Effects of melting inert particulate additives on ignition and flame propagation in dust/air mixtures

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Major losses in the process industry are caused by fires and explosions. An effective measure to minimize the impact and to prevent the occurrence of dust explosions is the use of dry suppressing agents, where the particles act as kinetic and thermal sink. In the field of explosion prevention the use of non-combustible solid material is well known and utilized. However, there is still a lack of information about mechanisms that are responsible for the explosion suppression effect itself. Especially, the role of inert particulate additives showing also relevant melting characteristics. Purpose of the following study was to identify the influence of melting particles on ignition and on flame propagation in combustible dust/air mixtures. Research has been carried out on reaction behaviour of the mentioned material to determine if and in which way the addition of melting additives influences the explosibility of combustible dust mixtures. Therefore, experimental methods and computational fluid dynamics models have been used to investigate the phenomenon. Flame characteristics were investigated in a tube-apparatus, where lycopodium has been used as combustible dust, zeolite as simple inert material and extinguishing agents as melting matter. In the mentioned apparatus flame speed as well as flame front temperature have been measured. The minimum ignition energy of different mixtures has been to further describe the ignition behaviour. By the use of numerical methods flame propagation was calculated in a 2D tubular profile and furthermore the ignition process investigated.

Keywords: dust explosion, flame propagation, ignition, melting additives

Introduction

To cover fire and explosion risks in the process industries two strategies are known: prevention and controlling. An effective countermeasure to minimize the impact and to prevent the occurrence of dust explosions is the use of dry extinguishing agents, where the particles act as kinetic sink. [Friedrich 1960] Research done by various authors on the topic of inhibition and extinction designate several mechanisms for the effects, which are the decisive factors: the extraction of heat [Cote 2003], the oxygen displacement [Cote 2003], the dilution [Cote 2003], the blocking of radiate heat [Cote 2003] and the interruption of chain reactions by trapping free radicals [Krasnyansky 2008]. Basically two ways of inerting can be classified: thermal inhibitors and chemical inhibitors [Dewitte et al. 1964]. The thermal inhibition, on which the main focus of the present work was placed, works on the basis of the extraction of the heat from the combustion zone. Studying the diagram of Semenov [Semenov 1928], it can be seen that below a certain level of heat loss the flame cannot persist by its self-generated heat. Heat loss exceeds the release of reaction energy and extinguishing takes place. Experimental research and numerical calculations on the ignability of different dust/air mixtures have been carried out in order to assess the interaction between combustible dust and inert particulate additives.

Method

In order to examine the ability of melting non-flammable powders to act as a suppressant in dust explosions determinations were carried out to identify the impact of the additives on the flame development. Therefore, experimental tests were carried out. According to EN ISO 80079-20-2 tests were performed on the minimum ignition energy (MIE) with the Kuhner AG® MIKE III Apparatus to identify the influence on ignition behaviour. For investigations on flame speed and flame propagation through a dust/air mixture a non-standardized method was used. This method was introduced by Kern [Kern 2013] and offers the opportunity to investigate the flame behaviour under low turbulence conditions in a dust/air cloud. The apparatus consists of an explosion tube with a length of 2,000 mm and a continuous spark igniter at the bottom. The dust feed system is arranged on the top, as well as an exhaust system and a flame arrester. The arrangement of the feeding device provides a proper dispersion of the dust and realizes a low turbulence level. [Kern 2013] Tests on the flame speed were observed through photooptical measurements. Four devices were installed between 100 and 290 mm (100 mm, 160 mm, 210 mm and 290 mm) above ignition. To investigate to what extent melting additives can absorb heat from the proceeding combustion, tests on the flame temperature were also performed on the mentioned apparatus. Therefore, thermocouples with a very fast reacting time were used at different levels above ignition. The measurement points were set at 80 mm and 100 mm above ignition. A graphic of the used apparatus for investigations on the flame can be taken from Figure 1.
All experimental tests were done with the same combustible dust, because the effectiveness of inertants is depending on
the composition of the used explosible dust. [Amyotte 2006] Lycopodium was the chosen powder caused by a
monodisperse behaviour and a uniform particle size of about 30 µm. The spore of club moss has a netlike structure
containing oleic acid, which causes a prompt deflagration after an ignition that is easy to achieve. [Skjold 2003] As inert
particulate additive a crystalline mineral, called Clinoptilolith, was used. This volcanic rock is characterized by a three
dimensional structure of silicon compound ([SiO₂]³) and alumina compound ([Al₂O₃]³) with naturally build cavities.
[Dyer 1988] For determining the influence of melting particles in the dust cloud a commercial chemical extinguishing
agent was used. It is a mixture of ammonium dihydrogen phosphate and ammonium sulphate. Advantages of such dry
chemicals are a quick extinguishing success, a high extinguishing rate and a great storability. [Friedrich 1960] This powder produces endothermic chemical reactions which precipitate the extinguishing effect, because it consumes the
energy of the flame, stop the combustion process and also stop the ignition. [Friedrich 1960] Moreover, the produced products show inhibitory effects. One effect of dry agents is the smothering effect, caused by decomposition of products
by the powder cloud. Both, thermal radiation caused by endothermic reactions of the powder, and heat transfer between
powder and flame leads, as a second effect, to cooling. [Friedrich 1960]

Numerical calculations were performed in the open-source computational fluid dynamics (CFD) software OpenFOAM®
(Field Operation and Manipulation). Therefore, a dust explosion in a dust/air mixture with melting inert particulate
additives was simulated, where the gaseous phase was regarded as a continuum in whose framework the dispersed solid
particles were tracked. As combustion model the “Partially Stirred Reactor” model, described by Ettore et al. [Ettore et
al. 2007], was suited, because both cases, the kinetic limited reaction regime and the diffusion limited regime, are
regarded in this model. [Tomasz 2017] An Euler-Lagrangian approach was chosen to compute the particle-laden flow
regime. [Fluent 2001] For an accurate modelling of the turbulent flows a common k-epsilon turbulence model was taken.
The model provides two conservation equations, one for turbulent kinetic energy k and one for the dissipated energy ε.
[Davidson 2018] To identify the impact of melting particles on flame propagation an existing model for surface reactions
was adapted in a way that it is capable of simulating a phase transition from solid to liquid. Therefore, a surface reacting
model (“COxidationDiffusionLimitedRate” model) had to be suited and modified. The physical process of melting can be
assigned to a fixed temperature-pressure combination. As long as solid material is present the total energy input is
applied to the phase transition and no temperature increase can be observed. The progression of the phase transformation
can be traced by the mass fraction of the particle. For the melting particles the properties were set to ρ = 2,300 kg/m³ and
c_p = 2,000 J/kgK. All cases were run with a concentration of 750 g/m³ and with a particle size of 50 µm, 30 µm, 20 µm
and 15 µm.

**Effects on ignition**

To identify the influence of inert particulate additives on the ignition of a combustible dust/air cloud tests were performed
on the minimum ignition energy (MIE) with the Kuhner AG® MIKE III Apparatus according to EN ISO 80079-20-2.
The higher the minimum ignition energy is, the higher the energy necessary to ignite the dust/air mixture. Therefore, tests
were done with various dust mixtures. The ignition process starts with the particle absorbs the ignition energy. Inert
agents prevent an ignition by absorbing thermal and radiant energy. As the amount of inert dust particles increases,
enough of the available energy gets absorbed such that the fuel cannot ignite. [Chatrathi et al. 2000] With the increasing
amount of inert additives the minimum ignition energy increases, therefore, more energy has to be taken into the system
to ignite. Experiments confirm these assumptions as it can be seen in Figure 2. On the contrast a system containing
melting particles produces endothermic chemical reactions, and hence, consumes more the energy of the ignition spark
than solely inert additives. The combustion process stops and also the ignition. However, the same level of minimum
ignition energy needs a lower amount of melting particles in the mixture. The melting particles are a mixture of

Figure 1: Schema of the apparatus for investigations on the flame propagation [Kern 2013]
ammonium dihydrogen phosphate and ammonium sulphate. To compare these components with each other, results done by Addai et al. were included in the figure, because these authors investigate a mixture of ammonium sulphate and lycopodium solely (grey circles).

![Figure 2: Experimental results minimum ignition energy (MIKE III) [Hüttenbrenner et al. 2018] with results from Addai, Gabel and Krause [Addai et al. 2016]](image)

Contemporary, ignition energies were calculated by CFD-modelling. The ignition energy was determined as the mean value between an energy input that is able to ignite the dust cloud and on that is not. In most cases they stretched over an energy range of 2 mJ [Hüttenbrenner et al. 2019]. Calculation results for each material/particle diameter combination for a concentration of 750 g/m³ can be taken from Table 1. The calculated MIE of Lycopodium was 25 mJ, slightly higher than experimental results (13 mJ). For simple inert particles a small increase of the ignition energy can be observed by decreasing the diameter of the dust particles. An augmentation of 5 mJ between the smallest and the biggest size can be explained by a rising number of particles more than 37 times. [Hüttenbrenner et al. 2019] However, the same effects cannot be seen at the other melting particles, which show additional heat sinks.

<table>
<thead>
<tr>
<th>type of additive</th>
<th>50 µm</th>
<th>30 µm</th>
<th>20 µm</th>
<th>15 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>simple inert particles</td>
<td>25 mJ</td>
<td>26 mJ</td>
<td>29-30 mJ</td>
<td>29-30 mJ</td>
</tr>
<tr>
<td>melting particles</td>
<td>24 mJ</td>
<td>24 mJ</td>
<td>25 mJ</td>
<td>25 mJ</td>
</tr>
</tbody>
</table>

To describe the ongoing combustion process the calculated combustion heat as a function of time for the complete geometry is displayed in Figure 3. There the energy input due to reaction including the rate at which the educts are converted to products can be seen in a system containing additives with a diameter of 50 µm in a concentration of 750 g/m³ with a modelled ignition spark of 28 mJ. The solid line refers to a system without inert particulate additives. A similar profile shows another system containing simple inert particles (dotted line). At the very beginning and during the first milliseconds of linear growth both graphs fit very well together. A steeper increase of the solid line (no additives) can be seen with proceeding time. An explanation can be found by observing the flame behaviour of both systems (see following chapter). For the first few time steps the flame propagation of the system containing simple inert particles shows a very inhomogeneous shape and the flame speed differ between both mixtures.

The combustion in mixtures containing melting additives proceeds very slowly and the released heat of combustion is primarily consumed by the heat of fusion. Solely natural convection causes flow in the geometry, and therefore, the decreased temperatures lead to lower turbulence and hence to bad mixing conditions. In accordance with Sutherland [Sutherland 1893] the decreased temperatures decline molecular diffusion which is also expected to be the reason for observed thicker reaction zones in those systems [Hüttenbrenner et al. 2019]. Compared to other calculated reaction profiles (cf. Figure 3) that all show very steep gradients at the end, the combustion in systems containing melting particles shows a rather homogeneous increase of combustion energy up to the final maximum, as it is displayed in Figure 4 [Hüttenbrenner et al. 2019].
Figure 3: Calculated released energy of combustion over time in a system with and without inert particles [Hüttenbrenner et al. 2018]

Figure 4: Calculated released energy of combustion over time in a system containing melting particles [Hüttenbrenner et al. 2019]

The introduced electrical spark in the combustible dust mixture forms a reaction zone and persists as long as oxygen is present. For most mixtures it sustains over a few time steps (<0.5 ms) and the combustion takes place only within a small cylindrical stripe. [Hüttenbrenner et al. 2019] If the reaction consumes oxygen faster than the reaction zone can propagate it does not proceed noticeably. On this, confer Figure 5, where the area around the ignition between the two electrodes is displayed, visualized by the oxygen mass fraction in the gas phase over some time.
Effects on flame speed

After the ignition process the reaction front starts to propagate through the flammable dust/air cloud with a dust specific flame speed. For numerical purposes the flame propagation in a tube with a length of 320 mm and a diameter of 80 mm was calculated in a 2D pipe profile. Both materials, combustible particles as well as inert particles, got a diameter of 50 µm and the dust concentration of the mixture was set to 750 g/m³. A circular hot zone ignited the stoichiometric gas composition at one end of the geometry. Results of these calculations can be taken from Figure 6, where the flame propagation velocity is plotted over time in a system containing on the one hand solely combustible particles (solid red line) and on the other hand simple inert particles in the mixture with combustible dust (dotted green line). The velocities were calculated through numerical differentiation of the flame front position over time. [Tomasch 2017] Observing the system containing solely combustible dust particles, it can be seen that the flame speed increases with progressing height of the considered tube. Explanations can be found in increasing turbulent conditions caused by wall and pressure effects as well as by remixing. In contrary, a dust/air cloud with inert particulate additives the flame velocity stays almost constant for a long time, and moreover, depletes far more time to pass the considered geometry. The increase of the flame speed at the very end of the geometry can be explained by the open end of it, and therefore, by the escaping of particles due to the pressure wave. Hence, these inert particles are missing for slowing down the propagation.

In a combustible dust/air system containing melting inert additives the flame propagation practically ceases. As it can be seen in Figure 7 the flame movement is limited to irregular expansions of the hot zone in the lower third of the geometry for quite a long time. Although the observed combustion is oxygen-limited, considerable amounts can be still found in a comparatively broad region behind the reaction zone. Mixing on a molecular level is poor, and therefore, higher reaction rates and faster flame propagation are prohibited. This theory can be supported by looking at the mixing parameter $k$ and
at the turbulent viscosity $\mu_t$. Basically, the mixing parameter $k$ describes to what extent either kinetics or mixing have an impact on the proceeding combustion. In the system the mixing parameter $k$ is very low in a relatively thick reaction zone compared to other observed systems. From the data of the turbulent viscosity $\mu_t$, it can be seen that apparently turbulence is weakest with melting particles. Even in boundary regions where due to turbulence the reaction normally converges kinetic limitation diffusion is still the crucial process. By using melting additives their behaviour constitutes the major heat absorption process as long as solid is available. For this reason it is possible to limit the release of fuel directly to the combustion zone and regions behind. This effect changes the flame propagation behaviour. The flame front is not fed from areas in front but instead from areas in the back, however, despite that the flame is able to sustain itself. The low buoyancy could be responsible for the preservation of the flame front.

![Figure 7: Calculated flame front position over time for a system containing melting particles](image)

Similar results can be seen by looking at experimental investigations in an apparatus consisting of a 2,000 mm long tube (see Figure 8). Caused by the experimental method, the flame front propagates as deflagration in a parabolic shape through the tube [Kern 2013]. The measured flame velocity is plotted over the amount of inert additives in the combustible dust/air mixture. The particles act as energy sink, which could be an explanation for the decreasing of the flame speed with increasing amount of inert particles in the cloud. The flame velocity of a dust cloud was determined as the average value of 8 experimental tests, where the speed is calculated as the time the flame front needs to cross a distance between two measurement points.

![Figure 8: Experimental results flame velocity (tube method)](image)

**Effects on flame structure**

To describe the flame behaviour results of numerical CFD-calculations are very useful (cf. Figure 9). The flame propagation in a combustible dust/air mixture through a tube can be seen in the first column in Figure 9. After ignition the reaction front starts to propagate through the flammable dust/air cloud within a small stripe. The particles in front of the propagating flame absorb energy from the flame through radiative heat transfer and convective heat transfer. [Chatrath et al. 2000] The propagation is very uniform and the reaction is diffusion-limited, therefore, the reaction rate
is low. The flame front of a system containing inert particles besides combustible dust propagates slow compared to other systems, nonetheless the propagation is very uniform (cf. Figure 9, second column). The reaction rate is diffusion-limited, and therefore low. Investigations on the mixing parameter show that the mixing is bad and the reaction zone is very thin. Combustion heat gets consumed by inert additives, thus the temperature decreases and slows down molecular diffusion. Kinetic limitation of the reaction due to decreasing temperatures is not playing a role for combustion. Investigating the sequence of flame propagation in a system containing melting particles (cf. Figure 9, third column) it can be seen that a hot zone separated from the flame front by an area of low temperatures appears and ignites spontaneously. The combustion zones are growing very fast until the whole geometry is affected. At around 0.39 s particles in the area above the hot zone are fused and melting takes place along streaks mainly over regions with maximum temperatures (dark red zone in Figure 9, third column). Slowly, the affected area enlarges and after 0.47 s the first few particles above the flame front are completely molten. In these cells where no melting is possible any more a temperature increase can be observed. Tomasch observed a phase transformation in front of the flame front on melting particles with a low enthalpy of fusion ($\Delta H_{\text{fus}} = 150$ kJ). Caused by a low needed energy, the particles transform to a liquid phase, and therefore, the heat sink is missing and the gas phase is warming up. [Tomasch 2017] On the one hand convection could play a role even with very low flow velocities, on the other hand, radiation could be an important factor due to the local random formation of hot regions above the flame front. This assumption fits together very well with observations made by Proust [Proust 2006], who states that radiation gains influence as an energy supply with growing flame thickness. The reaction zone can be observed as a very broad stripe, which can be explained by bad mixing conditions, and furthermore, by remaining converted oxygen in the back of the flame front.
Taking these assumptions into account, observed flame behaviour on experimental tests can be investigated (see Figure 10). The flame front propagates through a combustible dust/air mixture with melting additives through the tube. The flame front as well as the preheating zone in front of the flame front can be seen in the pictures.
As inert particulate additives act as thermal sink, a different temperature profile of systems with and without inert particles would be expected. As long as the energy input to the reaction zone is high enough, the flame can be self-sustaining. If the mean kinetic temperature \( T_m \) drops to its limiting value \( T_{m,\text{lim}} \) the flame cannot be self-sustaining [Dewitte et al. 1964] and the flame is extinguished because of thermal inhibition due to cooling down the burning gas mixture. The mean kinetic temperature can be calculated by the following equation from the measured flame temperature values \( (T_f) \), whereby \( T_0 \) is the gas temperature before ignition. [Dewitte et al. 1964]

\[
T_m = T_0 + 0.74 \times (T_f - T_0)
\]

By measuring the flame temperature in a combustible dust/air mixture an alteration in the temperature profile can be observed by adding inert particles. The flame temperature as a function of the amount of additives can be seen in Figure 11. A rising number of inert particles leads to a temperature decrease of the flame until the flame cannot propagate any more. In a system containing melting particles (black squares) the endothermic melting process consumes more energy, therefore the flame temperature in this system is decreasing faster than in a system with simple inert particles (red triangles). Melting agents have the advantage of thermal decomposition below the ignition temperature of the combustible dust (Lycopodium between 390 and 440 °C [IFA]), therefore energy gets consumed by the additives. The thermal decomposition of ammonium dihydrogen phosphate starts at 190 °C and ammonium sulphate at 235 °C. According to Jarosiński the flame propagation is quenched as the temperature is lowering to about 1,000 to 1,200 °C and the flame propagation velocity has a finite value of a few centimetres per second at the moment of extinction. [Jarosiński 1986] Experimental tests done by other authors [Smoot et al. 1977, Cashdollar et al. 1983, Veyssiére 1992] show that the measured temperatures of thermocouples are lower than theoretical values and real values caused by heat losses due to thermal radiation. Veyssiére considered although heat transfer through the flame front is governed by thermal conduction, radiative losses are not negligible for measuring devices and the values of thermocouples are 500 to 600 °K lower than by other measuring devices. [Veyssiére 1992] Therefore, Cashdollar and Hertzberg suggested a radiation correction after measuring the gas and particle temperature through infrared pyrometers to investigate the difference between both temperatures. The gas temperatures are significantly higher than dust particle temperatures [Cashdollar et al. 1983], at low dust concentrations up to 800 °K. Comparing their results, it can be seen that the uncorrected thermocouple readings comparable to particle temperatures at low dust concentrations are around 200 °K cooler than the pyrometer values. [Cashdollar et al. 1983] A possible explanation of this difference is according to Cashdollar and Hertzberg the continuous accretion of endothermically pyrolyzing particles on the thermocouples. Besides radiative losses from flame and from thermocouples, char and ash layers on the measuring devices could indicate measurement failures. [Smoot et al. 1977]
Figure 11: Alteration of the measured flame temperature in relation to the amount of inert particles in the dust/air mixture without radiation correction (tube method)

Conclusion

To identify the influence of melting inert particulate additives on ignition and flame propagation in explosible dust/air mixtures experimental tests and CFD-calculations were conducted. With increasing amount of inert additives the ignition energy increases, thus more energy is needed to ignite the dust cloud. For a system containing not only inertants, but also melting particles a lower amount of additives in the mixture is required caused by a higher energy consumption for fusion. In comparison with simple inert particles, which can delay the acceleration phase, melting particles act as thermal sink and therefore lead on to a diffusion limited regime in the system. However, this thermal sink is limited due to the enthalpy of fusion of the used particles. If all the required energy is consumed, the gas phase around cannot be cooled anymore and a time-delayed propagation of the flame can be observed.
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