Journal of Loss Prevention in the Process Industries xxx (2014) 1–4

Contents lists available at ScienceDirect

Journal of Loss Prevention in the Process Industries

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

Explosion of lycopodium-nicotinic acid–methane complex hybrid mixtures

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ARTICLE INFO

Article history:
Received 9 September 2014
Received in revised form
10 December 2014
Accepted 14 December 2014
Available online xxx

Keywords:
Dust explosion
Hybrid mixture explosion
20-L sphere
Maximum pressure
Maximum rate of pressure rise
Lycopodium
Nicotinic acid
Methane

ABSTRACT

With the terms "complex hybrid mixtures", we mean mixtures made of two or more combustible dusts mixed with flammable gas or vapors in air (or another comburent).

In this work, the flammability and explosion behavior of selected complex hybrid mixtures was studied. In particular, we investigated mixtures of nicotinic acid, lycopodium and methane. We performed explosion tests in the 20-L explosion vessel at different overall (nicotinic plus lycopodium) dust concentrations, nicotinic acid/lycopodium ratios, and methane concentrations.

An exceptional behavior (in terms of unexpected values of rate of pressure rise and pressure) was found for the complex hybrid mixtures containing lycopodium and nicotinic acid in equal amounts. This mixture was found to be much more reactive than all the other dust mixtures, whatever the dust concentration and the methane content.

1. Introduction

In 1885, Engler showed that the mixture of coal dusts with methane, at a concentration lower than the methane lower flammability limit, could be flammable thus producing unexpected hazardous conditions. Ever since, many studies have been focused on the flammability and explosion behavior of dust/gas mixtures subsequently named "hybrid" mixtures (Eckhoff, 2003; Garcia-Agreda et al., 2011; Sanchirico et al., 2011; Di Benedetto et al., 2012).

In chemical industries, such as food, pharmaceutical, wood, paintings and plastics industries, not only dusts and simple hybrid mixtures (one solid and one gaseous fuel component) are present, but also much more complex hybrid mixtures, such as mixtures of two or more dusts and gas/vapor, may be found. Typically additives, pigments, catalysts have to be added to other kind of reactants in powder form into reactors, large containers and hoppers which may contain a flammable gas or vapor (i.e. solvent) either already charged in the container or as residue from the previous operation or residue from an intermediate washing operation.

Some examples of complex hybrid mixtures are those occurring in the preparation of pharmaceuticals where active ingredient (i.e. paracetamol) and excipient (i.e. microcrystalline cellulose) dusts are mixed with a solvent (i.e. ethanol). Similarly in the painting industry pigments and resins in the powder form are mixed with organic solvent. Moreover, in the case of plastic industry, the production of copolymers (i.e. ethylene-propylene copolimer by the Spheripol process), involves the presence of two solids (i.e. polypropylene and copolymer) and a gas phase (i.e. ethylene) in the gas phase polymerization reactor.

Such complex hybrid mixtures have been scarcely studied. Few works were performed on mixtures of combustible dusts many years ago (Nagy et al., 1968). More recently, Denkevits and Dorofeev (2006) studied the explosion behavior of fine graphite and tungsten dusts and their mixtures. They showed that the mixture burns faster than both pure graphite and pure tungsten dust alone. Dufaud et al. (2012) investigated the flammability and explosion

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http://dx.doi.org/10.1016/j.jlp.2014.12.008
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behavior of various solid/solid mixtures, observing that the explosibility of the mixtures decreased with respect to the pure components. Recently, we performed explosion tests on dust mixtures made of nicotinic acid and lycopodium at different dust concentrations and relative amounts, showing the predominant influence of the most reactive compound (nicotinic acid) on the explosibility of the dust mixture (Sanchirico et al., 2014a). This effect was not encountered for the minimum explosion concentration.

The literature completely lacks of systematic studies on explosion by such complex hybrid mixtures. Therefore, this work aims at investigating the flammability and explosion behavior of complex hybrid mixtures in order to highlight the role of mixing (nicotinic acid, lycopodium and methane) with respect to the behavior of the simple hybrid mixtures (nicotinic acid/methane and lycopodium/methane). To this purpose, we performed explosion tests in the 20-L explosion vessel at different overall (nicotinic acid plus lycopodium) dust concentrations, nicotinic acid/lycopodium ratios, and methane concentrations.

2. Experimental set-up and materials

Experiments were performed in the standard 20-L apparatus consisting of a stainless steel spherical bomb surrounded by a water jacket for keeping constant the internal wall temperature. The system was modified to be used for hybrid mixtures by adding the feed line for gases. More details on the equipment are given elsewhere (Garcia Agreda et al., 2011).

In the present study, a permanent spark generator capable to supply 15 kV and 0.3 mA (module KSEP 320 produced by Kühner Ltd, CH) was used as ignition system. Sparks (duration equal to 2 s) were triggered with a delay of 60 ms in respect to the outlet valve opening.

Explosion pressures histories were measured by means of two piezoelectric transducers (Kistler Type 701A). A manometer (Dwyer Series 626) was used to measure the partial pressures for the gaseous mixture preparation.

Experiments were carried out in triplicate, minimum and maximum values of P_m an $(dP/dt)_m$ are reported in the results. The accuracy of our data is for P_m: ± 5% and for $(dP/dt)_m$: ±15%.

The dusts we chose are used as worldwide standard for explosion tests (Lycopodium and Nicotinic acid). They were supplied by Sigma Aldrich and used as received without further manipulations. The two dusts were mixed with a spatula before placing them in the dust holder, part of the equipment for explosion tests.

The reactive systems under study most likely are not recognizable in practical situations at industrial scale, however this choice aims at providing a suitable reference devoted to highlight possible deviations with respect to the explosive behavior of the single components, being their behavior well recognized in the literature.

Nicotinic acid (or Niacin) and Lycopodium were characterized by laser diffraction granulometry (Malvern Instruments Mastersizer 2000), scanning electron microscopy (Philips mod. XL30) and simultaneous TG/DSC analysis (TA Instruments SDTQ600).

In Table 1 the properties (i.e. humidity, density and particle size distribution) of the used dusts are given. In particular, for the particle size distribution, the samples were characterized by the d(0.1), d(0.5) and d(0.9) quantiles of the volumetric distribution (the d(x) diameter being defined as the size at which *x* fraction of the particles are smaller).

Table 1
Properties of lycopodium and nicotinic acid.

	Nicotinic acid	Lycopodium
Humidity, %wt	0	1.2
Density, g/m^3	1.47	1.18
Percentile diameter, μm		
d (0.1)	5	28
d (0.5)	32	38
d (0.9)	93	51

3. Results

In Fig. 1, the maximum rate of pressure rise ($(dP/dt)_m$) of the complex hybrid mixtures is plotted versus CH_4 concentration (vol/vol − %) at different lycopodium mass fractions in the dust mixture ($x_L = C_L/(C_L + C_N)$) (where C_L and C_N are, respectively, the lycopodium and nicotinic acid concentration in the mixture). The results were obtained at overall dust concentration (C_{dust}) equal to 63 g/m^3, which is much lower than the MEC of both dusts (125 g/m^3) (Sanchirico et al., 2011, 2014a, 2014b). It is shown that the addition of small methane concentrations (1% < LFL) may sustain the combustion process, as observed in the case of simple hybrid mixtures (Di Benedetto et al., 2012).

On increasing the methane concentration, the rate of pressure rise significantly increases at any value of x_L. Lycopodium ($x_L = 1$) is the less reactive dust, while nicotinic acid ($x_L = 0$) is the most reactive dust. When substituting lycopodium with nicotinic acid, an increase of reactivity is found. Quite surprisingly, the maximum value of $(dP/dt)_m$ is found at $x_L = 0.5$, at any CH_4 concentration.

In Fig. 2, the maximum value of pressure is plotted versus CH_4 concentration at different lycopodium mass fractions in the dust mixture ($C_{dust} = 63$ g/m^3).

At CH_4 concentration equal to LFL (5% vol in these conditions), P_m is almost the same for all the mixtures investigated. At lower methane concentrations, the maximum pressure of the lycopodium-CH_4/air mixture ($x_L = 1$) is significantly lower than the value of P_m of the other mixtures. When substituting lycopodium with nicotinic acid, P_m reaches the value of the nicotinic acid-CH_4/air mixture ($x_L = 0$). As in the case of the rate of pressure rise, at $x_L = 0.5$, the maximum pressure is the highest at any CH_4 concentration.

In Fig. 3, the P_m and $(dP/dt)_m$ values as obtained at different CH_4 concentrations are shown as a function of the lycopodium mass fraction in the dust mixture ($C_{dust} = 63$ g/m^3).

At $CH_4 = 1$% vol, it is found that the lycopodium-nicotinic acid-CH_4/air mixture does not ignite at any concentration, except for $x_L = 0.5$, neither the single dust air/mixtures. On increasing CH_4

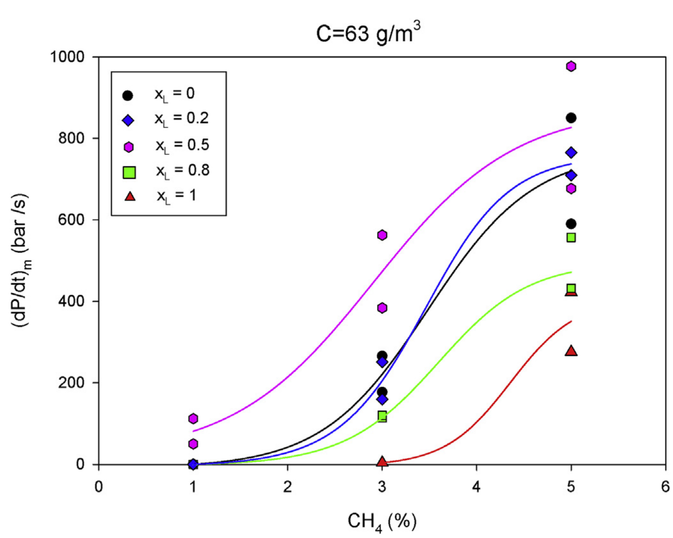

Fig. 1. $(dP/dt)_m$ as a function of CH_4 content at different lycopodium mass fractions in the dust mixture. $C_{dust} = 63$ g/m^3.