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Elucidating the effects of particle sizes on the fire extinguishing performance of core-shell dry water

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Abstract−Core-shell dry water (DW) has attracted significant attention as a promising candidate for future fire extinguishing agents, owing to its high water content, powdery structure and ease of handling. However, the lack of detailed information regarding the characteristics of DW has considerably hindered efforts to improve its fire extinguishing performance. This study is the first attempt to elucidate the origin of the effects of particle size of DW on fire extinguishment. Pristine DW was fractionated into three different particle sizes via careful sieving. Through systematic analyses, it could be determined that smaller DW could be vaporized at lower temperatures, thereby facilitating good cooling and smoldering of flames. However, small DW cannot sufficiently penetrate flames, which makes it difficult to reach the burning surface. However, medium-sized DW exhibited a balance in its cooling, smoldering, and penetration effects. Thus, it achieved better performance in fire extinguishment when compared to small- and large-sized DWs. It was also demonstrated that the fire extinguishing capability of medium-sized DW can be significantly enhanced by adding $NaHCO_3$ in the water core of the DW.

Keywords: Hydrophobic Silica, Core-shell Dry Water, Fire Extinguishing Mechanism, Particle Size Effects, Chemical Additives

INTRODUCTION

Fire suppression systems are essential for preventing fire damage and the resulting loss of life and structural damage. Several fire extinguishing agents, including water mist, carbon dioxide, commercial ABC powder, halons, and foam, are used [1,2]. Although these agents have played a key role when responding to fires, they have also caused unintended damage due to their side effects. For example, accidental exposure to carbon dioxide during the maintenance or testing of CO_2 systems has resulted in significant injuries and deaths [3]. In the case of the water mist extinguishing agent, if the momentum of the water droplets is low, their ability to penetrate flames is reduced, thereby degrading the effectiveness of the water mist in suppressing flames [4]. Moreover, commercial ABC powder can cause secondary pollution after it has been used [5]. In addition, concerns regarding fire extinguishing agents have been raised considering environmental issues. The use of halons, which had been extensively employed as fire suppression agents, is prohibited due to their ozone depletion potential [6,7]. Perfluorooctane sulfonate, a key component in the fluorosurfactant foam agent, was phased out by major producers because of its persistent bioaccumulative and toxic properties [8]. Considering the above-mentioned issues, it is imperative to develop a novel fire extinguishing agent that has excellent fire extinguishing performance without detrimental side effects.

Recently, there has been a growing interest in core-shell structured dry water (DW), which contains up to 98 wt% of water and exhibits characteristics similar to those of dry powders [9]. The core of DW is a significantly small water droplet with a porous shell of branched hydrophobic silica network that surrounds this water core [10]. It is considerably easy and convenient to handle and store DW because it maintains its powdery features even though it is mainly liquid water. The water core of DW can be released by evaporation or under mechanical stress [10]. Due to these characteristics, several studies have attempted to employ DW in various fields such as gas sensing [11], water pollution [12], storage and transportation [13,14], and fire extinguishing agents [15]. Dry core-shell DW has achieved excellent performance for extinguishing gasoline pool fires, and it is expected to possess sufficient scalability to enable its use in actual fire accidents [16].

Although previous studies have successfully demonstrated the potential of DW as a fire extinguishing agent, only a few studies have been able to unveil the important characteristics of DW that determine its fire extinguishing capability. To address this gap in the literature, we investigated the effects of the particle sizes of DW on fire extinguishing performance [17]. In our previous study, a careful sieving method was used to separate pristine DWs into three different particle size fractions, and it was found that medium-sized (approximately 210 μm) DW yielded better fire suppression performance when compared to small-sized (approximately 110 μm), large-sized (approximately 400 μm), and pristine DWs. However,

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we could not sufficiently explain this excellent fire-fighting performance of the medium-sized DW.

In this study, careful experiments and observations were carried out to unravel the effects of DW particle size on fire extinguishing performance. Moreover, clear and detailed evidence for the origin of particle size effects was also obtained. Furthermore, we demonstrated that the fire extinguishing performance of DW could be significantly enhanced by integrating particle size effects and the chemical additives of DW.

EXPERIMENTS

1. Preparation of DW

Core-shell DW can be easily prepared via high-shear mixing of hydrophobic silica nanoparticles in water. In general, hydrophobic silica nanoparticles do not mix with water due to their hydrophobicity. However, the high-shear mixing process can split water into large drops. Once these large droplets have been formed, further mixing leads to more homogeneous and finer droplets [10]. When the network of hydrophobic silica surrounds the water particle, a core-shell DW containing a water droplet as the core in the silica shell is formed. Therefore, the formation of core-shell DW depends on the shear force during the mixing process and the hydrophobicity of the silica particles used in this process. In this study, the optimum conditions for the preparation of core-shell DW were determined based on the reports of prior studies [5,9,18-21].

To prepare DW samples, hydrophobic fumed silica nanoparticles (R812S) were obtained from EVONIK (Germany). The silica nanoparticles (R812S) and distilled water were mixed at a mass ratio of 1 : 19 (silica: water). In particular, 35 g of the silica nanoparticles (R812S) was mixed with 665 g of distilled water in a glass bowl having a volume of 1.6 L. Thereafter, as shown in Fig. 1(a), a high-speed blender (IKFM-2000) was used to stir the mixture of the silica nanoparticles and distilled water for 30 s, at a mixing speed of 22,000 rpm. This simple mixing process resulted in the preparation of core-shell DW, as depicted in Fig. 1(b).

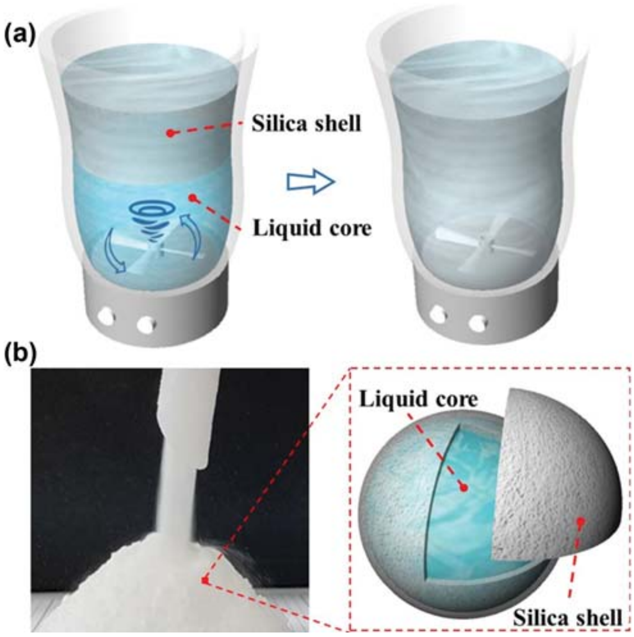

Fig. 1. (a) Schemes of preparation and (b) images of dry water.

Sodium bicarbonate ($NaHCO_3$) and ammonium phosphate dibasic ($(NH_4)_2H_2PO_4$) were obtained from Samchun Chemicals Co., Ltd., and used as chemical additives for DW. These chemical additives were dissolved in distilled water to obtain 1 mol/L concentrations. These 1 mol/L aqueous solutions of $NaHCO_3$ and $(NH_4)_2H_2PO_4$ were used instead of distilled water during the preparation of DW. Commercial ABC powder (Kukje Co., Ltd.) was also used as a reference fire-extinguishing agent.

2. Particle Size Separation of DW

As-prepared pristine DW has a broad particle size distribution. Therefore, we employed a careful sieving method to separate pristine DW into different particle size fractions. Six sieves with different hole sizes—850, 700, 500, 300, 150, and 75 μm—were stacked and pristine DW was passed through these sieves. However, only a considerably small amount of DW was screened by the sieves with hole sizes of 850-500 μm; therefore, these fractions were not used in the test. The fraction of DW that was collected through the sieve with a hole size of 75 μm was described as small-sized DW. In addition, the fractions of DW that were screened by the sieves with hole sizes of 150 μm and 300 μm were denoted as medium-sized DW and large-sized DW, respectively.

3. Characterization of DW

An optical microscope (DIMIS-M, Siwon Optical Technology) was used to observe the difference in the particle sizes of the prepared DW samples. The particle size distributions of the DW samples were measured via the Image J program.

The fluidity of the DW samples was also investigated based on the angle of repose. In general, an agglomerated powder with low fluidity exhibits a large angle of repose, whereas powders with high fluidity exhibit a small angle of repose. To measure this angle of repose, 50 mL of the DW sample was poured into a funnel and the height and angle of the accumulated cone were measured.

The water core of DW can play an important role in fire suppression. This core can cool the flame and surrounding gases via vaporization, and this vaporization can also dilute oxygen concentration. Therefore, it is important to investigate the difference in the vaporization according to particle sizes and additives of the DW samples. We employed thermogravimetric analysis (TGA) to compare the difference in the vaporization of the DW samples. A small amount, approximately 10 mg, of the sample was loaded in a test cell of D-TGA (Perkin Elmer TGA1). Changes in the mass of the sample were continuously measured, while the temperature of the sample was increased from 50 °C to 700 °C at a heating rate of 10 °C/min.

4. Fire Extinguishing Test of DW

To evaluate the fire extinguishing performance of the DW samples, class A wood crib fire extinguishing tests were conducted. Fig. 2 presents a scheme of the experimental setup for this test. The fire extinguishing test was conducted in a stainless-steel combustion chamber. Pinewood with a length of 150 mm, height of 30 mm, and width of 30 mm was used for the combustion. Before the combustion, the wood was dried for a minimum of 24 h in a dry oven maintained at 105 °C.

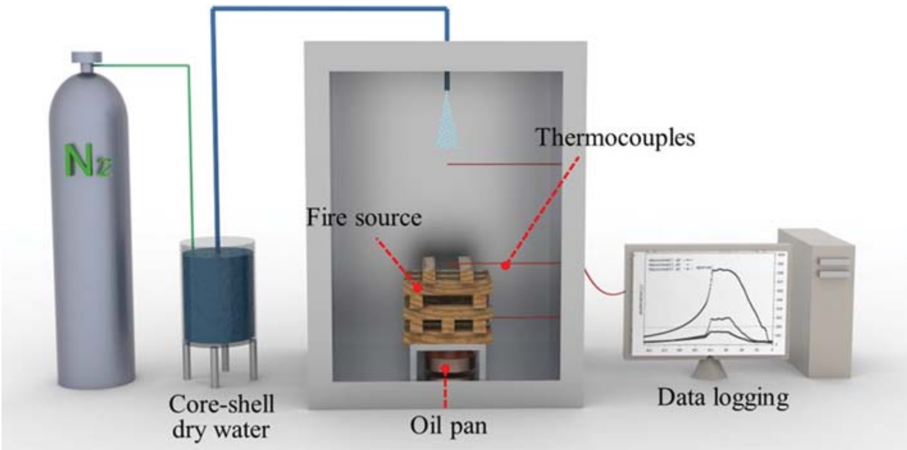

Fig. 2. Experimental setup for the fire extinguishing test.

Pieces of wood were stacked in six layers at the center of the chamber. In particular, three pieces of the wood were stacked in the first and second layers, two pieces in the third and fourth layer, three pieces in the fifth layer, and two pieces in the sixth layer. A thermocouple was installed between the third layer of the wood cribs to measure the temperature of the core of the wood during the fire. Additionally, two thermocouples were installed to measure the temperatures of the peak and bottom positions of the fire plumes.

Moreover, 10 mL of n-Heptane was ignited in a combustion zone under the wood cribs to initiate the combustion. Free combustion was performed for 2 min until the fire reached its peak. Thereafter, the DW sample was discharged at a pressure of 0.2 MPa through an injector, and the extinguishing performance was measured accordingly. It was confirmed that the DW in the extinguishing agent container was not destroyed and the water in the core of the DW was not released after discharging. To confirm the reproducibility of the extinguishing performance, the same experiment was performed thrice for each sample.

In general, the performance of the fire extinguishing agent is evaluated based on its flame suppression time. However, in actual fires wood can re-ignite even after the flame has been suppressed. Therefore, in this study, the fire extinguishing performance of the DW samples was evaluated based on the flame suppression time (T_1) as well as the extinguishing time (T_2) required for the core of the wood to attain a temperature less than 200 °C. The extinguishing time (T_2) can represent the complete extinguishment of fire because wood does not have sufficient energy for re-ignition after its temperature is reduced to less than 200 °C [22]. The flame suppression time (T_1) was obtained using a digital video recorder. The recorded video was divided into frames and the flame suppression time (T_1) was determined. The extinguishing time (T_2) required to attain a temperature less than 200 °C was evaluated by analyzing the core temperature with a thermocouple.

RESULTS AND DISCUSSION

1. Particle Size Distribution and Fire Extinguishing Performance

Fig. 3(A(a)) presents an optical microscope image of as-prepared pristine DW. It is evident that pristine DW consists of irregular and heterogeneous particles, and it also exhibits complex multimodal distributions in the particle sizes ranging from 50-500 μm. However, the sieved DW samples have uniform particle sizes. In particular, the small-sized DW exhibit more homogeneous distribution in particle size than medium- and large-sized DWs. In addition, as shown in Fig. 3(B(b))-3(B(d)), the average particle size of the DW samples measured from the images was similar to the average hole sizes of the sieves. These results confirm that the sieving method used in this study is highly efficient in separating DW into different particle size fractions.

Table 1. Fire extinguishing performances of the DW samples with different particle sizes

Samples	Flame suppression time (T_1) (s)	Fire extinguishing time (T_2) (s)
Small-sized DW	2.05	Failed
Medium-sized DW	1.82	60
Large-sized DW	2.24	73

The fire extinguishing performance of the DW samples differed significantly based on averaged particle sizes (as shown in Table 1). The small-sized DW sample suppressed the flame within 2.05 s; however, it was unable to cool the core of the burning wood and prevent re-ignition. During all three fire tests conducted for small-sized DW, the core temperature of wood did not decrease to less than 200 °C and the extinguished wood was re-ignited once. The large-sized DW sample also yielded insufficient performance in terms of flame suppression time (T_1) and extinguishing time (T_2). The flame suppression time (T_1) and extinguishing time (T_2) of large-sized DW were 2.24 s and 73 s, respectively.

Contrarily, the medium-sized DW sample achieved the best performance in fire extinguishment, as compared to the small- and large-sized DW samples. In particular, medium-sized DW suppressed the flame within a short flame suppression time (T_1) of 1.82 s, and the extinguishing time (T_2) of medium-sized DW was 13 s less than that of large-sized DW.

2. Origin of the Particle Size Effects

When the water core of the DW sample vaporizes, it reduces

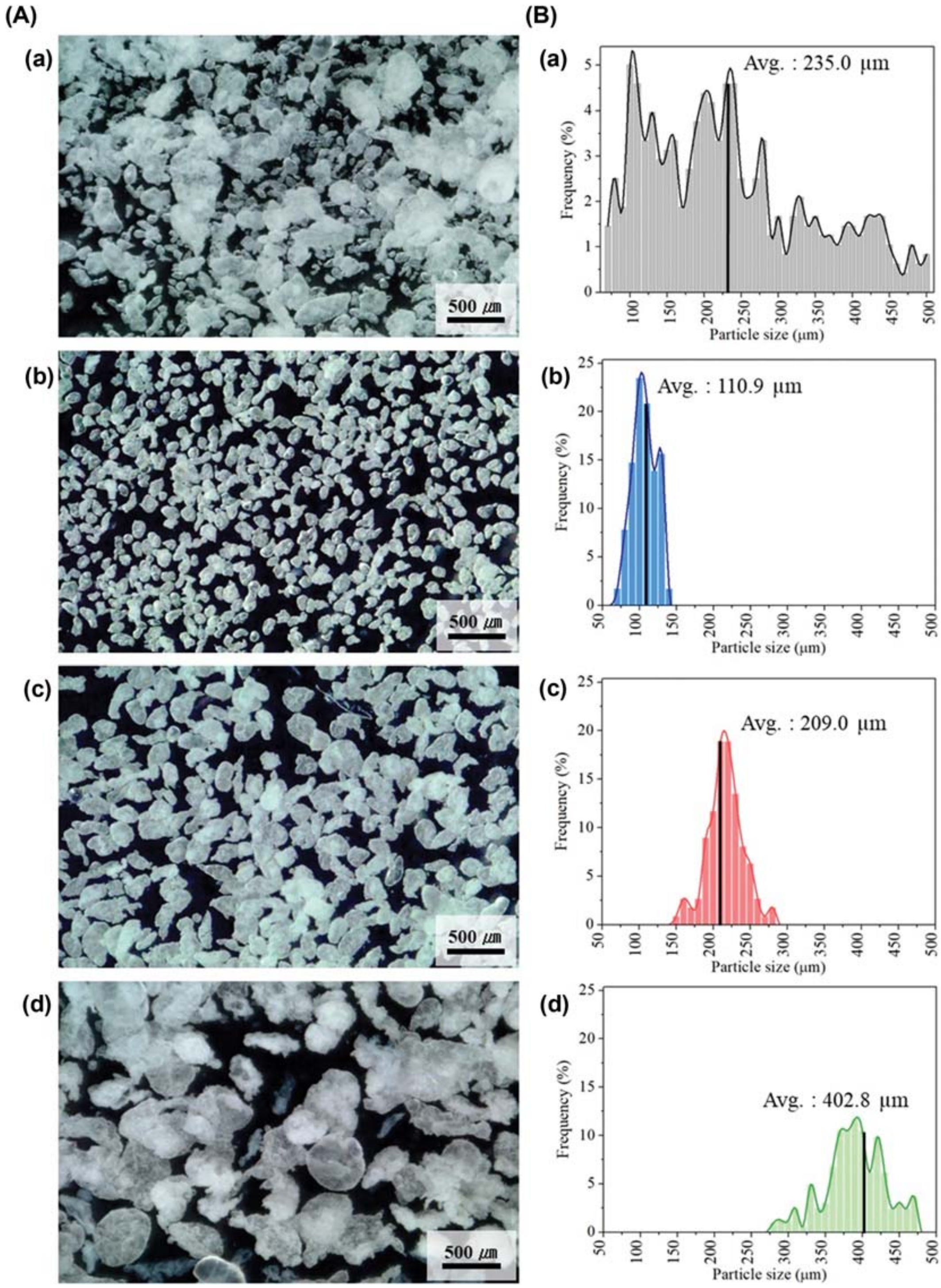

Fig. 3. (A) Microscopic images of dry water, and (B) particle size distributions of (a) pristine DW (b) small-sized DW (c) medium-sized DW, and (d) large-sized DW.

the heat of the flame. Thus, the temperature decreases and the flame is extinguished. The vaporization of the water core also results in a rapid expansion of water vapor, which dilutes the oxygen concentration in the air. Therefore, vaporization of the water core is one of the key factors that determine the cooling and smoldering effects when extinguishing a fire.

The TGA analysis and physical characteristics of the DW samples facilitate an understanding of the effect of particle size on the vaporization of the water core of DW samples. Fig. 4 depicts the results of TGA for the DW samples with different particle sizes, within a maximum temperature range of 200 °C. The DW samples consist only of silica nanoparticles and distilled water, and silica nanoparticles do not decompose at less than 200 °C. Therefore, the reduction in the mass observed in the TGA originates from

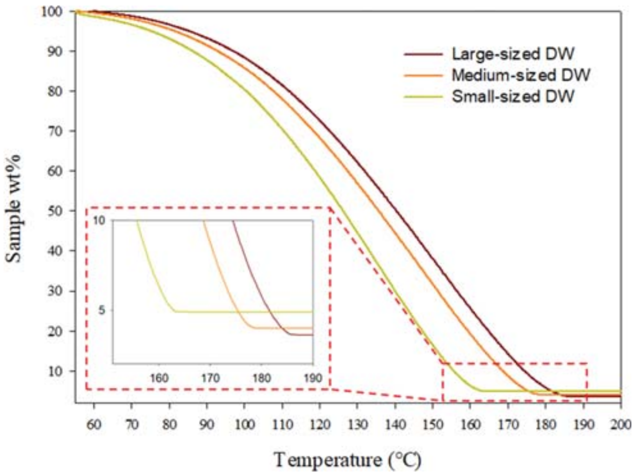

Fig. 4. Results for TGA of the DW samples with different particle sizes.

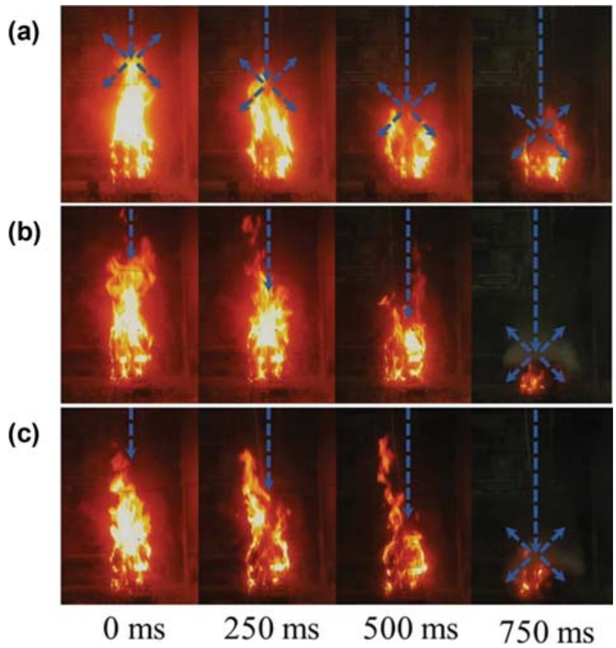

Fig. 5. Results for the frame by frame video analysis of flame suppression of (a) small-sized DW, (b) medium-sized DW, and (c) large-sized DW.

the vaporization of the water core in the DW samples.

Furthermore, it is evident that smaller DW vaporize at lower temperature. In particular, the water core of small-sized DWs vaporizes completely below 163 °C. However, the vaporization of medium-sized DW and large-sized DW was completed at approximately

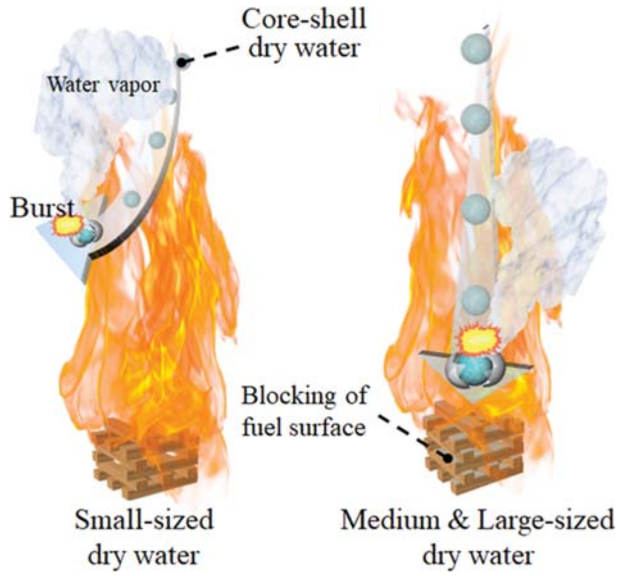

Fig. 6. Scheme for extinguishing mechanisms of dry water with different particle sizes.

178 °C and 186 °C, respectively. These results show that smaller DW can achieve cooling and smoldering effects at lower temperature. The thickness of the silica shell, which was calculated based on a previous study [9], can support the trends in the vaporization temperature of the DW samples. As shown in Table 2, the larger DW sample has a thicker silica shell and more water content than others; therefore, a higher amount of energy is required to vaporize its water core through the thicker silica shell.

However, the detailed frame-by-frame video analyses for fire flame suppression provided highly opposing trends regarding the effects of particle sizes of the DW samples. As shown in Fig. 5, the medium and large-sized DWs suppressed most of the flame after 750 ms of discharging. However, the small-sized DW did not sufficiently extinguish the flame after 750 ms of discharging. Most of the small-sized DW burst at the upper region of the flame; hence, it did not reach the source of the flame, i.e., surface of the burning wood (Fig. 6). In general, smaller water droplet diameters were found to increase the heat transfer rate [23]. Therefore, it is vaporized before penetrating the flame. This result is highly consistent with the poor flame suppression ability of small-sized DW.

In contrast, medium- and large-sized DWs sufficiently penetrated the flame and suppressed it. A closure analysis of the images at 750 ms indicates the difference between the medium- and large-sized DWs. As compared to the large-sized DW, the medium-sized DW achieved higher flame suppression and restricted the flames to smaller sizes. These results are amply supported by the fire sup-

Table 2. Physical characteristics of the DW samples with different particle size

Samples	Average particle size (μm)	Repose angle avg. (°)	Discharged mass avg. (g/s)	Shell thickness (μm)
Small-sized DW	110.9	33.7	17.8	8.0
Medium-sized DW	209.0	30.3	23.6	19.4
Large-sized DW	402.8	32.8	34.7	37.8

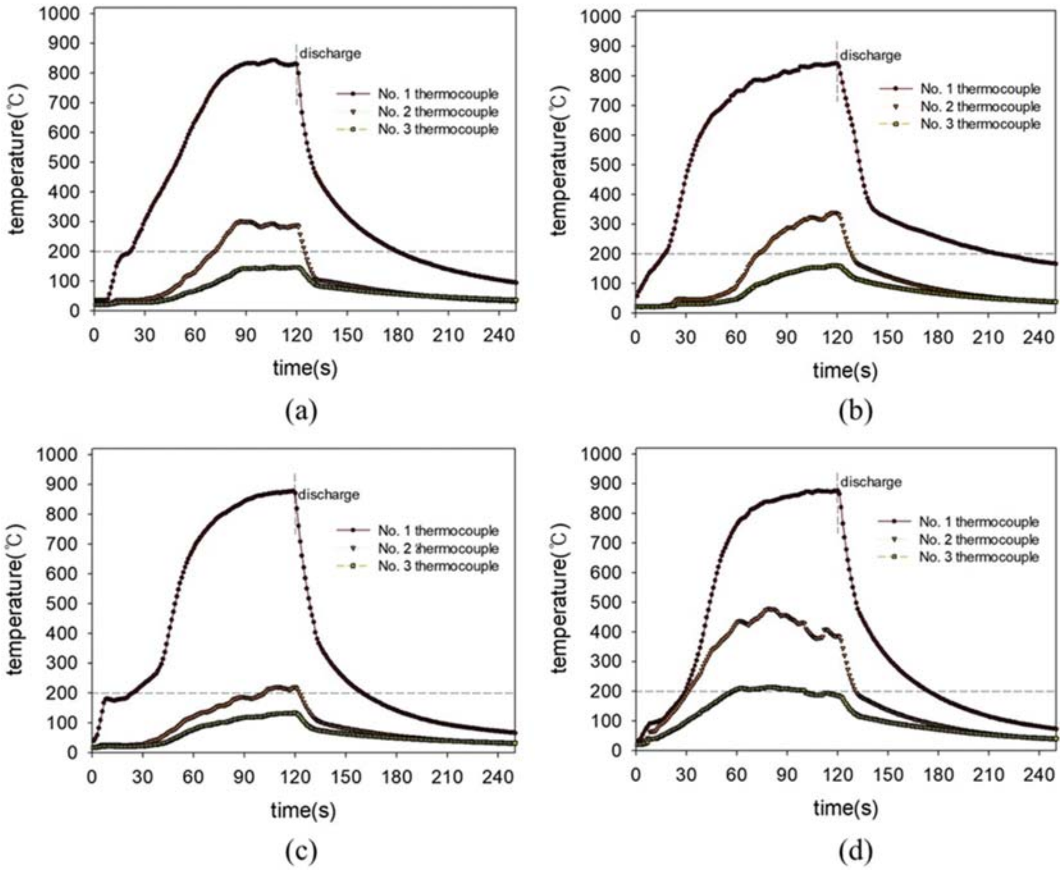

Fig. 7. Temperature profiles in the core of wood stack for (a) medium-sized DW with distilled water, (b) medium-sized DW with $NaHCO_3$, (c) medium-sized DW with $(NH_4)_2H_2PO_4$, and (d) commercial ABC powder.

Table 3. Comparison of fire extinguishing performance between medium-sized DWs with or without chemical additives and commercial ABC powder

Samples	Flame suppression time (T_1) (s)	Fire extinguishing time (s)		
		400 °C	300 °C	200 °C (T_2)
Medium-sized DW with distilled water	1.82	18	33	60
Medium-sized DW with $NaHCO_3$	1.69	13	22	40
Medium-sized DW with $(NH_4)_2H_2PO_4$	2.14	19	32	54
Commercial ABC powder	3.13	18	38	96

pression times (T_1) of medium- and large-sized DWs.

Based on these observations, it can be deduced that smaller DW can vaporize at lower temperature, thereby yielding good cooling and smoldering of flames. However, smaller DW cannot sufficiently penetrate the flame; hence, it is difficult to reach the surface of the burning wood. Contrarily, medium-sized DW achieves a balanced combination of cooling, smoldering, and penetration effects. Thus, it yields good performance for fire extinguishment.

3. Enhancing Fire Extinguishing Capability by Combining the Effects of Particle Size and Chemical Additives

Although medium-sized DW exhibited good performance in the fire extinguishment test, further investigations were performed to enhance the capability of medium-sized DW and compare it with that of commercial ABC powder. $NaHCO_3$ and $(NH_4)_2H_2PO_4$ were used as chemical additives for this enhancement because these are well known for their use in water mist. Medium-sized DW containing $NaHCO_3$ was prepared by using an aqueous solution of $NaHCO_3$ with concentration of 1 mol/L. In addition, an aqueous solution containing 1 mol/L of $(NH_4)_2H_2PO_4$ was used to prepare medium-sized DW with $(NH_4)_2H_2PO_4$. As presented in Fig. 7 and Table 3, the medium-sized DW with $(NH_4)_2H_2PO_4$ yielded a shorter extinguishing time (T_2) and a longer flame suppression time (T_1) in comparison to the medium-sized DW with distilled water. Therefore, the effects of the $(NH_4)_2H_2PO_4$ additives remained unclear. On the other hand, the commercial ABC powder took long time to suppress the flame and to completely extinguish the fire. The flame suppression time (T_1) and extinguishing time (T_2) of the commercial ABC powder were 3.13 and 96 s, respectively.

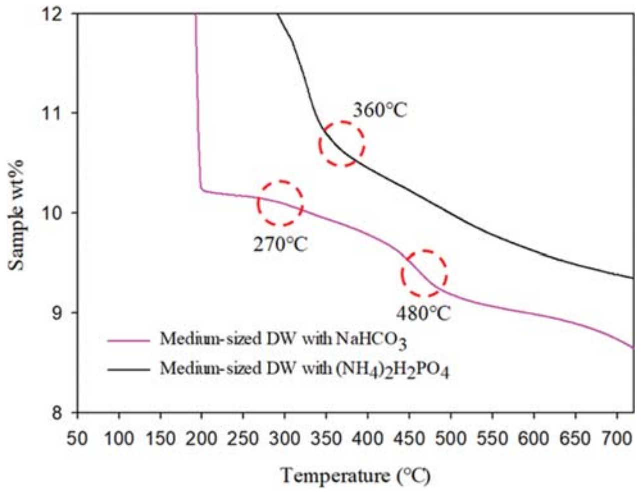

Fig. 8. Results for TGA of medium-sized DW with $NaHCO_3$ and $(NH_4)_2H_2PO_4$.

However, the medium-sized DW with $NaHCO_3$ was the quickest in suppressing the flame and extinguishing the fire. The flame suppression time (T_1) and extinguishing time (T_2) of the medium-sized DW with $NaHCO_3$ were reduced by approximately 50% in comparison with commercial ABC powder. The improved ability of the medium-sized DW with $NaHCO_3$ can be attributed to the endothermic and sequential pyrolysis reactions of $NaHCO_3$ at approximately 270 °C and 480 °C (as shown in Fig. 8). These results clearly indicate that combining the effects of particle size and $NaHCO_3$ additives can significantly enhance the fire extinguishing performance of DW, thereby facilitating its practical application.

CONCLUSIONS

Core-shell DW has been proven to be a promising candidate for future fire extinguishing agents owing to its high water content and powdery structure that facilitates ease of handling and storage. However, the detailed characteristics of DW that affect its fire extinguishing capability have not been elucidated thus far; this lack of information has significantly hindered efforts to implement it and improve its performance. This study is the first successful attempt to determine the effects of the particle size of DW on fire extinguishment. A careful sieving method enabled the fractionation of as-prepared pristine DW into three different particle sizes. Based on a systematic analysis, which included TGA, a frame-by frame video analysis, and particle analysis, we concluded that smaller DW can be vaporized at lower temperature, thereby yielding good cooling and smoldering of flames. In contrast, it is difficult to penetrate the flames and reach the burning surface when using smaller DW. Thus, medium-sized DW achieves a balance between the combination of cooling, smoldering, and penetration effects, thereby resulting in better fire extinguishment performance as compared to small- and large-sized DWs. It was also demonstrated that the addition of $NaHCO_3$ to the water core of medium-sized DW can lead to an excellent suppression performance of wood fire, surpassing the performance of commercial ABC powder.

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