Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Application of water@silica core-shell particles for suppressing gasoline pool fires

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HIGHLIGHTS

• A new type of fire suppressants with water@silica core-shell structures was fabricated as through a simple stirring method.

The capsular particles showed excellent performance in extinguishing gasoline pool fires in terms of time and agent mass.

• The work presented a novel route to produce small sized water droplets and store them without coalescence for long time.

ARTICLE INFO

Article history: Received 11 April 2017 Received in revised form 18 July 2017 Accepted 19 July 2017 Available online 21 July 2017

Keywords: Fire suppressant Capsular particles Water Silicon dioxide Gasoline pool fire

ABSTRACT

A new type of dry powders with capsular structure was fabricated for fire suppression, in which the content of water approached 60%. The capsules with the size of $3-5\,\mu$ m consisted of liquid core and solid shell, where the core was water droplet and the shell was assembled silicon dioxide particles with surface hydrophobic modification. The shell of close-packed silica particles surrounding each water droplet provided the structural rigidity of the capsules and enabled their application as powder fire suppressants. Two different scaled real fire tests showed that thus-prepared solid powders could extinguish 0.21 MW gasoline pool fire in 2.0 s with agent mass of 0.055 kg, and 1.0 MW gasoline pool fire in 5.0 s with agent mass of 0.49 kg. Such fire extinguishing performance greatly outperformed the conventional monoammonium phosphate (ABC) powders, neat silica powders and water mist, with significantly reduced fire extinguishing time and mass of agent consumed. Mechanism of the core-shell particles in fire suppression was discussed based on established theories and experimental results.

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1. Introduction

Gasoline is one of the most commonly known liquid fuels, which is highly ignitable and volatile. Gasoline has a comparatively low flash point of about -65 °C and the ignition temperature of about 232 °C. While burning gasoline has a temperature above 945 °C, which can heat objects in the fire area above its ignition temperature [1]. Meanwhile, gasoline is so volatile that a large amount of vapor is quickly generated from the liquid surface. The flammable range of gasoline is only 1.4%–7.1% [2]. When the gasoline vapor in an enclosure is ignited, it will burn explosively and causes extensive damage. Gasoline vapor is heavier than air. It tends to flow downhill and downwind from liquid gasoline, making it possible for explosive mixtures to collect in low points such as pipe trenches or terrain depressions. Usually, a crash is often followed by a gasoline

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http://dx.doi.org/10.1016/j.jhazmat.2017.07.040 0304-3894/© 2017 Elsevier B.V. All rights reserved. fire. At present, gasoline is widely used in cars, aeroplanes and some machines. The distressing and increasingly frequent incidence of fatal fires in employing gasoline [3], has repeatedly directed attention to the need for an effective fire suppressant for gasoline fires.

Highly efficient fire suppressants could fast control the fire and greatly reduce the loss. Since the phase out of halon, water mist as one of the halon replacer has been paid great attention for its high efficiency and environmental friendliness [4]. As naturally clean agent, water mist would not decompose or produce any toxic products when exposed to flame. In comparison to conventional water spray, water mist with much smaller droplet size (with 99% of the volume of droplets with diameters less than 1000 μ m) showed much higher efficiency in fire suppression. But water mist is not so efficient in extinguishing small liquid fuel fires in the open space because a small fire may not be able to generate enough heat for the transformation of water droplets into vapor to displace sufficient oxygen [5,6]. It is noted that even if a liquid fire is extinguished by water mist, re-ignition may occur at any time for the poor covering effect of water mist from contacting oxygen [7].



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To prevent re-ignition after extinguishment, water mist must be applied for sufficient time to allow hot objects in the fire area to cool below the ignition temperature of gasoline. This is time consuming and may cause water damage. Droplet size greatly affects the fire suppression capability of water mist [8]. It is difficult for water mist with small droplet size and low momentum to penetrate the flame fume to extinguish the fire. While water mist with big droplet size and high momentum would usually spoil out the liquid fuel or raise its level in a container and so result in larger combustible area. Production of water mist with proper droplet size was crucial for successful fire extinguishment. Conventionally, production of water mist depends on specific technique, such as specially designed nozzles and pressure. This makes the practical application of water mist become conditional. In comparison to water mist, dry powders as fire suppressants even showed superior fire extinguishing capabilities on a mass basis while consuming minimal space [9,10]. Furthermore, dry powders consisting of small particles could be easily discharged to the flame zone without any special nozzle.

Considering the shortcomings of conventional methods in producing water mist and the advantages of dry powders, here we reported a simple stirring route to produce a new type of water@silica capsular particles as fire suppressant. The water droplets with size of several microns were capsulated by silicon dioxide nanoparticles to form core-shell structures. Under the protection of outside hydrophobic solid shell, the particles with a high content of water approaching 60% behaved like dry powder fire suppressants with good flowability, which was named as "dry water" (denoted as DW) [11]. Details of the preparation, physicochemical properties and fire suppression performance of the DW suppressants were studied. Mechanism of the DW particles in fire suppression was discussed based on established fire suppression theories and experimental results.

2. Experimental

2.1. Sample preparation

All chemicals and reagents were used as received from commercial sources without further purification. Hydrophobic SiO_2 particles were purchased from Degussa. In a typical experiment, 100.0 g distilled water was mixed with 25.0 g SiO_2 and stirred at the rate of 13000 r/min for 30 s. The resulted samples were free-flowing white particles.

2.2. Characterization

Structure and morphology of the samples were characterized by X-ray diffraction (XRD, Philips X'Pert), ZEISS Axioskop2 plus optical microscopy, and scanning electron microscopy (SEM, QUANTA 200FEG). The Fourier transform infrared (FTIR) spectrum of KBr wafer was recorded using a Nicolet 6700 Fourier Transform Spectrometer. Thermogravimetry-differential scanning calorimeter (TG-DSC) curve was acquired through the SHIMADZUDTG-60H instrument.

2.3. Fire tests

Generally, the standard testing procedures for evaluating the fire extinguishing performance of dry powders includes ISO 7202-2012, NFPA 17, ANSI/UL 299, and etc. However, in these standards, the experimental setup is quite large, which is expensive and time consuming to build. For the limit of our experimental conditions, large fire tests following these standards were difficult to undertake. Two laboratory scaled tests were designed with relatively small fire sources and less agents to reduce the cost. But the test

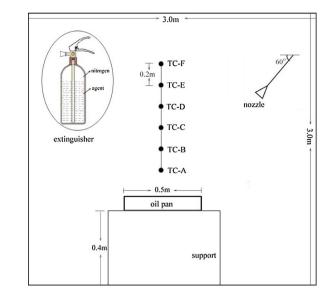


Fig. 1. Schematic illustration of the experimental set up in a 27 m³ compartment.

methods were basically in conformance with the regulations in international standards.

The small scale fire tests, were conducted in a 27 m³ $(3 \text{ m} \times 3 \text{ m} \times 3 \text{ m})$ confined space with natural ventilation. Details of the experimental apparatus were schematically shown in Fig. 1. Gasoline was contained in the oil pan with the diameter of 0.50 m. A thermocouple tree, containing six thermocouples with interval of 0.20 m and the lowest thermocouple 0.25 m above the fuel pan, was set up to measure the flame temperatures. In each test, 200.0 g powders were added into a tank with the volume of 1000 ml and pressurized by nitrogen to a pre-assigned value of 0.50 MPa. Before powder discharging, 400 ml gasoline was added into the pan, ignited and pre-burned for 30 s. The flame power was estimated as 0.21 MW. The distance from the extinguisher nozzle to the pan center was set as 1.0 m. The valve of the powder tank was turned off as soon as the fire was extinguished. The weight of the tank was measured before and after each test to determine the total mass of suppressants consumed for fire extinguishment. Each test was repeated at least three times to get a converged result. The fire suppression process was recorded by a video camera.

The bigger scale fire tests were conducted in a 1000 m^3 $(10 \text{ m} \times 10 \text{ m} \times 10 \text{ m})$ large space hall with natural ventilation to further evaluate fire extinguishing performance of as-prepared powders. 500 g powders were contained in a hanged powder extinguishing equipment and pressurized by nitrogen to 1.0 MPa. The circular oil pan with the diameter of 0.95 m contained 21.01 gasoline. The flame power was estimated as 1.0 MW. The perpendicular distance from the hanged extinguisher nozzle to the fuel surface was 1.5 m. The gasoline was ignited and pre-burned for 30 s before powder discharging. After the fire was extinguished, the agent mass consumed was measured and recorded. Considering the agent flow calibration uncertainty and measurement variance, the relative expanded uncertainty of the fire extinguishing time and the agent mass consumed in firefighting was estimated as $\pm 15\%$ and $\pm 10\%$, respectively.

3. Results and discussion

3.1. Structure and morphology

Fig. 2 showed a typical XRD pattern of as-prepared "dry water" particles, in which only a broad peak with 2θ centered at about 22° was seen. It indicated that the material was amorphous SiO₂

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