Risk of dust explosions of combustible nanomaterials

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Abstract. Nanomaterials have several valuable properties and are widely used for various practical applications. However, safety matters are suspected such as the influence on health and environment, and fire & explosion hazards. To minimize the risk of nanomaterials, appropriate understanding of these hazards is indispensable. Nanoparticles of combustible materials have potential hazard of dust explosion accidents. However, the explosion risk of nanomaterials has not yet been understood adequately because of the lack of data for nanomaterials. In this presentation, the risk of dust explosions of nanomaterials is discussed.

1. Risk evaluation of dust explosion

Recently, safety management of industrial process is performed by using risk evaluation. It is the most reasonable safety management method to evaluate and minimize the risk. Usually, the risk is expressed as the combination of probability of accident and consequence (loss) by the accident. The potential hazards of nanoparticles are damage on health and fire & explosion hazards. In this study, fire and explosion hazards are taken up. Especially, dust explosion is focused, because the risk will be the most serious in the case of the dust explosion. A typical scenario of dust explosion is shown in Figure 1. In the case of dust explosion, the probability might be governed by ignitability of the dust and the consequence (damage) might be governed by degree of explosion violence. In order to minimize the risk of dust explosion, appropriate risk estimation is needed. Therefore, the evaluations of the ignitability and explosion violence are essential. The well known parameters for the ignitability and explosion violence of combustible dust are as follows [1-3]:

- Ignitability: Minimum ignition energy (MIE), Minimum exploisible dust concentration ($C_{min}$), and so on.
- Explosion violence: Maximum rate of pressure rise ($\frac{dp}{dt}$)$_{max}$ or $K_{St}$), Maximum explosion pressure ($P_{max}$), and so on.

Dust explosion is a phenomenon that a flame is propagating in combustible particle cloud dispersed in the air. Therefore, above mentioned explosion hazard parameters are governed by the flame propagation mechanism. One of the important processes in the propagation mechanism is gasification of the combustible particle [4, 5]. The particle size has significant effect on the ignitability and explosion violence because the gasification strongly depends on the particle size. Therefore, these parameters of nanoparticles might be much different from those of the particles of micron scale.
2. Measured hazard parameters of dust explosion and their size dependence

There are only little available data on the explosion hazard of nanoparticles. Firstly, the available data on the hazard parameters for the ignitability and explosion violence of combustible dust of micron size particles are presented in this section. Then, the size dependence of these parameters is examined.

2.1. Minimum ignition energy (MIE, Ignitability)
Minimum ignition energy (MIE) is the minimum value of the energy that is needed to ignite the dust, which is an index of ignitability. The measured MIE and the size dependence are shown in Figure 2. It is found that values of MIE are order of a few tens mJ. As for the size dependence, MIE tends to decrease as the size of dust particle is decreasing. It means that the dust of smaller particle can be ignited more easily.

2.2. Minimum explosible dust concentration ($C_{\text{min}}$, Ignitability)
Minimum explosible dust concentration ($C_{\text{min}}$) is the lower flammable limit of flammable dust concentration, which is also an index of ignitability. The measured $C_{\text{min}}$ and the size dependence are shown in Figure 3. It is found that the Minimum explosible dust concentration ($C_{\text{min}}$) tends to decrease as the size of dust particle is decreasing. It means the lower explosion limit becomes smaller for the dust of smaller particle.
2.3. Maximum rate of pressure rise \((dp/dt)_{\text{max}}\), Explosion violence

Maximum rate of pressure rise is the maximum pressure rising rate, which is an index of the degree of explosion violence. The measured \((dp/dt)_{\text{max}}\) and the size dependence are shown in Figure 4. It is found that the Maximum rate of pressure rise \((dp/dt)_{\text{max}}\) tends to increase as the size of dust particle is decreasing. It means that the dust of smaller particle can cause more violent explosion.

2.4. Process of dust explosion and the dependence on particle size

The process of dust explosion is shown in Fig. 5 schematically. Usually, combustion reaction occurs in gas phase. Therefore, in dust explosion, at first, solid particle is gasified (evaporation, pyrolysis, and so on) by heat input from flame to generate combustible gas. A flame is formed by the reaction between the generated combustible gas and oxygen in air. The flame is propagating into the unburdened dust. The particle size strongly affects the explosion behaviour, because the gasification process depends on the particle size. Smaller particles can be gasified quickly because of their large surface area.
3. Risk of dust explosion of nanoparticles

3.1. Estimation of the explosion risk of nanoparticles

As shown in the previous section, the ignitability and explosion violence become more significant when the particle size becomes smaller, from the data of MIE, \( C_{\text{min}} \), and \( (dp/dt)_{\text{max}} \) for the dust of micron size particle. Then, the dust explosion risk of nanoparticles is supposed to become very high. However, it is questionable that this trend could continue endlessly as the particle size is decreasing to nano scale. It is considered that there is a limiting size, below which the risk ceases to increase. However, there are only little available measured data of explosion hazards for nanoparticles. Considering that the particle size is becoming smaller and smaller, the limit of the smallest particle should be molecule. Then, the comparisons between dust and gas are made on the explosion hazard parameters.

The measured value of MIE of ethylene gas is plotted in Figure 2. The comparison can be made between ethylene (gas) and polyethylene (dust) to expect the trend for smaller particles. Ethylene is monomer of polyethylene, therefore, the combustion characteristic might be similar. Figure 2 shows that MIE of the ethylene gas is far smaller than those of polyethylene dusts. It is supposed that MIE will be decreasing as the size of dust particle is decreasing to nano scale. MIE might not be decreasing endlessly, but it will approach the value of ethylene gas asymptotically.

The measured lower explosion limit (concentration) of ethylene gas is plotted in Figure 3. The figure shows that the lower explosion limit of ethylene (gas) is almost same as the minimum value of \( C_{\text{min}} \) of polyethylene (dust). It is supposed that the value of \( C_{\text{min}} \) might not decrease as the particle size is decreasing to nano scale. It is known that the minimum explosion concentration of combustible dust becomes lower than that of combustible gas [6]. There is another report [2, 5], in which the \( C_{\text{min}} \) of polyethylene (particle size < 10 \( \mu \)m) is 30 g/m\(^3\). This value is lower than that of ethylene gas (34 g/m\(^3\)). Table 1 shows the comparison of the minimum explosion concentrations between dust and gas. It is found that the minimum (lean) explosion limits of combustible dusts are much larger than those of combustible gases, compared in the unit of equivalence ratio. The reason of this phenomenon is considered that the combustible dust is non-uniform medium and the local concentration of combustible material can be higher than the combustible gas (uniform medium).
Table 1. Minimum explosible concentration (in Equivalence ratio) [6].

| Fuel gas     | Lean limit Equivalence ratio * | Dust       | Lean limit Equivalence ratio * |
|--------------|--------------------------------|------------|--------------------------------|
| Methane      | 0.50                           | Adipic acid| 0.28                           |
| Ethane       | 0.52                           | Lactose    | 0.22                           |
| Ethylene     | 0.40                           | Poly-ethylene| 0.34                         |
| Benzene      | 0.49                           | Sulfur     | 0.10                           |
| Methanol     | 0.46                           | Aluminum   | 0.29                           |
| Ethanol      | 0.49                           | Iron       | 0.35                           |

* Equivalence ratio = (Fuel / Oxygen) / (Fuel / Oxygen)stoichiometric

The measured maximum rate of pressure rise \((dp/dt)_{max}\) of ethylene gas is plotted in Figure 4. The figure shows that \((dp/dt)_{max}\) of ethylene (gas) is smaller than the maximum value of \((dp/dt)_{max}\) of polyethylene (dust). In the measurement for maximum rate of pressure rise, the dust is dispersed by air jet flow in the vessel to form particle cloud (dust). Therefore, \((dp/dt)_{max}\) for combustible dust is measured in turbulent flow condition, beside that for combustible gas is measured in quiescent flow condition without turbulence. If \((dp/dt)_{max}\) for ethylene gas is measured in turbulent flow condition, the value of \((dp/dt)_{max}\) will become a few times larger. Then, as the size of particle is decreasing to nano scale, \((dp/dt)_{max}\) might be increasing, however, it will not be increasing endlessly and approach the value of ethylene gas (with turbulence) asymptotically.

The explosion hazard parameters of nanoparticles are estimated by extrapolating the trend of size dependence in micro scale to nano scale. However, these results are just estimation. The accumulation of measured data of the hazard parameters of the nanoparticles and detailed analysis are needed.

3.2. Special effects of nanoparticles
    To examine the explosion hazard of nanoparticles, the effect of nano scale must be understood appropriately. There must be some special effects of nano scale particle other than the increase of surface area. One important effect is aggregation. Nanoparticles can aggregate more easily than the particle of micron scale. When aggregation occurs, the nano scale particles change to become larger aggregated particles with porous structure. The explosion behaviour of such aggregated particles was not understood adequately, but the effective surface area might decrease. In practical condition, most nanoparticles might be aggregated, and then the characteristic scale of the particles will become much larger than the scale of primary nanoparticles. More studies on such special effect of nanoparticles are indispensable.

4. Summary
    To minimize the risks of dust explosion of nanomaterials, the potential hazards of dust explosion have to be understood appropriately. However, the potential hazards of dust explosion are not clear because there are only few reported data. In this study, explosion hazard parameters of nanoparticles, such as ignitability and explosion violence, are discussed. There are no available data of these parameters for nanoparticles, therefore, the data of the particles of micron scale and gas are analyzed. Generally the explosion risk will increase as the particle size is decreasing. This trend will continue to nano scale, however, the value of the explosion hazard parameter will be in the range between the value for the particle of micro scale and that of gas. Also aggregation must have important effects on the explosion behaviour of nanoparticles. In any case, it is necessary to accumulate the data and make systematic analysis for achieving the appropriate risk estimation of nanomaterials.
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