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Self-ignition Behaviour of Bulk Materials: How Reliable is the Extrapolation of Laboratory Tests?

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The self-ignition behaviour of bulks is usually determined with the aid of isoperibolic or adiabatic hot storage tests; the sample volumes here are typically in the range of approx. 100 cm³ to several litres. The extrapolation to technically relevant volumes holds, however, considerable uncertainties. To reduce these uncertainties, a test stand was set up that allows to investigation sample sizes of up to 1000 dm³. These allow the study of self-ignition behavior closer to the conditions that prevail in practice. The suitability (or unsuitability) of the established methods (including dangerous goods classification tests) were to be demonstrated and influencing variables that cannot be measured on a laboratory scale were to be determined.

In addition, various analytical methods were used for the determination of reaction kinetic data of solid bulk materials and to predict the self-ignition behaviour of large storages. These are thermal analyses such as differential scanning calorimetry DSC, simultaneous thermal analysis STA as well as microcalorimetry for high-precision measurement of heat flows.

Complete test series using all mentioned test methods will be presented for crosslinked polyvinyl-pyrrolidone (PVP) and conclusions regarding the applicability of the extrapolation methods will be discussed. Hot storage tests up to semi-industrial scale and their combination with various thermoanalytical methods allow a much more precise prediction of the self-ignition behaviour of large bulks. A further promising approach to estimate their heat release rates, and hence, the risk of self-ignition under technical conditions, is the use of microcalorimetric methods.

1. Introduction

Spontaneous combustion of flammable materials can occur during both process engineering applications and the transport or storage of bulk materials. An overview of the methods for determining the spontaneous ignition behaviour is given by Fei and Liang (2011), for example. Various parameters (e.g. material properties, storage conditions and the geometry of the bulk solid) influence the spontaneous ignition process. For this reason, efforts have already been made in the past to better describe these processes through systematic laboratory experiments in combination with suitable model approaches and to transfer the results of the laboratory experiments to real scale with the aid of numerical methods, e.g. Fierro et al. (1999), Lohrer et al. (2005), Krause et al. (2006), Ferrero et al. (2009), Zhu et al. (2013), Everard et al. (2014), Degenkolbe et al. (2016), Wu et al. (2017) and Wu et al. (2019). Some of the work carried out so far also includes large-scale experiments. In this context, investigations of the spontaneous combustion processes in bulk materials on a real scale were carried out, such as coal stockpiles (Fierro, 1999) and wood chip stockpiles (Ferrero, 2009). However, these studies did not involve the systematic determination of critical storage conditions, as would be necessary for checking the extrapolation, but rather the investigation of selected scenarios.

The basic prerequisite for the successful application of extrapolation methods (including dangerous good classification tests) and further numerical calculation methods, however, is the knowledge of reaction-kinetic data of the processes taking place during the spontaneous ignition processes. These data are in turn determined from the laboratory tests already described and are thus subject to the uncertainties listed above.

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2. Experimental studies

2.1 Material tested

For this study, crosslinked polyvinylpyrrolidone was used. The reaction apparently proceeds according to an autocatalytic mechanism, which can be seen, for example, by a shift in the onset temperature from 5 K to 10 K when the heating rate is doubled in DSC measurements. No unusual auto-ignition behavior was observed in hot storage tests. This sample is well suited to perform extensive studies with different test methods and at different scales. Furthermore, this sample is of interest, because first results show that the extrapolated self-ignition temperature of a 27 m³ package is close to 50 °C, which is the relevant temperature for classification.

2.2 Isoperibolic hot storage tests

Isoperibolic tests have been performed in laboratory scale according to DIN EN 15188:2021 using cubic sample baskets of edge lengths from 5 cm up to 10 cm. In addition, semi-technical scale tests have been conducted using a unique test-stand. The setup for carrying out these tests consists of four heating chambers with an internal volume of about 3 m³ each, designed to store four 200 L barrels or containers up to a volume of 1 m³, see Figure 1 a). The air in the heating chamber is permanently circulated by means of a fan. Holes drilled in the rear wall ensure a four- to fivefold air exchange per hour. For safety reasons, it is planned to stop the tests at a point in time when an ignition could be clearly detected. For this purpose, a system has been installed which allows the oven to be switched off automatically and the oven chamber to be purged with nitrogen.
Wire mesh baskets with volumes of approx. 125 dm³ and 1,000 dm³ are available as sample containers. Each oven is equipped with a system to measure temperatures at up to 16 points in and around the sample. If necessary, it is possible to detect fire gases generated during the test. A mobile FT-IR spectrometer and oxygen analyser are available for this purpose.

Figure 1: Weather protection tunnel with 4 ovens and equipped sample container (1,000 dm³) with petroleum coke sample

For a simplified fast extrapolation, the so-called Pseudo-Arrhenius plot is often used where the volume to surface ratio of the sample (V/A) is plotted against the reciprocal self-ignition temperature ($1/T_{SI}$), see Annex A.5 of DIN EN15188 (2021). This method is used in section 3.1 to illustrate the results of the performed isoperibolic test series.

2.3 Adiabatic hot storage tests

In adiabatic tests, the ambient (oven) temperature is adjusted to correspond to the temperature in the center of the sample. Under these conditions, the Fourier heat equation is simplified in that way that no heat conduction in the sample and heat transfer from the sample to the surrounding occur and hence, the reaction kinetics may be determined from a single test. Adiabatic hot storage tests are described in Annex D of DIN EN15188:2021.

2.4 Thermoanalytical investigations

For thermoanalytical investigations, standard DSC tests as well as microcalorimetry tests were used. Microcalorimetry is based on the differential heat flow principle like DSC. It is distinguished by very high measurement sensitivity in the range from 1 mW/kg to 10 mW/kg and in a high baseline stability. This enables the measurement of low heat fluxes and thus an assessment of reactions at low temperatures. The type of microcalorimeter used is a Thermal Activity Monitor (TAM III) from TA Instruments. Within this device, a so-called perfusion cell is applied to measure oxidative self-heating processes. This enables air flow through the sample during the measurement in order to ensure a sufficient supply of oxygen. In this way, the heat production rate of comparatively large sample quantities of about 100 mg can be measured directly in the temperature range, which is relevant for self-ignition processes at an industrial scale.

Standard DSC tests were performed at different heating rates. With the help of model free methods such as Friedmann (1964), Ozawa (1965)/Flynn/Wall (1966), Kissinger (1957) and determination of initial slope kinetic parameters have been estimated. In addition, it has been discovered if a reaction follows rather complex or simple mechanisms.

3. Test results

3.1 Isoperibolic hot storage tests

The self-ignition temperatures (T_{SI}) determined from isoperibolic tests are listed in table 1. According to DIN EN 15188:2021, T_{SI} is defined as the highest temperature at which a given volume of dust just does not ignite. The selection of the oven temperatures for the decisive final two tests was set in such a way that the temperature of the test just produced ignition and that of the test did not produce an ignition differed by not more than 2 K.

Table 1: Self-ignition temperatures (T_{SI}) determined by isoperibolic hot storage tests

	laboratory scale				semi-technical scale		
volume in dm³	0.143	0.257	0.715	1.140	10.15	114	932
T_{SI} in °C	141.8	136.6	125.9	120.8	130.4	88.7	75.1

Figure 2 a shows the final tests with a sample volume of 1 m^3. While no ignition occurred at an oven temperature of 75.1 °C, the material ignited at an oven temperature of 77.4 °C about 95 days after the start of the test. The self-ignition temperatures determined for semi-technical volumes are slightly higher than the values predicted by extrapolation of laboratory tests. The measurement uncertainty of the extrapolation of laboratory tests as defined in DIN EN15188:2021 is shown by dashed lines in Figure 2 b.

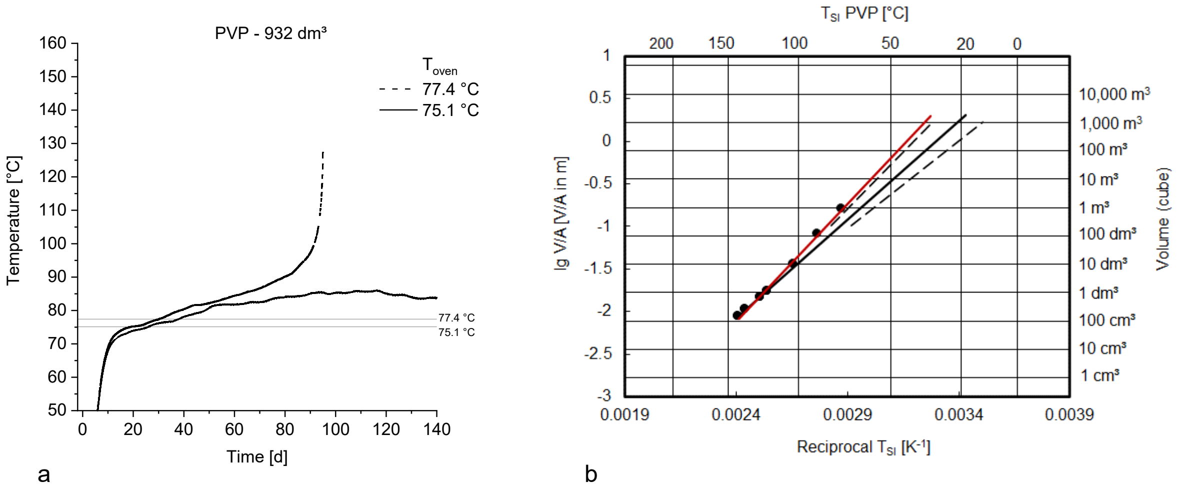

Figure 2 a: Temperature-time plots at the center of a 932 dm³ sample and b: Pseudo-Arrhenius Plot of isoperibolic test series with PVP with solid black line – extrapolation line of laboratory tests, dashed black lines – uncertainty of extrapolation of laboratory tests, solid red line – extrapolation line of all tests

3.2 Adiabatic hot storage tests in combination with thermoanalytical investigations

In adiabatic hot storage tests the sample reacts with an induction time of several hours when heated to 125 °C, see Figure 3. In Figure 4, the isothermal measurements in a microcalorimeter at 60 °C and 75 °C are plotted. The results from both test methods are combined in an Arrhenius plot (logarithmic heat flow over reciprocal temperature), see Figure 5. The apparent activation energy E_a is determined based on the adiabatic test with 99 kJ/mol. The micro caloric test result corresponds well to the extrapolation from the adiabatic test. Since micro caloric experiments allow for direct measurement of heat flux in a temperature range which is relevant for classification, they contribute to a significant increase of prediction accuracy. This is especially beneficial in cases in which adiabatic tests show ambiguous results.

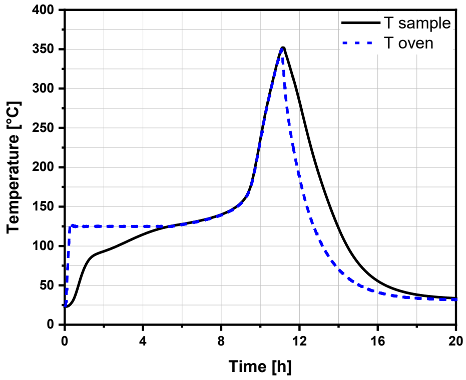

Figure 3: Adiabatic hot storage test initiated at 125 °C

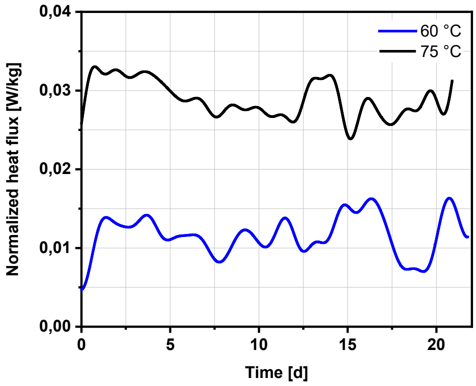

Figure 4: Isothermal micro caloric test at 60 °C and 75 °C

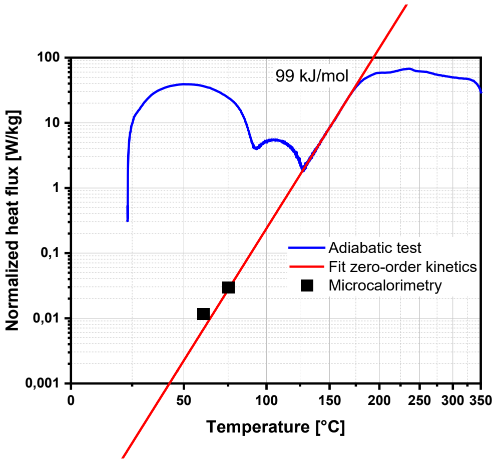

Figure 5: Heat flux over temperature, results from an adiabatic hot storage test initiated at 125 °C and from isothermal micro caloric tests at 60 °C and 75 °C

3.3 Screening method using direct measurement of heat flux

Direct measurement of heat flux can be beneficial for the prediction of self-ignition behaviour. Using Frank-Kamenetskii's theory of thermal explosion, the critical heat flux $\dot{Q}_{crit}$ which is required for thermal explosion can be calculated:

$$\dot{Q}_{crit} = \frac{R \cdot T^2}{E_a} \delta \cdot \frac{\lambda}{\rho \cdot r^2} \tag{1}$$

The Frank-Kamenetskii parameter δ is calculated according to Boddington-theory based on Bi-number and geometry (Boddington, 1971). λ is the thermal conductivity, ρ the bulk density and r the characteristic length of the geometry. The calculation is performed for a 27 m³ package at a storage temperature T of 50 °C as these are the relevant parameters for classification to UN sub-division 4.2. Hereby, different hypothetical activation energies between 50 kJ/mol and 200 kJ/mol are used. The results are given in Table 2.

The critical heat flux to detect at 50 °C is in the order of magnitude as the detection limit of the test device. For this reason, to derive a robust decision scheme, the corresponding critical heat flow at 75 °C is calculated assuming zero-order conditions and using Arrhenius-relation:

$$\ln \dot{Q}_2 = \ln \dot{Q}_1 + \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{2}$$

These results are also listed in Table 2. At 75 °C, the critical heat flux to detect is sufficiently large to allow for a reliable measurement. Based on these values, the decision if a substance is a candidate for sub-division 4.2 or not can be prepared. Particularly, if a heat flux smaller than 8.6 mW/kg is detected it can be concluded that the expected self-ignition temperature of a 27 m³ package is greater than 50 °C. Performing several micro caloric measurements at different temperatures allows for estimation of activation energy. In this way, the value of critical heat flux to be used for the decision can be sharpened.

Table 2: Critical heat flux threshold for self-heating of a 27 m³ package at 50 °C, estimated with FK theory, and corresponding critical heat flow at 75 °C

E_a in kJ/mol	50	100	150	200
$\dot{Q}_{crit}$(50 °C) in mW/kg	2.3	1.1	0.8	**0.6**
$\dot{Q}_{crit}$(75 °C) in mW/kg	**8.6**	16.4	41.6	119

3.4 Overview of results

The apparent activation energies obtained from different methods are listed in Table 3. The results are in good accordance regardless the method. The apparent activation energies determined including semi-technical volumes are slightly higher than the values predicted by extrapolation of laboratory tests.

Table 3: Apparent activation energy obtained from different methods

E_a Friedman [kJ/mol]	E_a Ozawa, Flynn, Wall [kJ/mol]	E_a Kissinger [kJ/mol]	E_a adiabat exp. [kJ/mol]	$E_a$isoperibol. exp. (FK/Thomas) [kJ/mol]
104 ± 4 [b]	101 ± 3 [b]	99 ± 5	99 [b]	96/82 [a] 112/103 [c] 99/76 [b]

[a] Measurements BAM ≤ 1 dm³, [b] Measurements BASF, [c] Measurements BAM ≤ 1,000 dm³

The self-ignition temperature calculated using different methods and experiments in different scales are listed in Table 4. Comparing the results from laboratory scale tests reveals a good accordance of predicted self-ignition temperatures, regardless the method used. The self-ignition temperatures predicted including semi-technical tests are shifted to higher values compared to prediction of laboratory tests.

Table 4: Predicted self-ignition temperature T_{SI} for an isometric cylinder with a volume of 27 m³

Method	1 isoperibolic test + 1 adiabatic test	5 isoperibolic tests (FK / Thomas) with V ≤ 1 dm³	7 isoperibolic tests (FK / Thomas) with V ≤ 1000 dm³
T_{SI} in °C	39 [b]	40 / 25 [b]	54 / 52 [a]

[a] Measurements BAM, [b] Measurements BASF

4. Conclusions

The reaction and self-ignition behavior of PVP has been studied on a laboratory scale using various methods. This included so-called hot storage tests, thermoanalytical methods as well as their combination. Both the prediction of self-ignition temperatures of technical bulks/storages and the determined formal kinetic data show a good agreement here.

Isoperibolic hot storage tests in semi-technical scale revealed that an extrapolation from laboratory scale is conservative. In addition to PVP, this could also be shown for other materials such as hard coal. Initial studies suggest that the limitation of available oxygen in the center of the bulk may be the main reason for the higher critical ambient temperatures (self-ignition temperatures). In the tests carried out so far up to 1,000 dm³ with further materials, the oxygen content in the bulk was reduced during the self-ignition process, but the oxygen was not completely consumed. It is possible that this reduction already led to a changed reaction behaviour.

However, to confirm this, further series of tests on both laboratory and semi-industrial scale with PVP are required to determine the reaction behaviour at reduced oxygen levels.

The combination of adiabatic hot-storage tests and microcalorimetric tests contributes to a significant increase of prediction accuracy compared to the solely adiabatic method described in Annex D of DIN EN15188:2021. The application of microcalorimetry is in general a promising approach for the assessment of self-heating behaviour since it allows for direct measurement of heat flux at temperatures relevant for technical storages. Such measurements may be the basis for a reliable and efficient screening method assessing the requirement of classification of a hazardous substance as self-heating. Particularly, an exclusion from classification would be possible if critical threshold values are not reached in the measurements.

References

Boddington T., Gray B.F., Harvey D.I., 1971, Thermal theory of spontaneous ignition: Criticality in bodies of arbitrary shape, Philosophical transactions of the Royal Society

DIN EN 15188:2021 Determination of the spontaneous ignition behaviour of dust accumulations. DIN Deutsches Institut für Normung e.V. Berlin, Beuth Verlag GmbH.

Degenkolbe S., Witt W., 2016, Self-ignition in structured packed columns, fundamentals of methodology development, Journal of Loss Prevention in the Process Industries 40: 437-448.

Everard C. D., Schmidt M., McDonnell K. P., Finnan J., 2014, Heating processes during storage of Miscanthus chip piles and numerical simulations to predict self-ignition, Journal of Loss Prevention in the Process Industries, 30, 188-196.

Fei F., Liang D., 2011, Research Progress and Comparison of Methods for Testing Self Ignition Materials, Procedia Engineering, 11, 91-99.

Ferrero F., Lohrer C., Schmidt B. M., Noll M., Malow M., 2009, A mathematical model to predict the heating-up of large-scale wood piles, Journal of Loss Prevention in the Process Industries, 22, 439–448.

Fierro V., Miranda J. L., Romero C., Andrés J. M., Arriaga A., Schmal D., Visser G. H., 1999, Prevention of spontaneous combustion in coal stockpiles – Experimental results in coal storage yard, Fuel Processing Techn., 59, 23–34.

Flynn J.H., Wall L.A., 1966, General treatment of the thermogravimetry of polymers, Journal of Research of the National Bureau of Standards Section A: Physics and Chemistry, 70A, 487 ff.

Frank-Kamenetzkii D.A., 1969, Diffusion and heat transfer in chemical kinetics. Plenum Press, New York, London.

Friedman H.L., 1964, Kinetics of thermal degradation of char-forming plastics from thermogravimetry, Application to a phenolic plastic. Journal of Polymer Science Part C: Polymer Symposia, 6, 183.

Kissinger H.E., 1957, Reaction Kinetics in Differential Thermal Analysis, Analytical Chemistry, 29, 1702-1706.

Krause U., Schmidt M., Lohrer C., 2006, A numerical model to simulate smouldering fires in bulk materials and dust deposits, Journal of Loss Prevention in the Process industries, 19, 218-226.

Lohrer C., Schmidt M., Krause U., 2005, A study on the influence of liquid water and water vapour on the self-ignition of lignite coal-experiments and numerical simulations, Journal of Loss Prevention in the Process Industries 18(3): 167-177.

Ozawa T., 1965, A New Method of Analyzing Thermogravimetric Data, Bulletin of the Chemical Society of Japan, 38(11), 1881-1886.

Wu D., Norman F., Schmidt M., Vanierschot M., Verplaetsen F., Berghmans J., Van den Bulck E., 2017, Numerical investigation on the self-ignition behaviour of coal dust accumulations: The roles of oxygen, diluent gas and dust volume, Fuel, 188, 500-510.

Wu D., Schmidt M., Berghmans J., 2019, Spontaneous ignition behaviour of coal dust accumulations: A comparison of extrapolation methods from lab-scale to industrial-scale, Proceedings of the Combustion Institute, 37, 4181-4191

Zhu H., Song Z., Tan B., Hao Y., 2013, Numerical investigation and theoretical prediction of self-ignition characteristics of coarse coal stockpiles, Journal of Loss Prevention in the Process Industries, 26, 236-244.