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Small-scale Screening Procedure to Identify Deflagration Potential of Bulk Solids

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A novel screening method is presented for the assessment of the deflagration potential of bulk solids. It is based on a combination of closed and open thermal stability measurement. The closed measurement is performed as Closed Pressure Vessel Test, which is already proven in use regarding explosives screening. The open measurement is performed as "Lütolf Quick Test for the Determination of Exothermic Decomposition". With the proposed test combination, the sample amount is significantly reduced to a minimum of 4 g. Based on numerous deflagrator samples, as well as of partly and fully de-sensitized deflagrators, mixed with inert Diatomaceous earth, the successful application of this test combination is demonstrated.

1. Introduction

Self-sustaining decomposition or deflagration in the absence of oxygen is often the cause of serious events in the chemical industry. Typically, local hot spots, e.g., hot-running bearings or foreign objects heated up by friction, in mills, mixers or stirred dryers, initiate the decomposition which then spreads through the bulk material via a flame front (Fierz and Zwahlen, 1989). Even under inert conditions or in the absence of oxygen, high temperatures can be reached, and large quantities of combustion gases are released. This may lead to a dangerous increase in pressure in closed equipment or equipment that is inadequately vented (Fink and Zwahlen, 1992).

Successful substance screenings are required to prevent such events. A common test method is the deflagration test according to VDI 2263-1 (1990). This test requires a large amount of sample (200 ml bulk volume per measurement), which is often not available in early stages of process development. Dynamic DSC (Differential Scanning Calorimetry) measurement with high-pressure crucibles is the most common initial screening tool. However, for reliable substance identification very conservative criteria need to be applied. A typical exclusion criterion for potential deflagrators is the specific heat of decomposition with $Q'_{dec.}$ < 300 J/g (exothermic), which leads to numerous false-positive results that require additional evaluation efforts.

2. Experiments

2.1 Deflagration test

The Deflagration test according to VDI 2263-1 (1990) was used as reference test against which two screening tests, Closed Pressure Vessel Test (CPVT) and Lütolf Quick Test for the Determination of Exothermic Decomposition (Lütolf-Test), were assessed. The test setup of the Deflagration test consisted of a 200 ml vertical glass tube filled with sample material as illustrated in Figure 1. The sample material, mostly pre-heated to 100 °C, was ignited from the bottom of the tube with a glow plug reaching about 800 °C. The test result was considered positive, when a propagation of the decomposition front through the glass tube could be observed visually or the temperature, recorded at three levels in the tube, increased by more than 150 °C.

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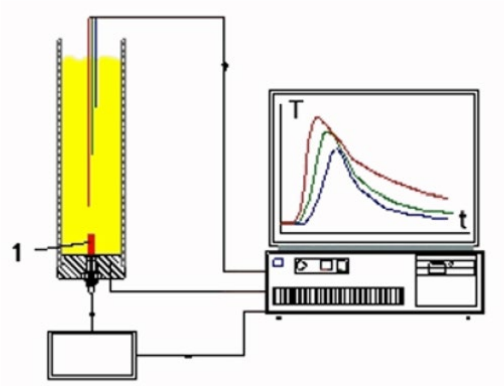

Figure 1: Scheme of the Deflagration test according to VDI 2263-1 (1990), in a 200 ml glass tube with a glow plug (1) as ignition source and temperature recording at 3 levels: low (red), medium (green) and high (blue)

2.2 Closed Pressure Vessel Test (CPVT)

The CPVT was one of the two screening tests applied. This test is typically used for the screening of substances with suspected explosive behavior (Knorr et al. 2007), which is of importance for the classification of dangerous goods i.e., hazardous materials. For this purpose, maximum pressure increase rates > 500 bar/s are evaluated. In this test the sample material (1 g) is placed in a mini-autoclave and heated at constant heating rate (2.5 K/min.) to about 400 °C. Temperature and pressure inside the mini-autoclave are recorded. The maximum pressure increase rate of a thermally initiated decomposition reaction can be evaluated thanks to the high resolution of the pressure signal recorded at 1 kHz rate. A more detailed description of the CPVT can be found elsewhere (Whitmore and Baker, 1999).
Instead of the usually performed explosives screening, we focused on significantly lower pressure increase rates for the assessment of the deflagration potential of bulk solids. Our experience over the past four years with negative explosives screenings based on the CPVT suggested that such deflagrators may be identified in the lower range of pressure increase rates as determined by this test at 5 bar/s.

2.3 Lütolf Quick Test for the Determination of Exothermic Decomposition (Lütolf-Test)

The Lütolf-Test, according to VDI 2263-1 (1990), was the second screening test applied in this work. It is a simple Differential Thermal Analysis (DTA) in which the sample material and an inert reference (usually graphite), 2g of each placed in an open glass tube, are heated at constant heating rate (2.5 K/min.) up to max. 450 °C.

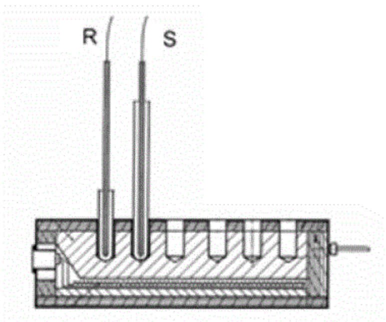

Figure 2: Scheme of the Lütolf-Test according to VDI 2263-1 (1990), with reference and sample vial

For the evaluation a thermogram was used in which the temperature difference between the sample and the reference (DT) was plotted against the reference temperature.

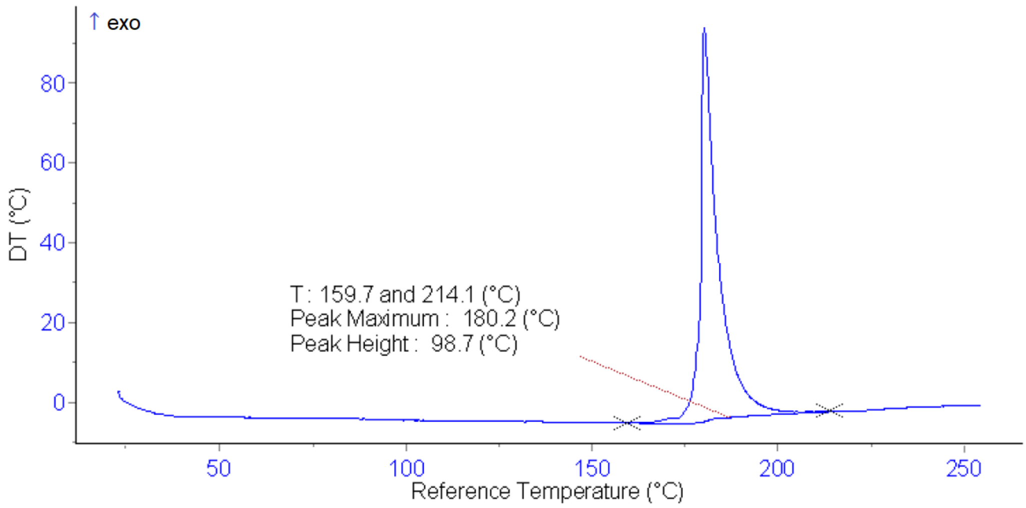

Figure 3: Thermogram of a Lütolf-Test with a sample in which the temperature difference DT is plotted against the reference temperature

At TÜV SÜD this test is used for many years as preliminary screening for powders prone to self-sustained decomposition. Together with other criteria e.g., presence of energetic functional groups in the molecule of concern and the overall decomposition energy determined by DSC (Differential Scanning Calorimetry) in closed crucibles. The Lütolf-Test criteria to identify such powders is the ratio between the maximum peak height (DT_{max}) and the onset temperature (T_{Onset}; corresponds to the temperature at the left limit of the peak) which must be ≥ 10 %. In the example, shown in Figure 3, this ratio is 62 % (= 99 °C / 160 °C · 100 %). Thus, the screening is positive which is true for the shown rather strong deflagrator.

3. Results

34 samples have been evaluated with above tests. All these samples showed an overall decomposition energy of > 300 J/g in the DSC. Among them were compounds containing the following functional groups: nitro-, azo-, and peroxo compounds, N-oxides, oxazoles, triazoles, sulphonyl hydrazides, olefins, haloanilines. Three of these compounds, all of them showing a strong self-sustained decomposition behaviour, were used to prepare “diluted” or phlegmatized samples by mixing them with Diatomaceous earth. With each sample a dilution series was prepared down to a concentration at which no more deflagration behaviour could be observed.
Half of the evaluated samples (17 of the 34) tested positive in the Deflagration test i.e., were identified as Deflagrators, and the other half negative. These results served as reference against the two screening tests, CPVT and Lütolf-Test.
The CPVT was considered positive, if the maximum pressure increase rate, observed during at least one of two measurements, was > 5 bar/s. This value was chosen as it is close to the lower detection limit, which is around 1 bar/s. Applying this criterion 16 positive tests and 18 negative tests were obtained. In comparison to the Deflagration test, which served as reference, the following screening results were obtained:

Table 1: Screening results based on the CPVT alone

Result	No. of samples
false positive	3
false negative	4
correct positive	13
correct negative	14

The 4 false-negative results indicate that the CPVT alone is not suitable for the screening of substances prone to self-sustained decomposition. However, when comparing with the Lütolf-Test, which is generally performed at the TÜV SÜD laboratories before any deflagration test is initiated, we noticed that this test successfully excluded the 4 samples with a false negative CPVT screening. Therefore, the combination of the two tests was further assessed.

As explained above, the Lütolf-Test is considered positive, when the ratio between maximum peak height and onset temperature is: $DT_{max} / T_{Onset} \geq 10$ %. Applying this “10 % criterion” 29 positive and 5 negative tests were obtained. In comparison to the Deflagration test (reference) the following screening results were obtained:

Table 2: Screening results based on the Lütolf-Test alone (10 % criterion)

Result	No. of samples
false positive	12
false negative	0
correct positive	17
correct negative	5

The 10 % criterion is known to be rather conservative as it is applied for many years with a known high false positive ratio, in this case 35 %, and no false negative results.
For a combined evaluation including Lütolf-Test and CPVT, which will be justified below, the criterion for the Lütolf-Test alone was increased to 20 %, as the two tests would complement each other. With the “20 % criterion” the following screening results were obtained:

Table 3: Screening results based on the Lütolf-Test alone (20 % criterion)

Result	No. of samples
false positive	7
false negative	0
correct positive	17
correct negative	10

As expected, the false positive ratio was lower (20 % instead of 35 %) and still no false negative result was observed.
However, the Lütolf-Test alone has inherent disadvantages. It is an open test from which gases, released during the reaction, can escape and a thus no pressure build-up can occur. As it is known that pressure build-up i.e., the presence of the decomposition gases may accelerate the decomposition reaction, a combination of the proven in use Lütolf-Test and the CPVT is evident.
The screening in which the Lütolf-Test and the CPVT were combined, and a negative test result on either test was considered as negative screening outcome (OR combination), led to the following results:

Table 4: Screening results based on the CPVT OR the Lütolf-Test (20 % criterion)

Result	No. of samples
false positive	8
false negative	0
correct positive	17
correct negative	9

Of the 34 samples, a total of 26 were correctly screened (76 %) with no false negative results. Compared to the Lütolf-Test with the 10 % criterion a significant reduction of false positive results was obtained (8 instead of 12 cases). Compared to the Lütolf-Test with the 20 % criterion, an additional false positive result was obtained. However, the Lütolf-Test with the 20 % criterion must not be used alone. This is an insufficiently conservative screening criterion, which years of experience with a much larger number of samples have shown.
The overall screening procedure to identify deflagration potential of bulk solids by applying the above tests is summarized in the following flow chart:

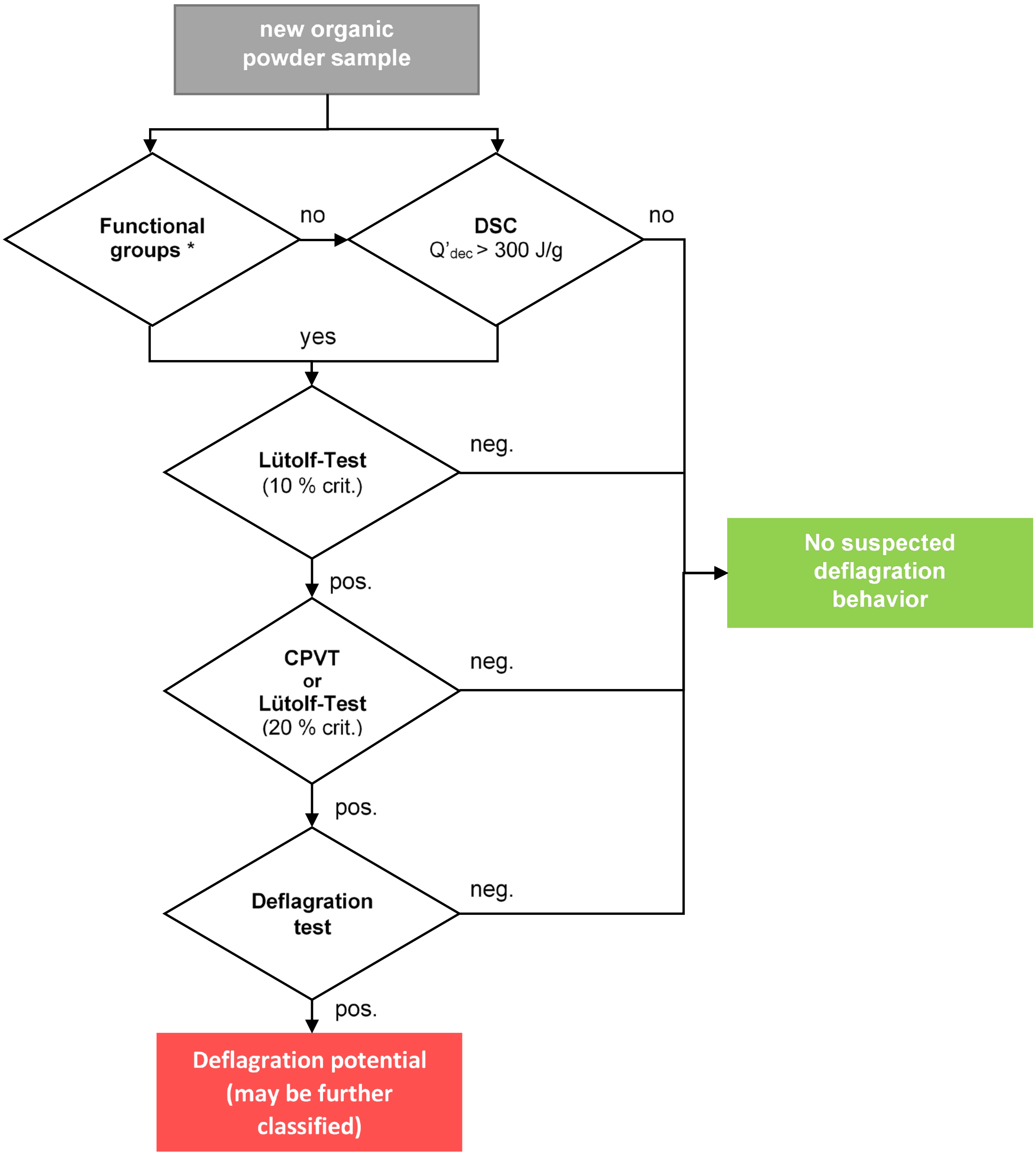

Figure 4: Suggested screening procedure to identify deflagration potential of bulk solids (Functional groups according to Appendix 6 of the UN DG Manual of Test and Criteria)*

Initially, the molecular structure may be screened for energetic functional groups according to Appendix 6 of the UN DG Manual of Test and Criteria (United Nations, 2019). If this is not possible, e.g., for a product mixture or if there are uncertainties, then the overall decomposition energy can be considered. This may be determined by DSC in a high-pressure crucible in the temperature range up to 400 °C. Afterwards, the different screening tests are applied as introduced above until a negative test result is achieved or the deflagration potential is justified in the Deflagration test.

4. Conclusions

A novel small scale screening procedure to assess the deflagration potential of bulk solids was developed. Until now, reliable screening was possible mainly with the deflagration test, as described above, which required at

least 200 ml of sample material. With the new approach, the demand on sample material is reduced to a minimum of 4 g.
The required robustness for such a small-scale screening is achieved by combining an open and a closed test, i.e., the Lütolf-Test and the CPVT. The Lütolf-Test alone is an already proven method for deflagration screening, which has been in use in TÜV-SÜD's laboratories for many years. The CPVT as an established explosive screening test complements the methodology by a closed test from which gaseous decomposition products cannot escape. This is particularly important since certain deflagration reactions are known to be accelerated by their decomposition gases under pressure.
Of the 34 screened deflagrator samples, a total of 26 were correctly screened (76 %) with no false negative results and 8 false positive results (24 %). For this novel, small-scale screening, the identified false positive rate is required in favour of sufficiently conservative screening.

Nomenclature

DT – temperature difference; T_{Sample} - $T_{Reference}$, °C
Q'_{dec} – heat of decomposition, J/g
T_{Onset} – $T_{Reference}$ at the left limit of the peak, °C
$T_{Reference}$ – reference temperature, °C
T_{Sample} – sample temperature, °C

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