Effects of ammonia on the explosion and flame propagation characteristics of methane-air mixtures

Zhenmin Luo [a], Tao Wang [a, *], Junying Ren [a], Jun Deng [a], Chimin Shu [a, b], Anqi Huang [b], Fangming Cheng [a], Zhenyi Wen [c]

[a] School of Safety Science and Engineering, Shaanxi Key Laboratory of Prevention and Control of Coal Fire, Xi'an University of Science and Technology, 58, Yanta Mid. Rd., Xi'an 710054, Shaanxi, PR China
[b] Graduate School of Engineering Science and Technology, National Yunlin University of Science and Technology, 123, University Rd., Sec. 3, Douliou, Yunlin 64002, Taiwan, ROC
[c] Institute of Modern Physics, Northwest University, 229, Taibai North. Rd., Xi'an 710069, Shaanxi, PR China

ABSTRACT

To further study the effect of ammonium dihydrogen phosphate powder ($NH_4H_2P_2O_4$) on methane explosion, a quartz tube test system with a length of 1400 mm and a 20 L spherical experimental system were employed to test the flame propagation and explosion characteristics of methane-ammonia-air mixtures. The mechanisms of the reaction processes were calculated using the Gaussian 03 quantum chemistry software. The results showed that NH_3 played a key role in the process of methane explosion. The addition of ammonia reduced both the upper and lower gas explosion limits, diminishing the range of explosion limits and mitigating the risk of explosion. Ammonia weakened methane explosion, and the more ammonia that was added, the more effective the weakening effect. This weakening of explosions was more efficacious for higher concentrations of methane than it was for lower concentrations of methane. According to the Gaussian calculation results, ammonia and amino groups more readily consumed oxygen and hydro and hydroxyl free radicals compared with methane and methyl groups. These consumptions caused a positive microcirculation feedback loop, which greatly reduced the quantity of methyl radicals and formaldehyde, thereby interrupting the chain reaction during methane explosion.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Gas explosion is one of the major disasters in process industries and causes tremendous loss of property and casualties. Technology for suppressing gas explosion aims at reducing an explosion's intensity or terminating an explosive chain reaction by adding inhibitory materials to the reaction system at the beginning of an explosion process (Moore, 1996; Pekalski et al., 2005). At present, the materials used to inhibit explosions include inert gases (Zhang et al., 2015; Di Benedetto et al., 2009), water mist (Yu et al., 2016; Cao et al., 2016; Shen et al., 2016; Modak et al., 2006; Yoshida et al., 2015), powders (Kosinski, 2008; Kuang et al., 2008; Ni et al., 2009; Amyotte et al., 2010), aerosols (Zhang et al., 2011), and porous materials (Nie et al., 2011).

Among these, powder suppression technology is one of the most important measures to mitigate gas explosions in industry. The unique advantage of powder suppressants is that they can prevent secondary explosions of gas and dust. Scholars have conducted numerous experiments to study the efficacy of various powders (Dong et al., 2005; Liu et al., 2013; Ni et al., 2009; Amyotte, 2006; Dastidar et al., 2001). Mikhail (2006) applied a novel extinguishing agent, based on a stable mixture of superfine ammonium phosphate and modified fumed silica, to suppress fire in an experimental chamber (100 m³) and an experimental tunnel 180 m in length. The results showed that the particle size of a powder in the aerosol and its fire-suppression concentration should not exceed 10 and 0.1–0.12 kg/m³, respectively. Experimental results indicated that urea, KCl, and $NaHCO_3$ are promising components of powder aerosols for the suppression of explosions. For the prevention of an explosion (flame velocity up to 35 m/s), the concentration of powder inhibitor should be between 0.15 and 0.20 kg/m³. For the suppression of a developed explosion (flame velocity up to 180 m/

s), the proper concentration is between 0.7 and 0.9 kg/m^3 (Mikhail, 2006). Chen et al. (2006) examined the suppression of oxyhydrogen gas explosions in an explosion tube with several suppressants, namely calcium carbonate ($CaCO_3$), bauxite (aluminum ore), silicon dioxide (SiO_2), ABC powder (ammonium dihydric phosphate), and BC powder (sodium oxide). The results showed that powders with high dust cloud densities and small particle radii demonstrated more effective suppression effects, and chemically active particles with low material density were effective suppressants. Moreover, Hoorelbeke et al. conducted a systematic experimental study on the mitigation of a gas vapor cloud explosion by solid inhibitors on both the lab scale and medium scale (Hoorelbeke and Mukharror, 2009; Hoorelbeke, 2011). The factors that influence the mitigation effectiveness, such as type of inhibitor, particle size, inhibitor concentration, type of gas medium, and the moment of injection of the inhibitor, were taken into consideration. The results showed that inhibitors that capture hydrogen or hydroxyl radicals had a better inhibition effect. In addition, the inhibitor effectiveness was heavily affected by the particle size.

Among the powders tested to suppress gas explosions, $NH_4H_2P_2O_4$ powder had a better inhibitor effect. Regarding the mechanism by which $NH_4H_2P_2O_4$ powder suppresses gas explosions, Luo et al. (2014) described the physical and chemical reaction processes during explosions and proposed that the pyrolysis products of $NH_4H_2P_2O_4$ powder may weaken and eliminate key free radicals during the explosion process.

However, the detailed mechanism of this effect has not been revealed. To analyze the explicit effect of $NH_4H_2P_2O_4$ powder on gas explosion suppression, the effect of ammonia, one of the thermal decomposition products of $NH_4H_2P_2O_4$ powder, on methane explosion was examined in this paper.

2. Experimental

2.1. Experimental system

The effects of NH_3 on the gas explosion limit range and flame propagation process were investigated using a standard gas explosion test device (GB/T12474-2008), the schematic of which is shown in Fig. 1. A 20 L cylindrical experimental system, whose schematic is shown in Fig. 2, was employed to test the effects of NH_3 on the gas explosion pressure. All the experiments were conducted at room temperature and atmospheric pressure with a relative air humidity of 38–50% RH.

The major components of the gas explosion device were the explosion pipeline, the stirrer, the ignition device, the manometer, the radio tube, and the vacuum pump. The explosion pipeline, with an inner diameter of 60.0 mm and length of 1400.0 mm, was made of quartz glass. The ignition device and a relief panel with a diameter of 25.0 mm were installed at the bottom of the explosion pipeline. After the gas compound had been mixed according to the partial pressure ratio method, the stirrer was turned on for 120.0 s to ensure an evenly distributed mixture of gas and air. A Memrecam HX-6 high-speed camera, made by the NAC Corporation, with a working speed 1000.0 fra/s and a duration time of 4.0 s, was turned on automatically at the moment of ignition. This camera recorded the whole process of flame propagation. As a safety consideration, the relief panel was open during the flame propagation tests.

The system composition, working methods, and working conditions of the 20 L cylindrical experimental system were equivalent to those described in Luo et al. (2014).

2.2. Concentration of NH_3

Ammonia is a colorless, explosive gas with an offensive smell. At atmospheric pressure and temperature, its density is 0.771 g/L, with explosion limits of 15.85–28.85% as measured in the GB/T12474-2008 explosion device. Wen et al. (2011) concluded that a density of 0.10 g/L $NH_4H_2P_2O_4$ showed the most favorable suppression of explosions for atmospheres containing 7.0–12.0% methane. The experimental results of Tian indicated that for methane concentrations of 7.0% and 9.5%, $NH_4H_2P_2O_4$ at a density of 0.30 g/L has the most favorable suppression effect. When the concentration of methane was 11.0%, the optimal inhibition density of $NH_4H_2P_2O_4$ was 0.25 g/L (Tian, 2013).

In this work, 0.1, 0.25, and 0.30 g/L samples of $NH_4H_2P_2O_4$ were fully decomposed, and the NH_3 molar fractions were correspondingly calculated to be 1.9%, 4.8%, and 5.8%, respectively. These materials were used for the experiments reported herein; their effects on flame propagation and the pressure level of methane explosion were tested, validated, and elucidated.

3. Experimental results and discussion

3.1. Impacts of ammonia on methane explosion limit

The methane explosion limits, explosion limit range, and risks of explosion are delineated in Fig. 3 when adding ammonia at volume fractions of 0.0%, 1.0%, 1.9%, 2.0%, 3.0%, 4.0%, 4.8%, 5.8%, 6.0%, 8.0%, and 10.0%.

Fig. 3 shows that the upper limit of methane explosion was 14.15%, the lower limit was 4.45%, and the width of the explosion limit range was 9.7%. For samples with greater amounts of ammonia, both the upper and lower limits of methane explosion had smaller values, and the explosion limit ranges were narrower. For a sample with 10% ammonia, the upper limit of methane explosion was 9.35%, and the lower limit was 1.85%; the width of the explosion limit range was 7.5%. For samples with ammonia concentrations ranging from 0.0% to 10.0%, the risk of methane explosion ranged from 0.44 to 0.56, revealing that the addition of ammonia can elevate the risk of methane explosion.

3.2. Impact of ammonia on the flame propagation characteristics

Several experiments were carried out to examine the explosion flame propagation characteristics when 0.0%, 1.9%, 4.8%, and 5.8% volume fractions of ammonia were added into volumes of air containing 7.0%, 9.5%, and 11.0% methane. The effects of different concentrations of ammonia on the methane explosion flame propagation rate are depicted in Fig. 4.

As shown in Fig. 4, from the ignition point of the pipeline, the methane explosion flame spread forward with fluctuations along the direction of the pipeline. The fluctuations decreased gradually, and at several times during the spreading process, back propagation and flame stagnation occurred.

The whole process of gas explosion flame propagation can be divided into three stages. The first stage starts from the moment of ignition and ends when flame stagnation occurs for the first time. At this stage, the explosion flame spreads upwards along the pipeline; its propagation rate first increases and then decreases to 0.0 m/s. During the second stage, the flame changes direction and propagates downward from the peak position; as in the first phase, the velocity initially increases and then decreases. At the third stage, the flame spread upwards again to the top of the pipeline until it is extinguished. During this process, small-scale back propagation occurs several times. Back propagation distances are much shorter than upward propagation distances; the flame finally moves to the top at a mainly constant speed of 0.5 m/s. In the propagation tests with methane at different concentrations, the flame speeds of the third stage were basically identical.