Suppression of methane/air explosion by ultrafine mono-ammonium phosphate in a 120 L combustion chamber

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Abstract. Experiments on the suppression effect of ultrafine MAP powder in methane/air explosions were conducted in a 120 L combustion chamber with a methane concentration of 10%. The use of ultrafine MAP powder was described with various triggering times and amounts of powder that could influence their effectiveness. The results showed that by increasing the amount of ultrafine MAP powder, the performance varied from promotion to suppression. The suppression action of the powder inhibitor was superior to the disturbance action, as reflected by the curve of explosion pressure and cross-sectional area normalization. By decreasing the triggering time, excellent suppression performance was presented and showed that suppression approached prevention. According to the experimental result, a few powder suppressant and nitrogen could not behave collaborative explosion suppression.

1. Introduction
Undesired gas explosions have occurred in relevant industrial conditions, leading to serious personal casualties and property damage, and in recent decades, efforts have aimed at prevention and mitigation of this explosion [1]-[2]. Explosion suppression is one potentially effective measure used to minimize explosive effects. Decreasing the blast pressure to ensure no flame propagation beyond the explosion kernel is enabled by activating the proper suppressors and injecting inhibiting material into the ignited flammable gas/air mixtures. Various suppressants have historically been adopted in industry as mature means of explosion mitigation [3][4].

The phase-out of Halon chemicals due to concerns over environmental protection have attracted renewed interest in the choice of explosion suppressants, which is attributed to development of technology for inhibitor preparation in more recent years. One example is the use of powder suppressants such as NH₄H₂PO₄ instead of Halon chemicals. The results showed that NH₄H₂PO₄ was generally effective in suppressing gas explosions, as presented by Chen et al. [5]. The chemical suppressant mono-ammonium phosphate (NH₄H₂PO₄, abbreviation: MAP) acts as a post explosion inerting agent if it remains in suspension in the transport medium. MAP limits the chain branching reactions by capturing the free radicals to mitigate flame propagation. This material is an ideal candidate for inhibiting gas explosions because this solid suppressant can more easily deliver high-rate-discharge (HRD) automatic explosion suppression. However, MAP powder with a small particle size has a better suppression-proofing effect because the reduction in particle size results in a matching increase in surface area and
residence time, which in turn leads to greater radiant heat absorption and improves mitigation performance[6]-[8].

Agglomeration of ultrafine solid suppressants has improved significantly due to progress in superfine powder preparation technology. This technology can effectively improve the vitality of powder, increase the bulk density and tapped density, and retain the chemical purity and valid ingredients[9]-[10]. Therefore, it is important to explore the explosion suppression performance of ultrafine MAP powder. This material has been tested extensively in 1 m3, 20 L or similar-size combustion chambers to explore its features. The results showed that addition of only 25 weight% ultrafine MAP powder was needed to suppress flame propagation in a gas explosion, whereas with standard MAP powder, 55 weight% was needed. Luo et al studied the detailed mechanism by which ultrafine ammonium phosphate powder suppresses gas explosion and marked the methane explosion limit depending on the effect of ammonia, one of the thermal decomposition products[11]. Premixed flammable mixtures with certain volume fractions of methane and ammonia were applied in the experimental procedure. However, only a few researchers have systematically examined suppressants injected into ignited flammable gas/air mixtures, especially with respect to the injection time of the suppressants. Most attention has been focused on the effects of intimate premixing with flammable and inert dust before ignition rather than explosion suppression. In fact, this mixing can lead to unacceptable product contamination when the application objective is inerting[12]-[13], and application of active explosion suppression technology under such conditions urgently requires much more detailed and direct research.

In this paper, we report gas explosion suppression effects by shortening the triggering time of the explosion suppressor using equal ultrafine MAP powder in a 120 L nearly spherical chamber and analysis using high-speed photography. The results reveal the connection and distinction of inerting and explosion suppression in active suppression using ultrafine MAP powder. The explosion pressure and cross-sectional area normalization of the fireball are compared to quantify the effect of the amount of ultrafine MAP powder. Whether a cooperative action between nitrogen and ultrafine MAP powder occurs is also analysed to reveal the gas explosion suppression more clearly.

2. Experimental

2.1. Experimental apparatus and procedure

The complete system, schematically shown in Figure 1, consists of a 120 L combustion chamber, gas premixing system, capacitor discharge ignition system high-speed camera, pressure transducer, explosion suppressor, data-acquisition system, and microcontroller-based trigger synchronization system. The combustion chamber was an approximately spherical device with a cross-section of 600 mm×600 mm. The two sidewalls of the explosion chamber were made of Perspex with 100 mm thickness to allow optical access, and the other sides were made of stainless steel. The bottom end of the combustion chamber was connected to a vacuum pump and gas mixing vessel. The explosion suppressor was installed in the top of the combustion chamber, and the powder suppressant was located inside the container. The ignition system consisted of a spark generator and a capacitor array for the emerging arc. A pair of tungsten-copper alloy electrodes 0.5 mm in diameter were located at the axis of the chamber and 25 mm above the bottom of the chamber. The ignition energy was adjusted to 10 J during all of the experiments. A NAC GX-8 high-speed camera was selected to capture the flame propagation procedure with a frame rate of 4000 frames/s at a resolution of 1024×1024 pixels. A piezoelectric pressure sensor (Model 113B21 made by PCB Piezotronics) with a 500 kHz frequency response was located at the central line of the stainless-steel wall of the combustion chamber to measure the pressure history during the experiments. A data-acquisition card (USB-2805C) with a sampling frequency of 100 kHz was used to collect the pressure signals.
A predefined amount of ultrafine MAP powder was placed inside the container, and the combustion chamber was evacuated using a vacuum pump. The pressurized premixed flammable mixtures with a certain volume fraction of methane and air were discharged into the chamber through the opening of the valve and reached 101.3 kPa to ensure that the experiment was conducted at normal atmospheric pressure. A controlled signal was sent by the computer, and the ignition electrode was discharged to ignite the premixed flammable mixtures. The pressure gain system began to collect the data and recorded the flame evolution procedure using the high-speed camera. When the triggering time was reached, the trigger signal of the explosion suppressor was emitted by the control system to react to a constantly developing flame. Overall, the trigger sequence of the explosion suppressor, ignition, high-speed camera and data gain card was controlled by the synchronization system. Each explosion experiment was conducted at least 5 times for repeatability.

2.2. Characterization of ultrafine MAP powder
Commercially available ultrafine MAP powder was selected as the suppression agent in the experiments and was the most typical representative of chemically active suppressants. The particle size distribution was measured by a MicrotracS3500 laser size analyzer, as shown in Figure 2. The results suggested that the powder has a concentrated particle size distribution with an 11 μm mean-volume diameter.

![Figure 1. Schematic diagram of the experimental system: (1) spark igniter, (2) pressure transducer, (3) explosion suppressor, (4) synchronization system, (5) computer-controlled data acquisition, (6) gas mixing vessel, (7) ignition electrode, (8) vacuum pump, (9) high speed camera.](image)

![Figure 2. Particle size distributions of ultrafine MAP powder.](image)
3. Results and discussion

3.1. Methane explosion procedure

Figure 3 shows the explosion pressure and matching flame pictures for a 10% methane explosion. The electrodes maintain an electro discharge to ignite the methane/air mixture after a few milliseconds. A spherical flame with a gradual increase in radius appeared centered on the ignition point (t = 40 ms). With the increase in diameter, the spherical flame touched the inside wall (t = 120 ms), followed by an acceleration of combustion. Finally, the spherical flame fully filled the chamber (t = 140 ms). The explosion pressure did not rise immediately when the gas mixture was ignited until the spherical flame spread over a certain distance, which was close to the inside wall of the explosion chamber (t = 80 ms). The explosion pressure (P_ex) started to obviously increase, and the maximum rate of pressure increase (dP/dt)max was 9.2 MPa.s\(^{-1}\), finally reaching a peak value (t = 180 ms) of 0.58 MPa. The change in the flame brightness can be observed in 0. With the advance of flame propagation, the flame brightness gradually increased and reached a maximum before the pressure increased to its peak value [14]. The flame subsequently faded away over a certain period.

![Figure 3. Explosion pressure relationship and flame pictures of 10% methane explosion.](image)

3.2. Effect of variation of triggering time

Figure 4 and Figure 5 present the explosion pressure and pressure increase rate of a 10% methane explosion suppression based on 40 g ultrafine MAP under four different triggering times of 30 ms, 51 ms, 56 ms and 74 ms. The triggering time of ‘30 ms, 51 ms’ represents the lower maximum explosion pressure (P_max) and a nearly constant rate of pressure increase (dP/dt)max compared with pure ignition. In contrast, the triggering time of ‘56 ms, 74 ms’ represents a higher P_max and (dP/dt)max. In the progression of the experiments, both P_max and (dP/dt)max first decreased and subsequently increased with increasing triggering time. After triggering for 30 ms before ignition, the values decreased to 0.0136 MPa and 0.001 MPa.s\(^{-1}\). With a triggering time of 51 ms, the values increased to 0.0397 MPa and 0.002 MPa.s\(^{-1}\). These results inferred that when the triggering time is less than 55 ms, the explosion flame could be prevented by ultrafine MAP in repeated experiments. If triggering for 56 ms, the explosion flame could not be fully suppressed, resulting in reignition, and the values increased to 0.60 MPa and 25 MPa.s\(^{-1}\). When the increase triggering time increased to 74 ms, the explosion flame could not be suppressed, and the values changed to 0.64 MPa and 17 MPa.s\(^{-1}\). It was assumed that when the triggering time exceeded 55 ms, the 10% methane explosion could not be effectively mitigated by ultrafine MAP in repeated experiments.
It is shown in Figure 4 and Figure 5 that the triggering time of 56 ms produced a lower Pmax than 74 ms. However, the time to Pmax was later, which is ascribed to reignition. Figure 6 presents the entire evolution of the flame behaviors and the matching explosion pressure in the chamber: triggering at 56 ms - contact at 58 ms - beginning of fireball control at 80 ms - fireball shrinkage by a large margin at 124 ms. Subsequently, the powder sprayed out, and the flame had not yet ended, which pointed to a new ignition source. In addition, the powder injected in the earlier stage started to roll up at the bottom of the equipment, and thus the fireball could produce a disturbance and reignition. In summary, suppression of the 10% methane explosion by the suppression system with addition of The triggering time gradually loses effectiveness to a certain degree.

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The effectiveness of the explosion suppression system lies in how rapidly the sensors can respond to the emerging explosion and on the efficiency of the suppressant injection system. In other words, the system requires the ability to inject a large quantity of suppressant in a short time and with acceptable reach to all regions of the protected space. The shortest triggering time was 30 ms in our experiments, and the matching amount of powder was 40 g. It was not difficult to imagine that the capacity of a high mass discharge rate could deliver a short triggering time, which blurred the distinction between explosion suppression and inerting. In addition, the intent was same as inerting, i.e., to remove the heat necessary for lasting combustion and thus limit generation of destructive overpressures in an enclosed chamber[15]. In industry, the inerting application must intimately premix the explosive gas and the inert material. Explosion suppression has a higher priority due to its widely applicability and avoidance of unacceptable product contamination. Innovations have always existed in which attempting to develop quicker explosion detection and suppression systems.

3.3. Effect of various amounts of powder
After performing a number of tests, the time necessary for powder spraying to deliver an excellent suppression effect was found. We know that when the triggering time is less than 55 ms, the maximum explosion pressure ($P_{\text{max}}$) and maximum pressure increase rate ($dP/dt)_{\text{max}}$ are reduced and present a remarkable restraint performance under the effect of ultrafine MAP powder. The induction period and time to $P_{\text{max}}$ are expanded. This trend was pronounced with a high amount of ultrafine MAP powder.

The 10% gas explosion suppression effect using different amounts of ultrafine MAP powder under 120 L was tested. We accepted a triggering time equal to 52 ms and a testing time of explosion pressure equal to 500 ms under three amounts of 20 g, 40 g, and 60 g. We observed the data of early rise time, $P_{\text{max}}$ and time to $P_{\text{max}}$ tested under different suppression conditions. The profiles are shown in 0, Figure 8 and Figure 9.
The addition of 20 g ultrafine MAP powder to a 10% ignited methane/air mixture is shown in Figure 7. The fireball, started to stimulate, had a speeded-up propagation stage and an uneven increase in cross-sectional area due to the disturbance action of the powder. The maximum of the cross-sectional area normalization was 0.67, the matching time was 74 ms, and the growth rate of the cross-sectional area normalization was 0.04 in the inhibitory stage. The cross-sectional area of the fireball began to decrease because of the inhibiting action of the powders. When the time after ignition was 90 ms, the cross-sectional area normalization fell to a minimum of 0.19. The powder inhibitor could not restrain the fireball because the fireball began to reignite in a large range, eventually filling the entire chamber. This similar trend was also reflected by the pressure curve in that the early rise time of the pressure was prolonged to 84 ms. The two other characteristic features of Pmax and time to Pmax showed a pressure of 0.69 MPa and a time of 135 ms, respectively. Compared with pure ignition, Pmax increased, and the pressure rise was sped up at the same time. From these typical features, the effect of gas explosion suppression using 20 g ultrafine MAP powder could promote development of the fireball and resulted in a poor explosion suppression effect. In addition, 0-120 ms was selected as the major stage of explosion suppression for a detailed study intended to describe the effect of 20 g ultrafine MAP powder on pressure. The period could be subdivided into several periods of time. The first node was the triggering time (i.e., Point A). This stage started from the moment of ignition and ended when suppressor triggering occurred for the first time. The fireball spread at a steady speed, and its propagation rate was similar to that of pure ignition. The second node was the contacting time (i.e., Point B), at which the fireball started to deform, as shown in the Figure 7, during the period from powder spraying to contact with the fireball. The pressure increased to a certain extent due to turbulent action. In this case, the degree of pressure increase reached 25 MPa.s\(^{-1}\) (i.e., A-B). Subsequently, stages B and D showed complex interactions between the powder and fireball, resulting in pressure oscillation. The fireball started to shrink and subsequently existed on the top of the chamber for a moment. After point D, the inhibiting effect of the powder gradually lost its effect, the explosion pressure began to increase again, and the fireball reignited on a large scale.

Figure 7. Curve of the relationship between explosion pressure and cross-sectional normalization area of fireball for 10% methane/air mixtures with addition of 20 g ultrafine MAP.
Similar existed in spraying 40 g ultrafine MAP powder, as shown in Figure 8. As shown, auxo-action to the fireball remained, and it was not as obvious as with 20 g. In this test, the maximum of cross-sectional area normalization decreased to 0.45, the matching time was prolonged to 75 ms, and the growth rate of the cross-sectional-area normalization was 0.014 in the entire inhibition stage. In response, the fireball decreased to a greater extent. When the time after ignition was 120 ms, the cross-sectional area normalization fell to 0.07 such that only a small fireball was observed in the chamber. The fireball subsequently began to reignite, and the growth rate of the cross-sectional-area normalization was 0.04 in the reignition stage. An increase in the ultrafine MAP powder caused a further decrease in the early rise time of pressure, which was prolonged to 188 ms, and the time to Pmax was 265 ms. The result assumed that the entire rising trend was similar to that of adding 20 g ultrafine MAP powder. Pmax dropped to 0.66 MPa, and the pressure rise appeared to extend, which proved that an inadequate amount of powder promoted instead of realized effective explosion suppression. A detailed study (i.e., 0-140 ms) on the effect of the powder on pressure shown fireball surge, complex interactions resulting in pressure oscillation and fireball reignited with pressure rising still existed. The difference was that the degree of pressure surge produced a value of 3.875 MPa.s\(^{-1}\) (i.e., A-B).
Figure 9 presents the course of the pressure in the explosion chamber in the case of spraying of 60 g ultrafine MAP powder. The maximum of the cross-sectional-area normalization sharply decreased to 0.35, the matching time was shortened to 72 ms, and the growth rate of the cross-sectional-area normalization was also reduced to 0.009. The increase in the explosion pressure in this case was low and equal to approximately 0.017 MPa, which in turn efficiently improved the effectiveness of the explosion suppression period. The results are shown in the detailed study (i.e., 0-120 ms). When powder was added, the increase in pressure caused by the disturbance action was reduced, and the degree of pressure surge showed a value of 0.043 MPa.s⁻¹ (i.e., A-B). Thus, pressure varies slightly, and the period of the fireball is presented to prove that. It should also summarize application of 60 g ultrafine MAP powder, which gave much better results for effective explosion suppression in our 120 L explosion chamber compared with the results gained from the other two tests.

Based on the three groups of different amounts of powder, the impact on the explosion pressure and cross-sectional area normalization of the ultrafine MAP powder was studied. According to the experimental results, inadequate powder could increase the $P_{\text{max}}$ and speed up the pressure rise, as shown by the results in Figure 7 and Figure 8. With the increase in powder, the $P_{\text{max}}$ of the three types of powder decreased, and the pressure rise period was slowed. In addition, the pressure growth rate of ultrafine MAP powder significantly decreased, especially when the amount reached 60 g.

3.4. *Synergic action of nitrogen and powder*

To analyze the direct effect of ultrafine MAP powder on gas explosion suppression, the effect of nitrogen produced by a gas generator and used in powder spraying was examined in methane explosion, as shown in 0.
It is generally assumed that for methane at a fixed concentration, addition of a small quantity of powder suppressant and nitrogen improves the inhibitory effect. In this work, powder suppressants and nitrogen as if already became a fixed thinking which sum up as "the Synergic action" [16]. Objective in our study, we found that distinguishing existed. For a sample with nitrogen and no powder, P_max was 0.61 MPa, and the early rise time of pressure was 45 ms. The time to reach P_max was 140 ms, and the time of the total period of restraint was 95 ms. However, we knew from previous experiments that when 20 g ultrafine MAP powder is added to a same sample with the equivalent nitrogen, the matching values were 0.69 MPa, 84 ms 135 ms and 95 ms. With addition of powder, the feature P_max (nitrogen < nitrogen + powder) was defined as reflecting the effectiveness of synergism during a contained deflagration to explore the nitrogen and powder suppressant. The pressure rise showed that the time of pressure rise by spraying of nitrogen combined with powder was faster than that of nitrogen. The explosion pressure did not drop quickly immediately after the explosion suppressor was triggered, coming down to the previous result, and did not show an obvious synergic action.

4. Conclusions
In the gas explosion experiments in a 120 L explosion chamber, application of a high-speed camera proved to be an asset in recording the gas explosion. For a 10% methane/air mixture, the results showed that the fireball began to speed up the combustion that occurred when it touched the inside wall. The rise in the explosion pressure and fireball propagation were presented out of sync in the entire evolutionary processes.

The maximum explosion pressure (P_max) and pressure increase rate (dP/dt)_ex of the 10% methane explosion were significantly decreased with the decrease in triggering time. Present wrapping the fireball by ultrafine MAP powder quickly after using a short triggering time, heightened effect on suppression action. For rekindling should be owing to longish triggering time, disturbance action of the powder was inferior to suppression action in turn unable to restrain the fireball development. In the industries, explosion suppression technology takes higher applicability result of avoiding product contamination. Further work is necessary to develop high-efficiency explosion suppression.

When applied in different amounts (20 g, 40 g and 60 g), the ultrafine MAP powder presented different inhibitory performances. Compared with pure ignition, the first two amounts could promote gas explosion progress and the latter could effectively suppress the explosion. In contrast, the growth rates of the cross-sectional-area normalization under the three amount conditions were 0.04, 0.014 and
0.009, respectively, and the minimum values of the cross-sectional area normalization in the inhibitory period were 0.19, 0.07 and 0, respectively. The results showed that the suppression action of the powder was superior to the disturbance action as the amount of powder increased.

We recognize that ultrafine MAP powder and nitrogen could play a synergic role in the mitigation effect of methane/air explosion in the entire system. In our study, the distinguishing result shown when the powder suppressant was inadequate was that an obvious synergic action did not appear.

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