

The Relationship between the Explosion Indices of Dispersed Dust and Particle Surface Area and the Heat of Combustion

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The German Social Accident Insurance has been studying dust samples from trade and industry for many years with regard to their explosion indices, and makes these data available free of charge and accessible from around the globe in the GESTIS-DUST-Ex database. The dusts studied vary widely in their chemical composition and particle size distribution. The substantial data collective nevertheless permits study of the possible relationships between the various safety indices. The focus of this study lies upon the influence of the median upon the maximum explosion pressure P_{max} and the rate of pressure rise dp/dt . The median reduces a complete particle size distribution to a single value and is therefore an imprecise measure of the active surface of the dusts. For this reason, precise BET surface analyses of 129 dusts were performed in a further study in order to determine possible correlations between P_{max} and K_{st} . In addition, the heat of combustion of these dusts was determined calorimetrically in order for further information on the explosion reaction and the K_{st} value to be obtained.

1. GESTIS-DUST-Ex database

The database was launched and developed at the beginning of 1980 with financial support from the European Union. It has since been extended to cover over 6,000 dusts, and is available in English, German and French. The database contains the explosion safety indices of flammable dusts from all industrial applications. The dusts consequently comprise a range of metals, organic and inorganic substance components, and mixtures thereof. Their particle size distributions may also vary. This information is stored in the database and is now updated and maintained solely by the DGUV (GESTIS-DUST-Ex 2015).

1.1 Correlation of P_{max} and K_{st} to the median

The database contains static data records on the maximum explosion pressures of $N=2391$ dust samples. The explosion pressures are determined following dispersion of the dust in closed, pressure-tight laboratory apparatus under standard conditions to EN 14034-1. Figure 1 shows the distribution of the samples across pressure ranges; samples determined as not being explosive have been excluded ($N=702$).

Approximately 50% of the samples studied lie within the 9-7 bar pressure range. Particularly critical dusts with explosion pressures greater than 10 bar frequently consist of fine aluminium or magnesium dusts or highly reactive organic dusts. This is shown in the correlation of P_{max} to the median (Figure 2). The graph can be divided into an upper region ($P_{max} > 8$ bar) and a lower region ($P_{max} < 8$ bar). In the upper region, an approximate hyperbola ($1/x$ where x =median value) is observed; high explosion pressures are possible only with very fine dusts (K. L. Cashdollar 2000). All medians are contained within the lower region of the curve, and the distribution equates more to a frequency distribution of P_{max} with no visible correlation to the median. This is attributable to the material properties of the dusts, notably their chemical composition, and also to the elasticity and hardness of the dust particles. Dispersion of the dusts at a preliminary pressure of 20 bar increases the fine component of brittle particles (e.g. lignite, bituminous coal, waxes) and thus displaces the actual median at the instant of ignition towards lower values, i.e. the laboratory analysis yields higher maximum explosion pressures for these dusts. Since this process may also occur during industrial handling of these dusts, this false positive assessment is accepted in the majority of laboratories.

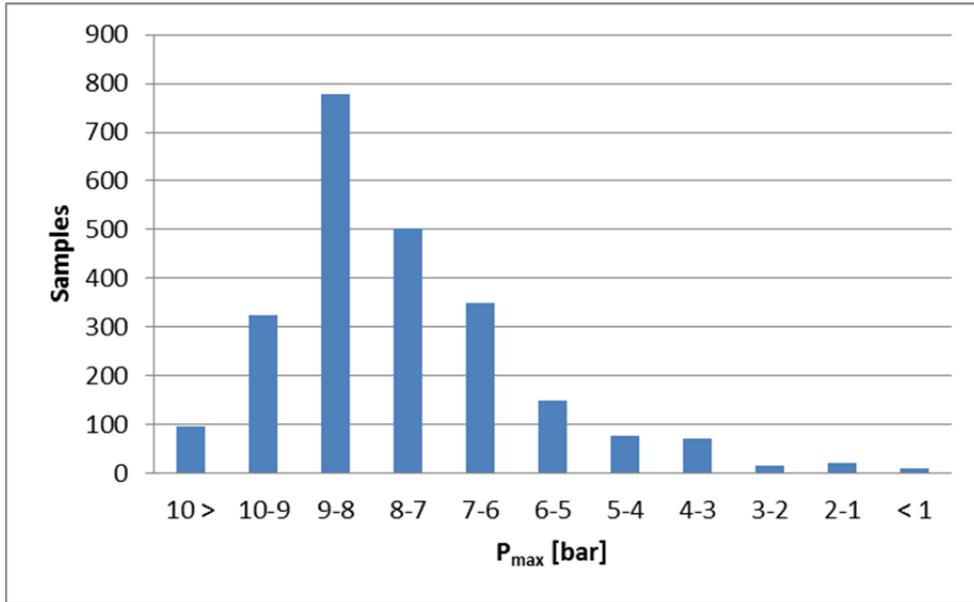


Figure 1: Distribution of the analysed samples between pressure regions

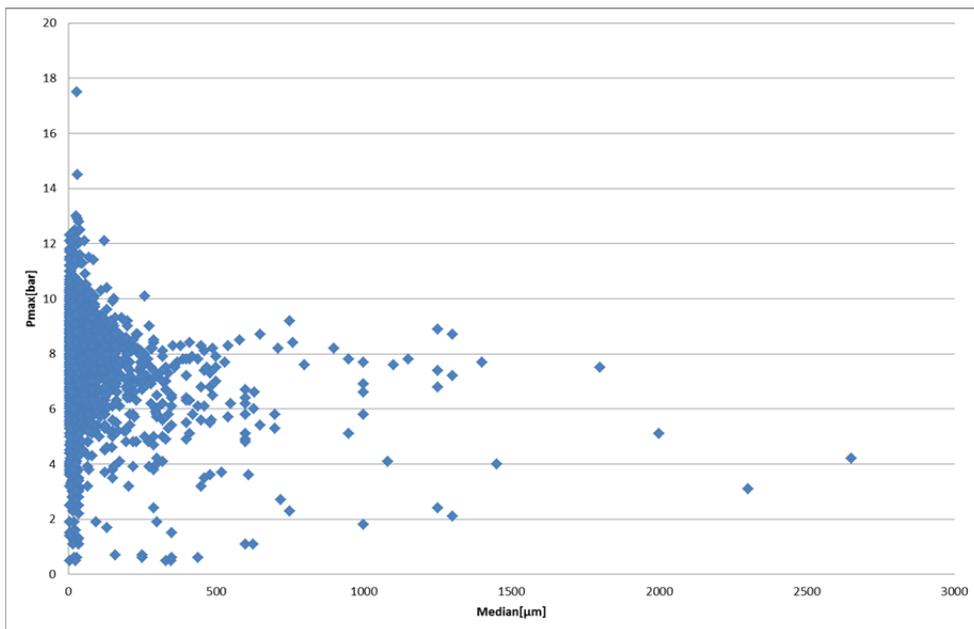


Figure 2: Correlation between median and P_{max} ($N=2391$)

1.2 Rate of pressure rise dp/dt and median

The rate of pressure rise dp/dt of a dust explosion is determined according to EN 14034-2. The maximum is determined by systematic variation of the dust concentration. Since the dp/dt values are dependent upon the volume of the test vessel, the values obtained are converted to a standardized volume of 1 m^3 . This standardized rate of pressure rise is termed the K_{st} value.

The GESTIS-DUST-Ex database contains K_{st} values that have been determined for 3,093 samples in the closed 20 l sphere or the 1 m^3 vessel. In Figure 3, the K_{st} values have been divided into 4 ranges, and the distribution of the samples in these ranges is shown. Almost 70% of the samples lie within the pressure range up to $K=200 \text{ bar}\cdot\text{m/s}$. 702 dusts were assigned to the "no explosion" range. A dust is assigned to this range when it demonstrates very little or no explosion pressure in the test. According to this test criterion, pressure-free combustion of the dust is possible without being classified as an explosion.

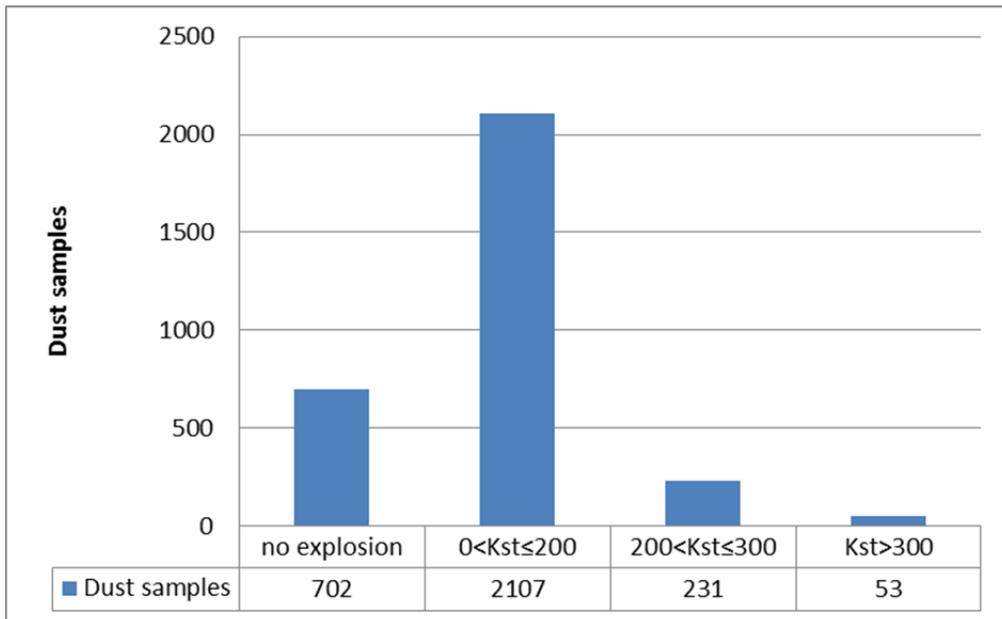


Figure 3: Distribution of the analysed samples between the dust explosion classes (N=3093)

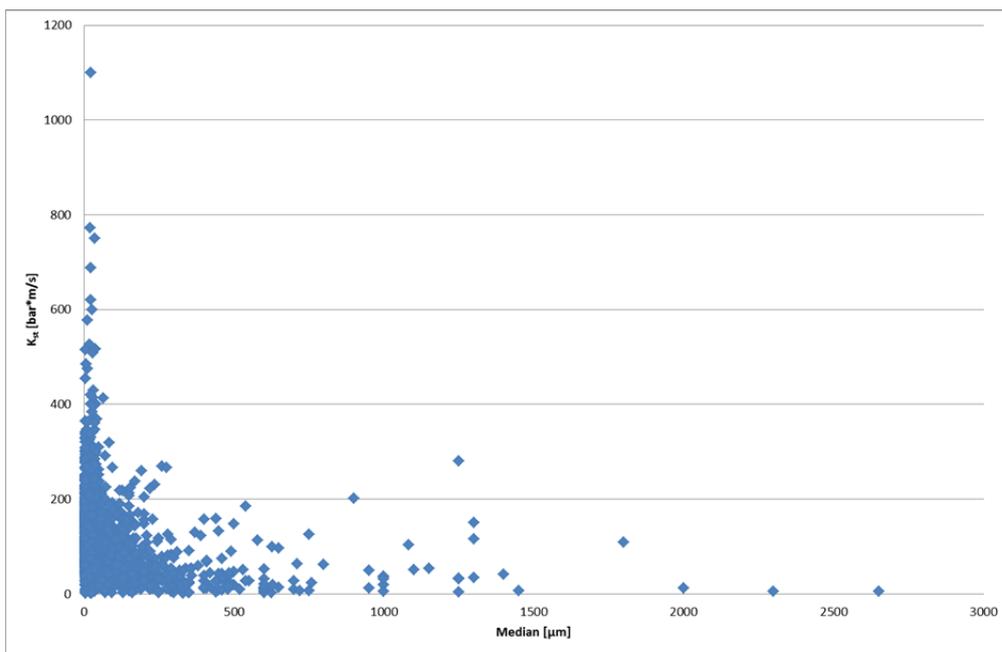


Figure 4: Correlation between maximum K_{st} value and median (N=2391)

Rates of pressure rise are kinetic variables, i.e. knowledge of the reaction equation is required for interpretation of the K_{st} values. Figure 4 shows the K_{st} values (excluding "no ignition") as a function of the median. Even across the highly heterogeneous substance collective, a correlation is clearly visible and provides an indication of possible relationships. The median generates a unitary quantity from a particle size distribution. This unitary quantity represents the focus of the particle size distribution and therefore, with limitations, a measure for the reactive surface of a particle collective. It must still be clarified what may actually constitute a reactive surface during explosion reactions.

2. Kinetics of the explosion reaction – Arrhenius equation

The K_{st} value describes the kinetics of the explosion reaction. This is dependent upon multiple factors, including the technical parameters of the selected analysis method, such as vessel geometry, dispersion system and ignition energy; the physical properties of the dust, such as density and particle size and geometry; and the chemical properties of the dust. If only the chemical reactivity of the dust is considered in the first approximation, the K_{st} value and thus the change in pressure over time can be described by the Arrhenius equation.

$$\frac{dp(t)}{dt} = k_0 \cdot e^{\frac{-E_a}{RT(t)}} \cdot [S(t)]^a \cdot [O_2(t)]^b \quad (1)$$

$p(t)$: explosion pressure at time t

k_0 : pre-exponential frequency factor

E_a : activation energy [$J \text{ mol}^{-1}$]

R : general gas constant [$JK^{-1} \text{ mol}^{-1}$]

$T(t)$: temperature at time t

$S(t)$: surface area [m^2/g] at time t

$O_2(t)$: oxygen concentration at time t

a, b : order of reaction

In the above equation, the solid concentration is stated as a surface area per gramme: this already follows from the known fact that higher K_{st} values are generally reached with a finer grain of a given substance.

For the temperature rise over time:

$$T(t) = \frac{([O_2(t=0)] - [O_2(t)]) \cdot \Delta H_c}{c_v} \quad (2)$$

$[O_2(t=0)]$: oxygen concentration at the start of the reaction [mol/m^3]

$[O_2(t)]$: oxygen concentration at time t [mol/m^3]

ΔH_c : heat of combustion

c_v : specific heat capacity, in this case: sum for gas and dust [$J/\text{mol K}$]

The rise in temperature over time as a consequence of the reaction conversion leads to an exponential rise in the reaction and thus to explosion. A condition for this is that no thermal losses occur in the initial phase of the reaction, i.e. it is virtually adiabatic. The reaction heat ΔH_c is important here. If the thermal generation term remains below a certain limit, an exponential rise does not occur. Equally, it is conceivable for the c_v value to rise so strongly owing to the addition of solid matter that no reaction occurs. It is thus clear that the combustion enthalpy (H. Selle 1954) and the surface area are two important quantities with a substantial influence upon the rate of pressure rise.

3. Correlation of P_{max} and K_{st} to the particle surface area and the heat of combustion

3.1 Performance of the experiment

The particle surface area and the heat of combustion were determined in addition to the standard indices of P_{max} , K_{st} and median for $N=129$ industrial dusts primarily of chemically organic composition (no metals). The particle surface area was determined by BET (Micromeritics Gemini VII) (ISO 9277, 2003). This method enables the outer particle surface area to be determined including the roughness and the internal surface area of pores. Nitrogen was employed as the adsorptive gas. The method assumes a number of physical criteria, such as energetically uniform adsorption sites, good nitrogen adsorption properties, etc. These criteria are not met in full by the dust mixtures. The BET method is nevertheless suitable for differentiating crystalline surfaces from highly porous and rough surfaces. A photometric method (Retsch, Camsizer XT) (ISO 3222-2, 2005) was also used to determine the surface area of some samples. This method digitally records and measures the geometry and surface area of a large number of dust particles. This method determines the outwardly projected surface area of the particles in the analysed surface without recording any increase owing to roughness or pores. The heat of combustion at constant volume was determined in a calorimetric bomb at an oxygen pressure of 30 bar (DIN 51900-1, 2000). The safety indices P_{max} and K_{st} were determined in closed systems as described above.

3.2 Results

In the Arrhenius approach, the influence of the BET surface area and the heat of combustion upon the K_{st} is particularly significant. Figures 5 and 6 show the K_{st} value as a function of the BET surface area and the heat of combustion ΔH_c .

Large BET surface areas ($BET-S_m > 3 \text{ m}^2/\text{g}$) do not result in a substantial increase in the K_{st} value. Besides the outer surface, the BET method considers the inner porous surface and the roughness of the dust particles. The latter do not appear to be relevant to the explosion reaction under atmospheric conditions. Surface areas in the order of approximately $1 \text{ m}^2/\text{g}$ with high K_{st} values are produced by substances that, as a result of the ignition energy ($\Delta T = \text{approx. } 400 \text{ K}$ with 10 kJ of igniter), fuse to form droplets with a reactive layer of vaporous and solid phase components (A. di Benedetto 2010) (Cashdollar und Zlochower 2007). It is also apparent that a minimum reaction surface area exists in the order of approximately $0.1 \text{ m}^2/\text{g}$: at a density of 1 and with spherical particles, this corresponds to a median of approximately $60 \text{ }\mu\text{m}$.

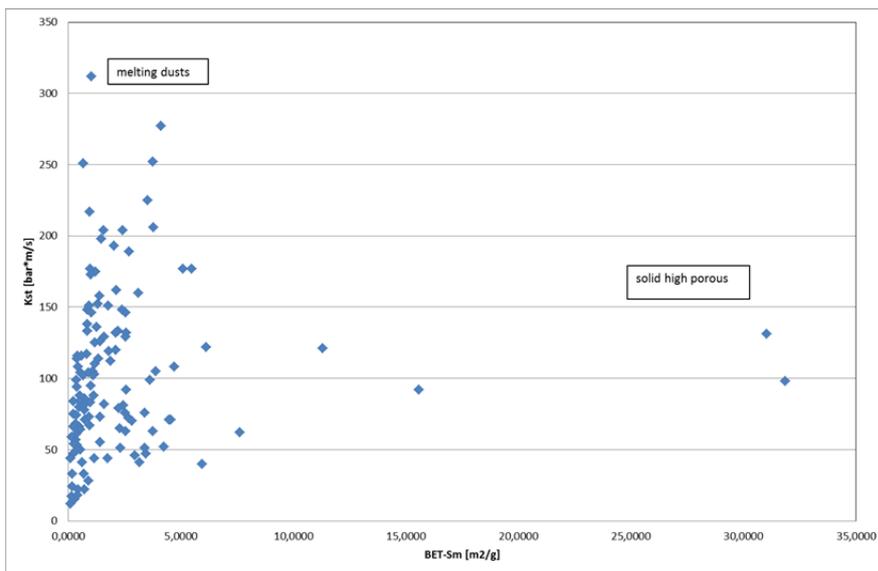


Figure 5: Correlation of the BET surface area to the K_{st} value ($N=129$)

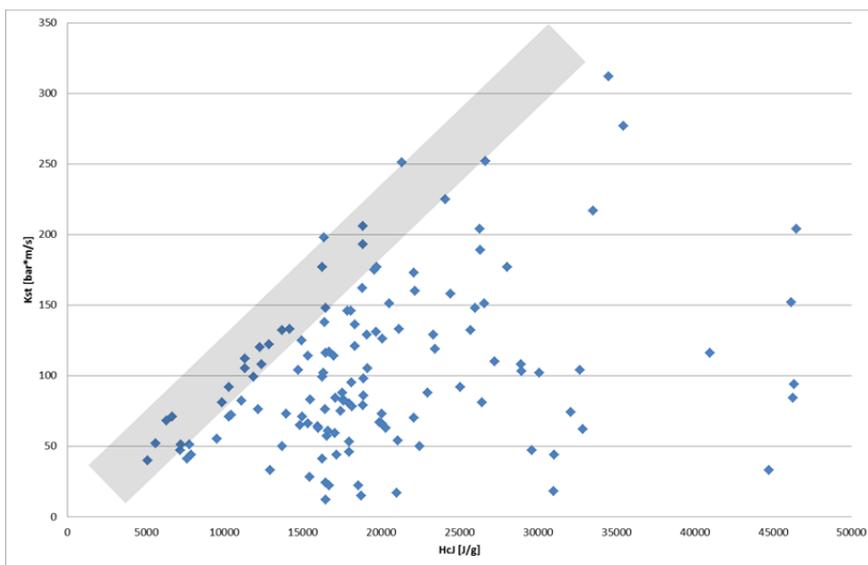


Figure 6: Correlation of the heat of combustion ΔH_c to the K_{st} value

This is substantially lower than the threshold particle size of 500 μm frequently applied in explosion protection, but is a consequence of the BET analysis method, which detects a greater surface area and results in apparently smaller particle sizes being calculated.

Use of the Arrhenius equation normally requires the correlation between the K_{st} value and the heat of combustion to be presented logarithmically; for better comparison with Figure 5 however, the K_{st} values in Figure 6 have not been presented logarithmically. At first sight, a satisfactory correlation is not evident. This is due to the fact that the heat of combustion for generation of complete conversion is determined calorimetrically at an oxygen pressure of 30 bar. Under atmospheric conditions, the reaction heat developed during the explosion is not complete at any given time, and the term for heat development in the Arrhenius equation is dependent upon the conversion over time (Equation 2). The region highlighted in grey in Figure 6 shows dusts with substance compositions containing chemically bound molecular oxygen, which permits higher conversion rates with corresponding K_{st} values (e.g. maltodextrin, niacin, cyanuric acid, polyester). Substances with a very high heat of combustion but comparatively low K_{st} values (such as PE, PP, PS, paraffin wax) lack this additional oxygen, as a result of which the maximum possible thermal conversion is limited solely by the atmospheric oxygen. Since the study collective consists of industrial dusts differing in their substance composition, these relationships exhibit correspondingly wide scatter. Further studies involving dusts of defined substance composition, including chemical sum formulae, would be useful in this respect.

4. Summary and prospects

The safety indices P_{max} and K_{st} value determined according to EN 14034 are influenced by the technical parameters of the analysis method and also substantially by the substance properties of the dust studied. It was shown for organic dusts that the inner surface of particles had no influence upon the reactivity of the dust particles and consequently no influence upon the K_{st} value. The reaction takes place primarily on the outer surface, i.e. in the surface/vapour layer. The heat of combustion is a thermodynamic substance variable that influences the P_{max} at relevant conversions. The conversion under atmospheric conditions is limited by the partial oxygen concentration of the ambient air. Additional chemically bound oxygen in the dust material increases the conversion, resulting in an increase in the reaction temperature and the K_{st} value. Comparative studies, based upon these results, of dusts of defined chemical composition and with different components of bound oxygen would be advantageous.

References

- A. di Benedetto, P. Russo, P. Amyotte, N. Marchand. „Modelling the effect of particle size on dust explosions.“ *Chemical Engineering Science* 65, 2010: 772-779.
- Cashdollar, Kenneth L. „Overview of dust explosibility characteristics.“ *J. of Loss Prevention* 13, 2000: 183-199.
- Cashdollar, Kenneth L., und Isaac A. Zlochower. „Explosion temperatures and pressures of metals and other elemental dust clouds.“ *J. Loss Prevention in process industries*, 2007: 337-348.
- GESTIS-DUST-Ex. „<http://staubex.ifa.dguv.de/explosuche.aspx?lang=e>.“ 2015.
- H. Selle, J.Zehr. „Beurteilung der Experimentalwerte für die untere Zündgrenze von Staub/Luft-Gemischen mit Hilfe thermochemischer Berechnungen.“ Düsseldorf: VDI, 1954.