Extinction effectiveness of pyrogenic condensed-aerosols extinguishing system

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Abstract–We studied the extinction effectiveness of pyrogenic condensed-aerosols in gaseous fire extinguishing systems through the ISO (International Organization for Standard) 15779. The thermal characteristics of solid aerosols as an extinguishing agents were evaluated by using TG and DTA. The modified closed pressure vessel test (MCPVT) and the conductivity of the solid aerosol extinguishant were also measured to ensure the safety of extinguishant. The TG and DTA result showed that the resin added to the main component of Potassium Nitrate (PN) has the effectiveness to mitigating the exothermic reaction of the pyrogenic condensed-aerosol extinguishant. The results of maximum height test revealed the extinguishing capability of a pyrogenic condensed-aerosol extinguishing agent as a gaseous extinguishing system.

Key words: Pyrogenic Condensed-aerosol Extinguishant, Halon 1301, Gaseous Extinguishing System, GWP

INTRODUCTION

The gaseous pyrogenic condensed-aerosol extinguishing system has been under development as a new type of alternative Halon 1301 (bromotrifluoromethane, $CBrF_3$) gaseous fire extinguishing agent as it is connected to depletion of the ozone layer [1-3]. Also, in accordance with the development of construction technology, many high-rise buildings above fortieth floors are causing major difficulties for fire departments in reaching these heights with ladders. The most important advantage of gaseous pyrogenic condensed-aerosol extinguishing systems is their easy installation, which includes no piping and only occupying a small space. For the alternative gaseous fire extinguishing systems of halon, there are dry chemicals, water sprays, carbon dioxide, Inergen, hydrochloroflurocarbons (HCFCs) and chloroflurocarbons (CFCs) within the fire extinguishing systems [4-9]. Among them, the fluorinated gaseous fire extinguishing systems contain a problem in that they produce a great deal of hydrogen fluoride (HF), which possess a high level of global warming potential (GWP). None of the gas systems, including the dry chemical and water spray systems, show weaknesses in their chemical residue after the fire suppression. An Inergen fire extinguishing system is safer from the viewpoint of no toxins being produced from the inert gas, yet it requires a large quantity of extinguishing agents and a large space for its storage system, resulting in a higher expense [10-16]. The pyrogenic condensed-aerosol extinguishing system, in which the GWP factor and ozone depletion are zero, respectively, stands as the most suitable candidate for the next halon alternative gaseous fire extinguishing system [17-19]. However, this system has not been widely used, while the tests on how solid aerosol extinguishing agents affect humans, the tests on its design concentration, its reliability, and its toxicity have yet to be concluded; therefore,

installation of the solid aerosol extinguishing systems within residential areas has yet to be considered. Recently, there has been a movement worldwide that HCFC and CFC gaseous fire extinguishing agents should be restricted as they are one of the fluorinated gaseous extinguishing agents that involve a high GWP. For the halon alternative extinguishing agents, a system containing a lower GWP is becoming an essential factor for selection [20-23].

In this study, the extinction effectiveness of pyrogenic condensed-aerosols possessing the main component of potassium nitrate (PN) in a gaseous fire extinguishing system was investigated according to the maximum height test method of the ISO 15779 [26-28]. Also, experiments on the thermal behaviors of the component of the solid aerosol extinguishing agents were conducted regarding the safety use of the extinguishing agents.

EXPERIMENTAL

1. Thermal Analysis

The curves of DTA (Differential thermal analysis) and TG (Thermal gravity) were obtained by using MAC Science/9801FA2. The DSC (Differential scanning calorimetry, DSC 1 Mettleer) was carried out by placing 2 mg samples of PN into an aluminum cell with a carrier gas of N_2 at a flow rate of 50ml/mi at various heating rates from 10 to 50 K/min. An alumina was used as a reference sample.

2. MCPVT (Modified Closed Pressure Vessel Test)

The MCPVT was used to measure the pressure generated from the solid aerosol extinguishing system. As the MCPVT is a small pressure vessel test modified by the ISO 10156, the temperature and pressure of the inside chamber can also be determined [24].

3. Extinguishing Performance Test (Maximum Height Test)

The test of the extinguishing efficiency of a solid aerosol extinguishing agent was conducted in a $100 \, m^3$ fire model in accordance with the ISO 15779 and the NFPA 2010 code [26-28].

4. Material

The PN used in the study was manufactured in Chile with a purity

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level of at least 99%. Resin was used as the laboratory reagent.

RESULTS AND DISCUSSION

The pyrogenic condensed-solid aerosol extinguishing system generated the combustion of propellants in which K containing compounds were able to terminate the chain reaction with H or OH radicals. Potassium nitrate (PN, KNO_3) is one of the most effective and useful materials among the pyrogenic condensed-solid aerosol fire extinguishing agents. The main mechanism for pyrogenic condensed-solid aerosol extinguishing agents focuses on the rapid suppression of a fire by efficiently generating the extinguishing agents (solid aerosols) which include nitrogen, carbon dioxide, potassium oxide, etc. [17-19].

In this pyrogenic condensed-aerosol extinguishing system, the fire extinguishing agent is burned and discharged along the following steps:

Step 1: Ignition of the solid extinguishing agent

Step 2: Formation of gaseous combustion products from a quick combustion reaction

Step 3: Movement through a filter system which minimizes or inhibits the emission of dust

Step 4: Movement through a cooling system, which cools down the high temperature of the combustible gas

Step 5: Emission of a gaseous aerosol extinguishant on the outside.

The pyrogenic condensed-aerosol extinguishing agent needs to be adjusted to the temperature of the pyrogenic aerosol being discharged from the generator because PN decomposes and burns at a high temperature. The resin is required to be added to the pyrogenic aerosol extinguishant for reducing the temperature of pyrogenic aerosols which are exothermically produced and for assisting to balance the thermal reaction of PN.

Fig. 1 displays the TG and DTA curves of pure PN and resin, respectively. PN produces an exothermic reaction during its thermal decomposition (Fig. 1(b)). It is necessary to reduce the heat capacity at the same range regarding the exo-thermal heat of PN. The curves of Fig. 1(b) reveal that within the same areas in which
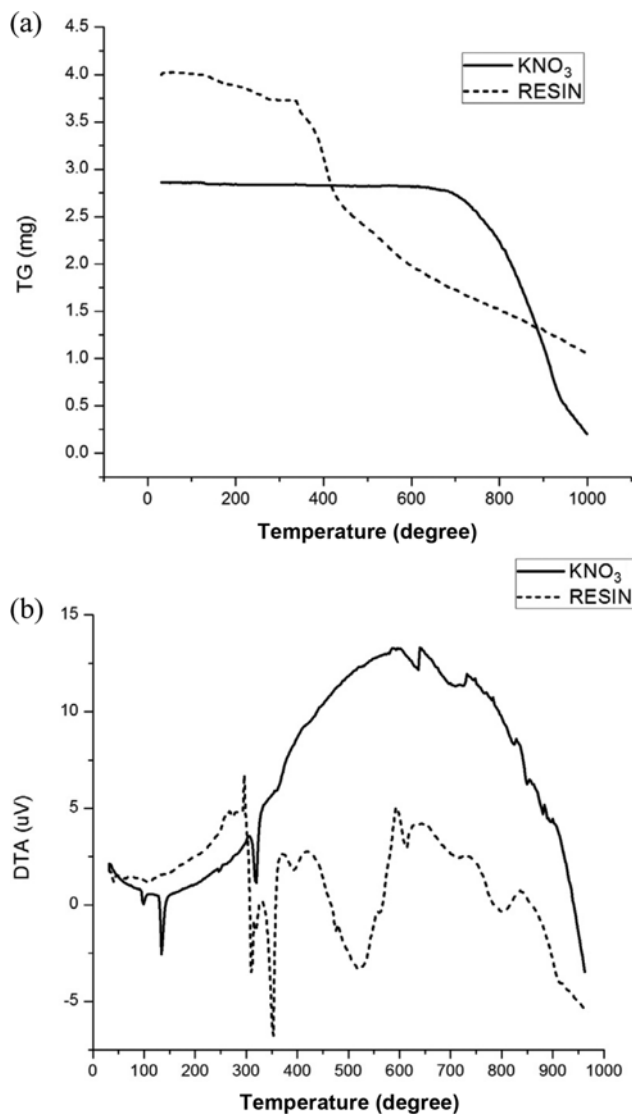

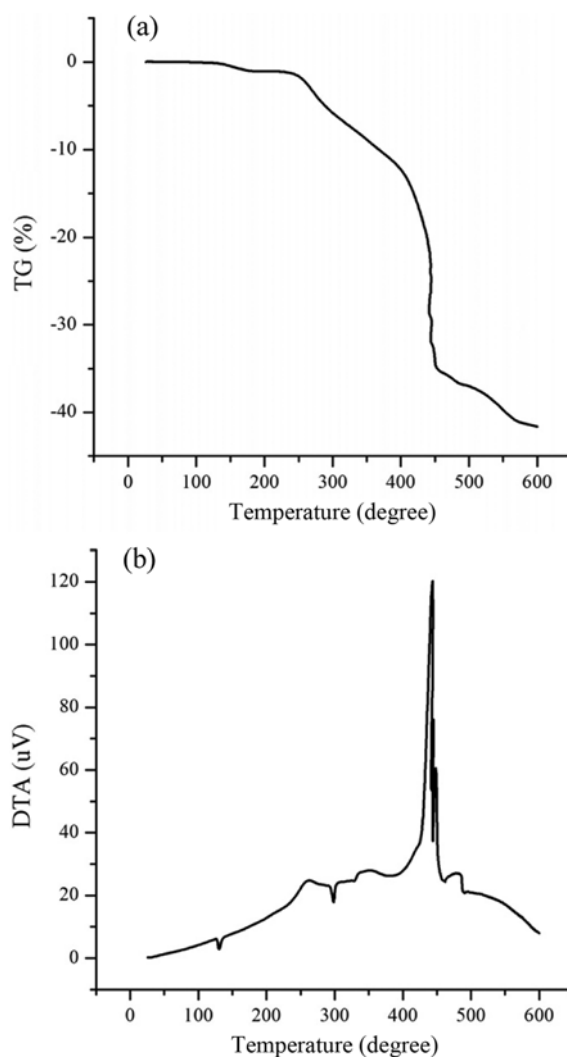Fig. 1. TG(a)/DTA(b) curves of PN and resin at a heating rate of 5 °C/min.

Fig. 2. TG(a)/DTA(b) curves of a solid aerosol extinguishant at a heating rate of 5 °C/min.

Table 1. The T_{peak} of pure PN (upper) and with resin (lower) for DSC curves under various heating rates

Heat rate Φ (K/mim)	T_{peak} (℃)		T_m (K)		$1/Tm10^3$	
10	126.59	314.52	399.74	672.89	2.501	1.486
15	125.50	316.75	398.65	671.8	2.508	1.489
20	126.36	316.10	399.51	672.66	2.503	1.487
25	127.50	318.75	400.65	673.8	2.495	1.484

Heat rate Φ (K/mim)	T_{peak} (℃)		T_m (K)		$1/Tm10^3$	
10	129.64	307.88	402.79	581.03	2.484	1.721
15	130.49	305.85	403.64	579.00	2.478	1.727
20	132.01	309.03	405.16	582.18	2.469	1.718
25	132.52	-	405.67	-	2.466	-

PN is an exothermic reaction and the resin is an endothermic reaction, respectively, the temperatures are at around 400 ℃ to 600 ℃. It is expected that the additional resin mixed with PN deters the exothermic reaction of PN during decomposition.

Fig. 2 shows the curves of TG and DTA for the composition of a pyrogenic aerosol extinguishant with 80% PN and 20%. The peak at around 250 ℃ in Fig. 2(a) is of resin decomposition while the PN decomposes at 450 ℃. From the PN exothermic reaction, the temperature of the pyrogenic solid aerosols being discharged from the generating system is higher than 450 ℃. A cooling element is needed for the high temperature of the discharged pyrogenic aerosols as well as for the generator system regarding the resistance of the high pressure. From 300 ℃ to 500 ℃, the resin reacts endothermically, leading to the lowering of the decomposition temperature of PN in Fig. 2(b). By adding resin to PN, the resin inhibits the exothermically decomposed reaction of a solid aerosol extinguishant, resulting in a reduced temperature for the aerosols being discharged from the generator.

By the Kissinger method, the activation energy of PN was determined to investigate the effects of resin on PN. Table 1 contains the temperature of T_{peak} of pure PN regarding a DSC analysis with various heating rates of 10, 15, 20, and 25 ℃/min. The T_{peak} of PN at 314.52 ℃ shifts to a higher temperature as the heating rate increases.

The Arrhenius Equation explains the dependence of the rate constant k of chemical reactions on temperature T and the activation energy Ea in the following Eq. (1):

$$k=A \times e^{-(Ea/RT)} \tag{1}$$

In this equation A is the pre-exponential factor and K is the absolute temperature in Kelvin, while R is the universal gas constant (8.314 J/mol-K), and Ea is the activation energy. The units of the pre-exponential factor A are identical to those of the rate constant and will vary depending on the order of the reaction. When the activation energy decreases, the rate of the reaction increases. The natural

Table 2. The activation energy of pure PN and PN with resin in an extinguishing agent

Materials	Activation energy (J/mol)	Curve
Pure PN	138.05	Y=− 16.605x 42.837 (R²=0.96)
PN with resin	172.07	Y=− 20.696x 52.425 (R²=0.98)

logarithm of the Arrhenius equation is as follows:

$$\ln(k)=-Ea/R \times 1/T + Ln(A) \tag{2}$$

Therefore, when a reaction has a rate constant, a plot of ln(k) versus T^{-1} produces a straight line, whose gradient and intercept can be used to determine the Ea and A [25,29].

The activation energy of PN increases from 138.05 J/mol to 172.07 J/mol in the sample containing resin. The resin in the solid aerosol extinguishing system produces an effect to increase the activation energy of potassium nitrate, resulting in slowing the progress of the reaction of potassium nitrate. As the heating rate increases in the pyrogenic condensed-aerosol extinguishment system, the combustion time of the solid aerosol by-products filling the generator is reduced, speeding up the discharge rate. If the solid aerosol extinguishing agent burns too quickly, the pressure of the generator increases rapidly. If the pressure increases according to the reaction dynamic theory, the reaction rate increases as well. In terms of the reaction cycle, as the burning rate increases, the pressure increases. As the heating rate increases, the pressure increases. For safety purposes, the gas vent in the generator, which is used in the pyrogenic condensed-aerosol extinguishment system, needs to be strongly promoted. Installing the pyrogenic condensed-aerosol extinguishing system in buildings, etc., fire safety should be guaranteed at lower temperatures below 300 ℃. In Table 3, the MCPVT results are described of a pyrogenic condensed-aerosol extinguishant a change in pressure, resulting in increased temperatures.

The rise in pressure of the gas produced by solid aerosols was measured using the MCPVT. Through mini-pressure vessels, the MCPVT can accurately measure the temperature and pressure in the inner sections of the vessel. The MCPVT, the transformed version of the large scale DTA system, can measure the temperature and pressure of the ISO. The sample weighed 1.1 g and applied heat at an increased increment rate of 10 K/min. The pressure rise of the aerosol emitted from the aerosol extinguishing system should be guaranteed safe at temperatures below 300 ℃. Table 3 shows that there were no significant pressure increases in the area from room temperature to 300 ℃. These results confirmed that the pyrogenic condensed-aerosol extinguishing system in regards to the discharging extinguishant would be safe in a normal environmental condition.

The extinction effectiveness of the pyrogenic condensed-aerosol extinguishing system was conducted in accordance with the maximum height test method of ISO 15779 (Fig. 3(a)). The test can was placed on the floor and attached to the ceiling, each placed within

Table 3. The pressure variation according to an increasing temperature

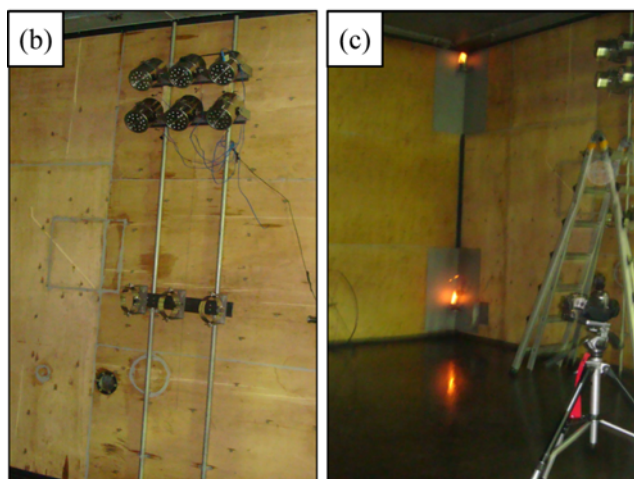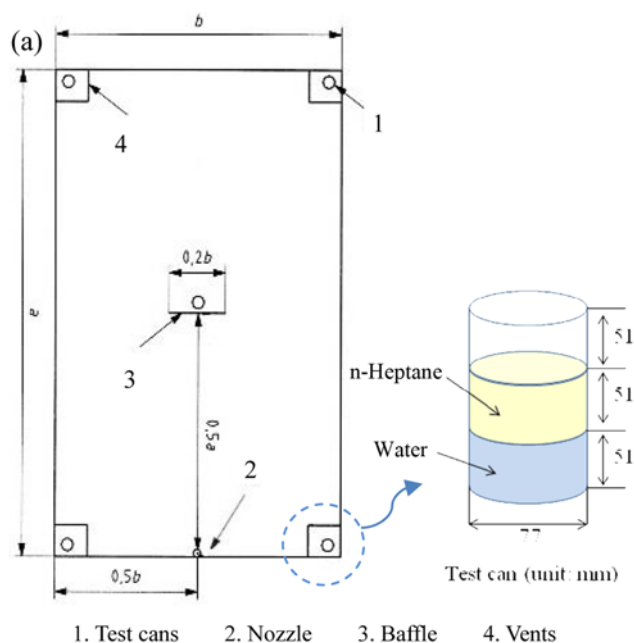| Temperature (℃)	30	50	100	150	200	250	300
Pressure (MPa)	0.01208	0.01812	0.03019	0.04227	0.06039	0.10266	0.19324

Fig. 3. Plan view (a) and photos (b), (c) of the instrumentation placement for the maximum height test of ISO 15779.
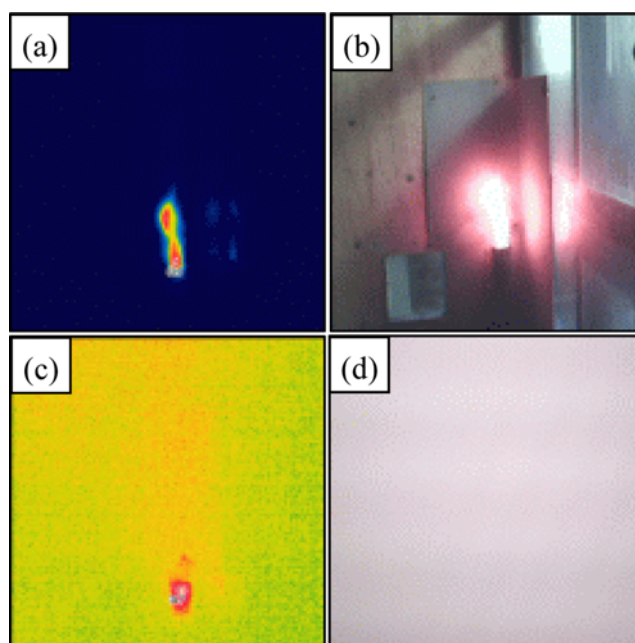

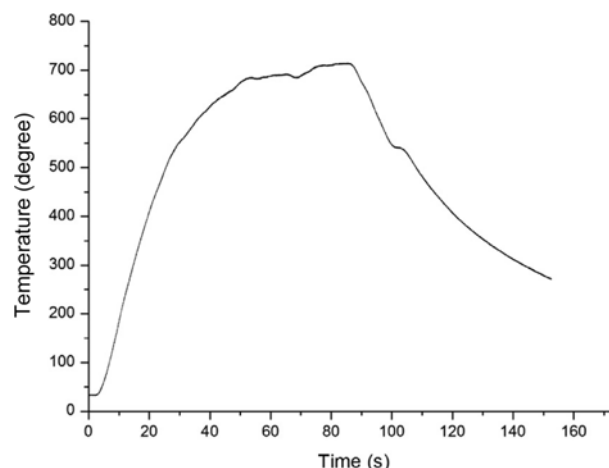Fig. 4. Infrared (a), (c) and general (b), (d) photos for the maximum protected height limitation test in 100 m³ units.

Fig. 5. The temperature change of the fire on the can during the maximum protected height limitation test in 100 m³ units.

50 mm away from the corner of the unit, according to the enclosure arrangement model in Fig. 3(c). Each test can was placed 300 mm behind the center of the floor, and 300 mm away from the upper and lower sections. Fig. 3(b) illustrates the nozzle installation which is on the center of the wall in the test room. The test begins by igniting the cans; then, the nozzle discharges the solid aerosol extinguishant toward the baffle in the direction placed in the middle of the enclosure (NFPA 2010, ISO 15779).

Fig. 4(a), (c) displays the infrared pictures of fire on the can. When the solid aerosol gaseous extinguishing agents are discharged from the extinguishing system, the color of the atmosphere in the test room turns from blue to green. The pyrolyzed aerosol heats the test room and flows internal within the atmosphere because of the discharged pressure and the difference in the specific gravity. After releasing the solid aerosols of the extinguishant from the generator, the protected area is rapidly filled, which was recorded by using a general camera (Fig. 4(b) and (d)); however, the change of the flame

was viewed more clearly with the use of an infrared camera (Fig. 4(a) and (c)). Fig. 5 illustrates the temperature change of the fire on the can during the maximum protected height limitation test. The temperature rise at around 700 °C but the temperature falls sharply after the discharge. The graph indicates that the fire in the can was successfully suppressed.

K compounds discharged from the solid aerosol extinguishing agent, combined with O, H, and OH radicals, extinguished the fire under a chemical chain reaction without consuming any air. The other discharged products, including the inert gases of carbon dioxide and nitrogen, extinguished the fire as a result of physical extinguishing reaction. Through the mechanisms of physical fire suppression of an inert gas and the chemical fire suppression of radicals of potassium oxide, the solid aerosol extinguishing system produced a very effective gaseous fire suppression system compared to Halon 1301

in the area of a gaseous fire extinguishing system.

CONCLUSION

The extinction effectiveness of pyrogenic condensed-aerosols in a gaseous fire extinguishing system was demonstrated through the maximum height test fire experiment of ISO 15779 in which the burn time and discharge percentage of pyrogenic condensed-aerosol emitted met the ISO requirements. The activation energy determined by the Kissinger analysis showed that the resin added to PN increases the activation energy of PN, resulting in the lowering the decomposition rate of PN through deterring the exothermic reaction. The MCPVT results displayed that there was no significant change of the pyrogenic condensed aerosol extinguishant under 300 °C. The results of the maximum height test of ISO showed that the extinguishing capability of a pyrogenic condensed-aerosol extinguishing agent is competitive to the alternative of Halon 1301 in a gaseous extinguishing system.

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