PE. It can be deduced that forming NO affected to production of HCN due to thermal NO_x reaction occurred in PE burning that could produce HCN as an intermediate product [17]. Therefore, the additional irritating gases could be produced with water mist application.

In case of the water mist composed of Sauter mean droplet diameter less than 270 μm , the surface area of water mist was relatively large, as a result, they could absorb heat more quickly than large size of water droplets. Also, water mist discharge can slow down the combustion reaction rate and can control the combustion of polymeric material [18]. However, the possibility of produced toxic gases was increased with the influence of size distribution of water mist discharge on polymer burning as the result of the state of combustion and types of solid fuel.

5. Conclusion

In this paper, the concentrations of toxic gases that were produced from the combustion of natural and thermoplastic polymers with the influences of water mist droplets size were investigated. The following conclusions were obtained from this study.

1. The influence of water droplet size distribution produced from the water mist nozzles on polymers burning are significantly related to the time to extinguish burning them and the flame characteristics. In some cases, the combustion cannot be completely suppressed, however, water mist would play a dominant role to control the flame size instead of fire extinguishment.
2. The produced toxic gas concentrations especially CO are associated with the size of water mist spraying on the combustion of natural polymers. The small droplet size of 33.75 to 202.5 μm in this study may cause the water gas reaction.
3. Produced toxic gases concentrations from synthetic thermoplastic polymers burning with water mist spray on the combustion state of polymers and types of solid fuel. The results found that HCN and acrolein were generated with large size of water mist, mean droplet diameter approximate 262.7 μm .

The velocity and flow rate of water mist droplets depended on the operating pressure will be studied in the future for a better understanding on the fire suppression effectiveness and toxic gases produced by the combustion of polymeric materials.

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