Effect of CO2/N2 on explosion vent behavior of lycopodium/air mixtures in a 20-L sphere

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Abstract. To investigate the inerting effect of CO2/N2 on the explosion venting behaviors of lycopodium/air, a standard 20 L spherical chamber, with a thermo-gravimetric analyzer TGA Q500 was adopted to determine the explosion severity and mechanism of inhibition. In the heat flow of the N2 atmosphere and CO2 atmosphere, the pyrolysis processes of lycopodium powder show obvious differences from 370°C approximately. Through the whole explosion process, CO2 plays a key role and it can effectively cut off the contact between dust and oxygen. The particles with free radicals decomposed from heat lycopodium powder such as nitrogen and carbon will react lowly under the blocking effect of CO2. Meanwhile, carbon, nitrogen and other atoms can participate in chain reaction and react with active groups, which greatly reduces the risk of powder explosion. The explosion pressure $P_{ex}$ and the maximum reduced pressure $P_{red}$ were obtained with lycopodium powder explosion under a wide range of CO2 concentrations. Compared with the pure physical suppression principle of N2 in the explosion process, CO2 can participate in the explosive reaction more effectively, and hence has a better suppression effect of the explosion than N2. An unexpected behavior has been found in relation to the explosion venting behavior. Under the smaller vent diameter or at higher static activation overpressures, the suppressive effects of carbon dioxide to lycopodium/air venting explosion are better than those of nitrogen.

1. Introduction
In recent years, dust explosion accidents in the industrial process often occur [1]. Risk mitigation is becoming an issue of paramount importance in powder industries, both products production and powder handling operations [2, 3]. Meanwhile, the hazard caused by organic dust explosions is one of the most common hazards. In 2017, the number of dust explosion accidents due to organic powders was nearly seventy [4]. Many researchers have studied with the effect of inhibitor powder and inert atmosphere to reveal the explosion process [5-9]. Explosion behaviors were investigated under different conditions with the influence of adding an inert gas such as nitrogen and carbon [10, 11]. Detailed comparisons of measured char combustion rates show that replacing the inert nitrogen gas in the oxidizer with carbon dioxide has less influence on the coal combustion [12]. Whether the inert gas can further reduce the risk of powder explosion when the vessels occur explosive venting process after the safety relief device acted on.

This work aims to clarify the effects of the addition of inert gas on a typical lycopodium powder
explosion process and venting explosion process. Inert gas nitrogen was employed as comparison atmosphere with the purpose of studying the impact of carbon dioxide on the explosion process. The inhibitory effect of different CO₂ concentrations in various lycopodium powder concentrations in the lycopodium explosion venting process under various venting conditions was studied. The relevant kinetic analysis of the powder explosion under different inert gas was also presented.

2. Methodology

2.1 Experimental systems.
Basing on the characteristic of an explosion venting process, this system was autonomous refitted based on the 20-L spherical explosion chamber in accordance with the principles of the standard E 1226-10 (2010). More details on the equipment can be found in our previous work [13,14]. It consists of explosion reactor, powder injection systems, the gas mixing system, ignition system, pressure acquisition system, as shown in figure 1.

In addition, both the validity and precision of the entire apparatus have been verified in previous studies conducted by the present authors [13]. The atmospheric pressure was set at 0.101 MPa (absolute pressure) and the ambient temperature was about 23 °C during the experiments. Each test was done repeatedly to insure the reliability and reproducibility. It should be noted here that all pressures in this paper are gauge pressure unless otherwise specified.

![Figure 1. The 20-L spherical explosion chamber.](image1)

2.2 Materials.
Carbon dioxide and nitrogen as the most common and readily available inert gas were selected as the suppression gas. Carbon dioxide was employed as the main inhibiting gas in the study, while nitrogen was used for comparison. Research on the inhibitory effect of carbon dioxide can be obtained in many previous literatures [11,16]. In this paper, lycopodium powder as one of the most common organic powders in studies and widely used as a reference dust in general testing and as a calibration in standards was selected due to its preferable dispersibility and flowability. Studies on its explosibility and flammability can access to previous advance [17-19]. The chosen particle size might be beneficial to obtain results which had better general applicability [15]. The particle size distribution and microstructure via by a laser diffraction analyzer and SEM observation, as shown in Figure 2. According to these analyses, well dispersive lycopodium powder was mainly composed of tetrahedral shapes of particles with bowing trench. The powder was systematically dried at 40 °C for 2 h before each test.

![Figure 2. Particle size distribution of lycopodium.](image2)

3. Results and discussion

3.1. Determination of pressure behaviors on various concentrations.
Explosion pressure curves of different lycopodium concentrations with various CO₂ concentrations are shown in Figure 3. Adding 5% concentration of CO₂ to the concentration of 250g/m³ lycopodium powder can significantly delay the explosive time when the explosion reaches the explosion pressure
peak and compared with the explosion of pure lycopodium powder, the explosion pressure in the vessel reduces by 20%. Adding 5% carbon dioxide to the concentration of 500g/m$^3$ and 750g/m$^3$ lycopodium has a certain delay effect on the explosion, but has little effect on the peak value of the system explosion pressure. Adding 10% CO$_2$, compared with the explosion of pure lycopodium powder, the explosion curve is gentle and explosion pressure in the vessel reduced by 40%. Moreover, compared with the pure dust explosion, the pressure drop rate after reaching the peak was obviously slower when carbon dioxide added to the system. The mitigating and retarding effects of carbon dioxide on the explosion should be considered.

![Figure 3. Evolution of explosion pressure of different lycopodium/CO$_2$ concentrations](image)

![Figure 4. Effects of membrane layers and vent diameters on static activation overpressures.](image)

Results show, the low concentration of carbon dioxide (less than 3%) has a low suppressive sensitivity to low concentration of lycopodium powder explosion, and the suppressive effect of adding 3% carbon dioxide to the entire concentration range of lycopodium powder explosion is not obvious. Optimistic explosive concentrations in a lycopodium powder range are 500g/m$^3$-750g/m$^3$, and the sensitivity of the inert gas to the explosion inhibition of the system increases sharply after the carbon dioxide is higher than 15%. There is a carbon dioxide suppression sensitive point over each lycopodium concentration tested, and the explosion pressure of the system drops rapidly when the concentration of sensitive points is reached. Meanwhile, explosion suppression sensitive point, probably occurs before the minimum inert concentration, reduced 5%, approximately, exact results in Table 1. Moreover, CO$_2$ can reduce the lycopodium explosion intensity and decrease significantly the risk of powder explosion. By increasing CO$_2$ concentration (volume fraction more than 5%), the explosion pressure decreases dramatically.

![Table 1. Carbon dioxide concentration to explosion suppression effect of lycopodium.](image)

### Table 1. Carbon dioxide concentration to explosion suppression effect of lycopodium.

| Lycopodium concentration | Minimum inert concentration | Suppression sensitive point |
|--------------------------|----------------------------|-----------------------------|
| 125g/m$^3$               | 8%                         | 3%                          |
| 250g/m$^3$               | 13%                        | 8%                          |
| 500g/m$^3$               | 17%                        | 12%                         |
| 750g/m$^3$               | 20%                        | 15%                         |

3.2 Pressure parameters of venting explosions.

Before conducting the venting experiments, the static activation overpressure test was performed first, depicted in Figure 4. As can be seen, the static activation pressure mainly determines by the vent diameters and the number of layers. The static activation is proportional to the number of layers and inversely proportional to the vent diameter. Linear mathematical relational expressions are as follows: Vent diameter of 20mm: $P_{stat} = 0.042n$ (MPa) 40mm: $P_{stat} = 0.023n$ (MPa) 60mm: $P_{stat} = 0.014n$ (MPa)

$n$: layers of polyethylene membranes

Figure 5 shows the maximum reduced pressures varied with the concentration of CO$_2$/N$_2$ and static activation pressures under 20mm, 40mm and 60mm vent diameters. The concentration of lycopodium
powder in all the venting experiments was 500g/m$^3$. For 20mm vent diameter, the suppression effect of carbon dioxide is better than nitrogen, but as the vent diameter increases, the advantages of carbon dioxide suppressive effect at lower static activation overpressure are not fully manifested, which do not much differ from the suppression effect of nitrogen. When the static activation overpressure is 0.216 MPa at 40 mm vent diameter, the suppressive effect of carbon dioxide is better than that of nitrogen, but when the static activation overpressure is 0.162 MPa, the suppressive effect of N$_2$ is superior to CO$_2$. As the vent diameter further increases to 60mm, the inhibitory effects of various concentrations of carbon dioxide and that of nitrogen on the maximum reduced pressure are basically the same, and the reduction of the explosion intensity is not sensitive when the inert gas is added.

The results demonstrate that the anti-explosion effect of carbon dioxide is better than that of nitrogen under small vent diameters and higher static activation overpressures. Therefore, the use of carbon dioxide is more effective than nitrogen when the explosion is more severe. At high explosive temperatures, the activity of carbon dioxide is greater, and it easily reacts with lycopodium. Larger vent diameter leads to lower maximum reduced pressure, resulting in a slow temperature rise process that cannot fully stimulate the chemical activity of carbon dioxide.

Figure 5. The maximum reduced pressures $P_{red}$ in dependence on CO$_2$/N$_2$ concentration for different static activation pressures with vent diameter of 20mm, 40mm and 60mm.

3.3 TGA/DTG tests.

In order to understand the role of carbon dioxide and nitrogen in suppressing the reactivity of lycopodium powder, TGA SDTA851 thermo-gravimetric analyzer was applied to test the thermal characteristics of lycopodium in carbon dioxide and nitrogen surroundings respectively. Under atmospheric pressure, experimental temperature increased from 20℃ (ambient temperature) to 800℃ at a rate of 10℃/min. Figure 6 shows the results in terms of weight loss and its derivative (DTG) vs. temperature for lycopodium/CO$_2$, lycopodium/N$_2$.

According to the thermogravimetric curve, the heat loss process of lycopodium powder can be divided into two stages. The first stage is the beginning of heating to 130℃. At this stage, the moisture
in the dust particles is mainly evaporated, and the overall water loss rate is about 5%. After the heating started, the powder quality began to decrease, the corresponding TGA curve began to decrease, the weight loss rate gradually increased, and the corresponding DTG curve reached a peak at 65 °C. Thereafter, the weight loss rate gradually decreased to a minimum at 120 °C, and the TGA curve tended to be flat, as well as the dust quality appeared a short period of stabilization. At this stage, there was basically no difference in the quality change of lycopodium in a carbon dioxide atmosphere and nitrogen atmosphere. Subsequently, the weight loss of dust enters the second stage-pyrolysis stage. It results that the oxidation of the Lycopodium occurs in a smaller range of temperatures (140 –550°C) in the carbon dioxide surroundings with respect to nitrogen surroundings (140 –730°C). The overall pyrolysis rate of powder in the carbon dioxide atmosphere is little faster than that in the nitrogen atmosphere. This behavior is due to the composition of lycopodium made of different components which have different oxidation temperatures, i.e., oil, polysaccharides (inner layer) and Sporopollenin (external layer). The loss of dust quality at this stage is mainly due to the pyrolysis of fatty oil in lycopodium powder. In the case of the carbon dioxide surroundings, the TGA curve shows a first peak which is at a lower temperature (199.15°C) with respect to that of the nitrogen surroundings (194.8°C). Two further peaks (306.8 and 321.59°C) at the little different temperature of those of Lycopodium, and the weight loss rates were 31.13% and 30.32%, respectively.

Moreover, the pyrolysis process of lycopodium in a nitrogen atmosphere and carbon dioxide atmosphere began to differ significantly from 370°C approximately. Compared with the nitrogen atmosphere, the DTG curve during the pyrolysis of the carbon dioxide atmosphere was steeper and reached another peak at 415°C. When the temperature reaches 500°C, the change in dust quality tended to be stable and basically no longer changed. In the nitrogen atmosphere, the pyrolysis of lycopodium basically stopped at 700°C, indicating that pyrolysis process and products after heating in nitrogen and carbon dioxide atmospheres are different, and the fluctuation of the DTG curve was related to the fatty oil content in the lycopodium powder. Compared with nitrogen, carbon dioxide is weakly oxidizing, and can react with lycopodium at a higher temperature. These results confirm the synergetic effect observed in the explosion tests. According to the results of TG, it can be assumed that carbon dioxide with respect to nitrogen in the pyrolysis reaction of lycopodium powder acts as a catalyst.

Figure 6. TG and DTG curves of lycopodium in CO2 and N2 atmospheres.

3.4 Regime diagram of CO2 suppression to lycopodium explosion.
Many studies have shown that inhibition of carbon dioxide compared to nitrogen better [11,12]. Since nitrogen it is an inert medium itself does not participate in the reaction, but it can play a role in diluting oxygen and reducing temperature. Some scholars have studied the impact of carbon dioxide on the explosion process and made a series of mechanism speculations [20-22]. The main effects of both CO2 and N2 on explosion are on the specific heat of the mixture. The inert level of the chemical inhibitor (the amount of inhibitor required to prevent explosion) is lower than that of the inert inhibitors. The CO2 has greater thermal capacities than N2 and reduces the laminar flame speed to a greater extent. From a macro perspective, the suppressive effects of N2 and CO2 on flame propagation are mainly caused by reducing
the reactant concentration and modified heat capacity. Both of which result in a decreased flame temperature, while besides that, CO₂ further influences the chemical kinetics because it is a major product of combustion.

Figure 7 demonstrates the chemical kinetics of carbon dioxide suppression to lycopodium explosion. From a microscopic molecular perspective, the inhibition of carbon dioxide lies in capturing the electrons released during the explosion. Low temperature CO₂ continuously absorbs heat during the explosion, causing its own activation energy to decrease and release electrons, and then immediately triggers a series of chain reactions in the explosive environment. As a weaker oxidant, CO₂ participates in the decarburization reaction (CO₂+C → CO+CO), and the non-conductive character can block the movement of electrons. Moreover, carbon dioxide at high explosion temperatures can react reversibly with the water generated by the explosion reaction product to form carbonic acid, which destroyed some of the chain carriers in the reaction. In the high temperature environment of instantaneous explosion, water molecules and carbon dioxide molecules collide with carbonized lycopodium particles to generate free radicals. Furthermore, CO₂ also influences the chemical kinetics, because CO₂ is a major product of explosion, and the addition of CO₂ will chemically reduce radical concentration of H, leading to the decrease in concentration of other free radicals, such as O and OH. The content of O radicals dropped sharply, which greatly reduced the concentration of the chemical reaction activation center, thereby hindering the chain reaction of the lycopodium powder explosion, reducing the reaction rate of the dust explosion. Both CO₂ and water vapor have a high heat capacity, not only absorbing a large amount of reaction heat during the heating process, but also radiating heat generated by the explosion flame. As a more stable third-body molecule, CO₂ and water vapor also participate in the ternary collision of the chain reaction, so that a large amount of free radical energy is transferred to itself, and the effect of weakening the chain reaction is achieved. In addition, CO₂ has a good effect of replacing the oxygen.

4. Conclusion
Lycopodium dust explosion poses a considerable threat in herbal medicine industries. In this study, an experimental investigation is conducted to determine the suppression performance CO₂ and N₂ on lycopodium dust explosions. In order to reduce the severity of the consequences of lycopodium dust explosion, the mechanism of carbon dioxide suppression was further discussed. The conclusions obtained were as follows:

1. Under the gradient of various lycopodium concentrations (125g/m³, 250g/m³, 500g/m³, 750g/m³), the minimum explosive suppression concentrations with CO₂ are 8%, 13%, 17% and 20% respectively.
2. Carbon dioxide plays a great role on decreasing explosion strength. However, the effect of adding 3% carbon dioxide to the entire concentration range of lycopodium powder is not obvious. Moreover, the low concentration of carbon dioxide has low sensitivity to the lycopodium powder under optimistic explosive concentration.
3. For the case with same N₂ and CO₂ volume fraction, the CO₂ has a better suppression effect to lycopodium /air explosion compared with N₂ under the situation of a violent explosion.
4. For smaller diameter venting (20mm), the addition of carbon dioxide will have a greater impact
on the explosion venting process, which will greatly reduce the explosion pressure of lycopodium power. At the same time, it is found that the magnitude of the venting explosive pressure $P_{red}$ in the container is not related to the higher initial static activation pressure. However, the suppressive effect of CO$_2$ and N$_2$ may be indiscriminate under the case of larger vent diameter and lower static activation pressure.

5. Through the analysis of the TGA curve, carbon dioxide not only has the physical suppression effect of nitrogen but also the possibility of chemical suppression.

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