

The Relationship between a Thermal Analysis and a Safety-Relevant Problem

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Many processes require a safety related reflection, regarding to the fire and explosion hazards. But a reflection can be difficult, especially the consideration of fire and explosion hazards, according to process conditions require a special knowledge and experience from the experts.

As a part of a research project “explosion protection in spray dryers” the self-heating reactions of milk powder as a possible and effective ignition source should be determined. Therefore, it was necessary to perform thermal analyses with a coupled Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). The measured rate of mass loss permits under advantage of the Flynn-Wall-Ozawa method a calculation of the kinetic data of the decomposition process of milk powder. The gaseous decomposition products were also analysed with infrared spectroscopy.

On basis of the experiments it was possible to define the main decomposition steps of milk powder. Furthermore, equivalent parameters to characterize the possible risk of self-heating and further of self-ignition, according to the process conditions, were prepared. Therefore, different scenarios have been created to estimate the risk. In the first case a theoretical milk powder deposit in the form of a sphere and of a plate was developed. Secondly, the theory of heat transfer and chemical kinetics by Kamenetskii were used to calculate the critical layer thickness and a heat balance.

The present contribution shows the transfer of a small - scaled thermal analysis on a large- scale and safety-relevant self-heating problem. The shown approach (measurement, evaluation etc.) will be reflected critically. Especially the comparability of a small-scale analysis with a real safety relevant problem will be discussed.

INTRODUCTION

Knowledge of the thermal stability and the possible chemical hazardous reactions are an indispensable element of the process development. Self-heating is an example for a typical safety relevant problem in the process industry, which should be determined and controlled. Especially organic material is susceptible to self-heating in different unit operations, particularly in drying operations. Per the process parameter, the self-heating can develop to a self-ignition and furthermore to a smoldering fire, respective to a glowing ember, cf. (Babrauskas 2003). Glowing embers are known as an effective ignition source in the fire and explosion safety, which has the potential to ignite a dust-air-mixture, cf. (Zockoll 1988). Self-heating is a very probable cause in the case of spray drying processes, which can lead to a fire event or even to an explosion event, cf. (BEEVER 1985; Maiwald et al. 2016; VDI Richtlinie 2263; Beever 1985).

The presented problem is an appropriate example of a safety-relevant question which must be confirmed by laboratory tests. The present contribution is intended to describe and illustrate the problems of the self-heating of milk powder deposits in spray dryers and describes possibilities of using data from a thermal analysis to control hazards.

SELF-HEATING IN THE SPRAY DRYING PROCESS

Spray drying is a drying process which effects a phase transition from liquid to solid by finely atomizing the liquid substance into a warm air flow. In general, spray drying is known as a very gentle drying process since the dry material is only subjected to a small degree of thermal stress. For this reason, spray drying is applied to thermally sensitive products such as milk powders. Furthermore, spray drying is characterised by two main effects, drying and agglomeration. With the help of spray drying, particles with specific particle properties, for example particle size or spherical characteristics, are produced by vaporization of the binder. In addition, the particles agglomerate to the desired particle characteristics as a function of the residence time, the particle moisture, the stickiness and the collisions with other particles. **Figure 1** shows a typical arrangement of a spray drying system.

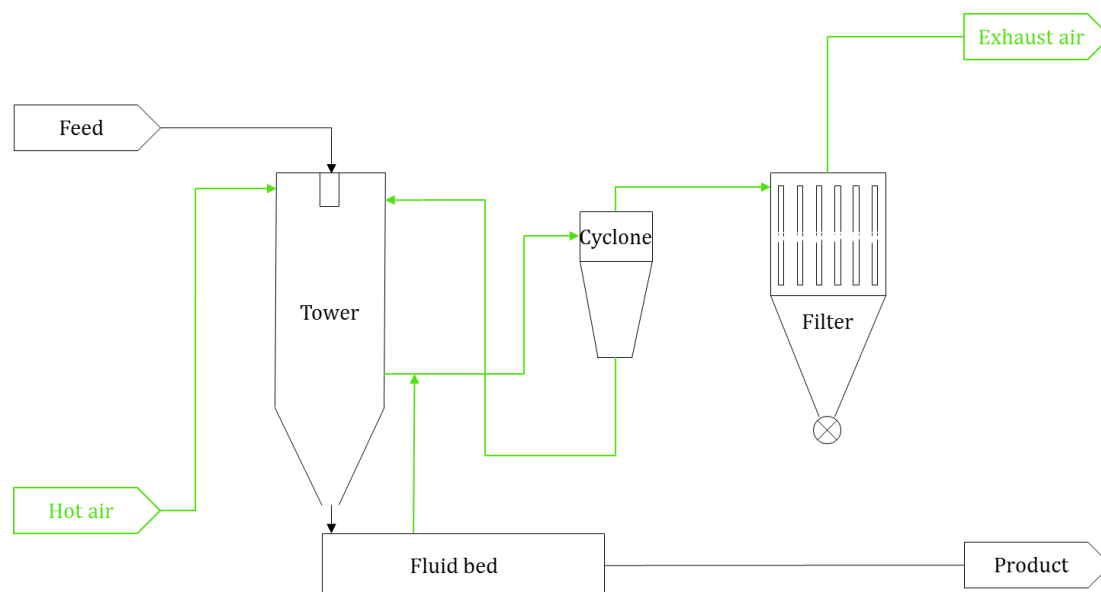


Figure 1: Typical arrangement of a spray drying plant, cf. (Liske 2016).

Disturbances, such as unwanted increasing of the residence time or an adjusted flow pattern in the spray tower, can lead to unwanted deposits in the spray tower. About the prevailing elevated temperatures, the good air supply of the convection allows a rapid drying of the deposit. According to the operating time, a long residence time of the deposit in the drying chamber is possible. Because of the constantly acting heat, the deposit can first be warmed up by means of a preheating process, whereby self-heating is possible in the following step. Heat is generated in the deposit by initiated exothermic reactions. In the spray drying process, a phase transition from the liquid to the solid state takes place due to the drying. Coupled with the high flow velocities and high particle loading in the drying chamber, a layer growth of the deposit is possible. The layer growth is promoted by the product moisture and a possibly high fat content with a high stickiness. Thus, increasing layer thicknesses and an increasing poorer heat dissipation are to be assumed. Heat dissipation is an important factor in self-heating. If the heat released by chemical reactions exceed that of heat removal, there is a risk of self-ignition, cf. (Steen 2009). Depending on the local arrangement a milk powder deposition, variations in the geometrical form and composition of the deposit are conceivable. For example, a deposit on the chamber walls can develop a plate-shaped milk powder deposit, whereas a deposit on the nozzles can have a spherical geometry and an increased water content. During self-heating, the heat in the deposit can rise so far that it can lead to an ignition which can cause a smoldering fire. If the smolder front achieves the deposit surface in connection to sufficient oxygen, a glowing fire can be observed with temperatures between 500 °C and 900 °C, cf. (Schmidt S. 2016; Zockoll 1988).

In the case of the milk powder, the Maillard reactions, also known as non-enzymatic browning, are the dominant reactions in the initial steps of self-heating. Further corresponding oxidative reactions of the milk powder components are conceivable, including autoxidation and hydrolysis of the fats, decomposition of carbohydrates and combustion, respective oxidation of formed decomposition products, cf. (Raemy und Lambelet 1991).

EXPERIMENTAL

Thermogravimetry (TGA) and Differential Scanning Calorimetry (DSC) are common methods by which the thermal behavior of materials can be experimentally tested. With the help of the thermal analysis, a qualitative assessment of the decomposition behavior of the milk powder was done. For this purpose, investigations were carried out in a coupled TGA/DSC under an air-similar and an inert atmosphere. The inert atmosphere makes it possible to suppress the oxidative decomposition, thus the role of the Maillard reactions can be determined. With the help of sieving, a certain standard particle fraction of the milk powder between 250 µm and 125 µm was selected and used recurrently for the measurements. The milk powder is used as a baby food supplement.

A temperature-controlled measuring program with different heating rates (5 K/min; 10 K/min and 20 K/min) was carried out. Each sample was enclosed in an open aluminium crucible. An empty crucible was used as a reference. The initial weight of the samples ranged around 6 mg. The gaseous decomposition products were analysed in a separated measurement with different conditions with coupled Fourier transformed spectroscopy (FT-IR). Therefore, a sample of milk powder was measured with a heating rate of 20 K/min under an air atmosphere.

RESULTS AND DISCUSSION

TGA AND DSC ANALYSIS UNDER AIR ATMOSPHERE

Based on the generated TGA/ DSC curves, so called thermograms, three exothermic decomposition reactions can be observed. The course of reactions are further explained by using the 10 K/min heating rate as an example. Therefore the parameter “onset-temperature” is needed, which is defined as the initial temperature at which a chemical reaction takes place. At the beginning of the measurement a slight mass loss can be observed up to approx. 150 °C. This mass loss can be attributed to the evaporation of water. A first exothermic reaction can be observed from an onset temperature of approx. 150 °C, too.

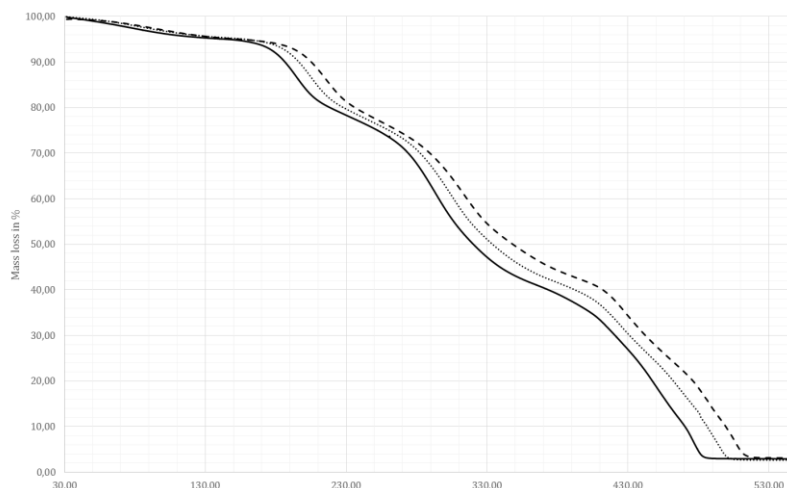


Figure 2: TGA thermogram of milk powder under air atmosphere.

By this reaction, a mass loss of 16.4 mass-% is achieved. No significant heat release can be observed using the thermogram of the DSC measurement.

In the following course, a second exothermic reaction can be observed whose onset temperature is about 232 °C, the mass loss of this reaction is 37.51 mass-% of the initial weight. In addition, a heat release of approximately 657 J/g can be observed. Finally, a third reaction is carried out at an onset temperature of about 380 °C with a mass loss of 38.3 mass-%, with a heat release of about 6646 J/g and a maximum at 494 °C.

The first pronounced heat release peak takes place at a temperature of 336 °C and can be assigned to the second decomposition stage. After completion of the measurement, a residual mass of about 2.7 mass-% remained in the crucible. The associated thermograms are shown in **Figure 2** and **Figure 3**.

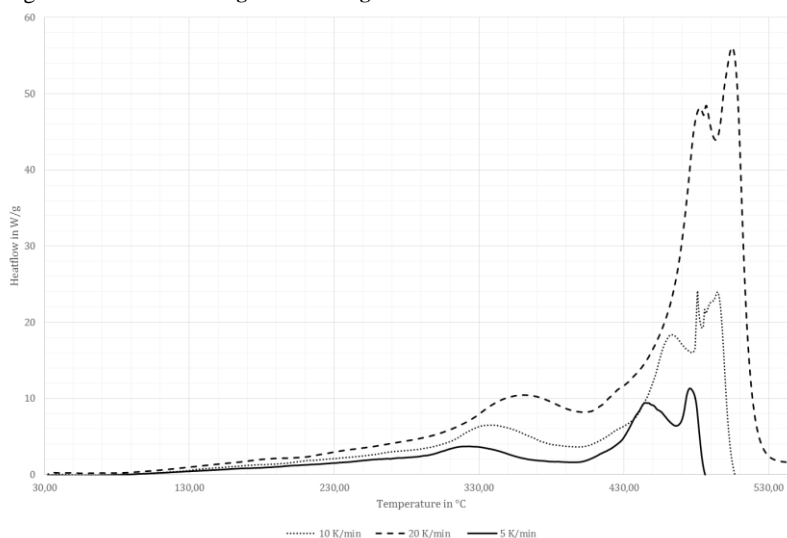


Figure 3: DSC thermogram of milk powder under air atmosphere.

TGA AND DSC ANALYSIS UNDER INERT ATMOSPHERE

Three reactions in the decomposition process can also be determined under nitrogen atmosphere. The first reaction has its onset temperature at about 150 °C. The highest reaction rate is reached at about 204 °C. The mass loss of this reaction is about 18.9 mass- %. These observations are equal to the first decomposition reaction under air conditions. The Maillard reaction takes place at 150 °C and 170 °C in decomposition process of milk powder, cf. (Raemy und Lambelet 1991; Chong et al. 1996). Furthermore, the Maillard reaction takes place independent from oxygen. Thus, it is highly probable that the first decomposition step is the Maillard reaction. Per the less heat release at the first decomposition step, it is assumed that the Maillard reaction is not the main reason for a thermal runaway and further a self-heating. Probably the Maillard reaction is an initial step, which helps to overcome the activation energy for further reactions and initiates the temperature increase in the self-heating process, cf. (Raemy und Lambelet 1991).

The second reaction of the decomposition follows at an onset temperature of about 260 °C and results in a mass loss of 29.1 mass- %. The maximum of the reaction rate in the second reaction is about 310 °C. The second and the third reaction, which were observed in the measurements under air-similar atmosphere are mutually interrelated, so that no onset temperature for the third reaction can be read off. Finally, the mass loss rate is constant and has a residue of about 19.2 mass- %. The maximum value of the heat release is determined at about 280 °C with about 2 W/g. In the further measurements within the scope of this series, a similar reaction behaviour could be observed. The results of the series of measurements under an inert atmosphere are shown in **Figure 4** and **Figure 5**.

In a comparative evaluation of the TGA/ DSC curves under air-similar and inert conditions, differences during the decomposition can be observed in the second and third reaction. At the start of the second reaction, a deviation occurs during the reaction. The reaction begins at the same onset temperature of about 260 °C. However, the reaction under an inert atmosphere is not as pronounced as under air-like conditions. Contrary to the course of the reaction under air, a further decomposition reaction takes place under an inert atmosphere at about 340 °C to 400 °C. This reaction is not observed in the decomposition process under air in the mentioned temperature range. After this reaction completion, the decomposition process is completed under an inert atmosphere at a temperature of about 500 °C. During the decomposition process under air-like conditions, a decomposition reaction begins at 380 °C with a comparatively massive extent in mass loss and in heat release. A large reaction with a maximum reaction rate at approx. 470 °C can be observed. The reaction is complete at about 500 °C. The described reaction cannot be observed in the inert decomposition process.

Following these observations, the second decomposition reaction at 230 °C is probably a coupled decomposition and oxidation of the individual milk components such as fats and carbohydrates, cf. (Raemy und Lambelet 1991; Raemy und Schweizer 1983) The last decomposition reaction could only be observed under air-like conditions. The heat release rate of 6646 J/g suggests a smoldering fire and thus an oxidation. The temperature range from 400 °C to 500 °C also indicates a smoldering fire, cf. (Babrauskas 2003; Hurley et al. 2016).

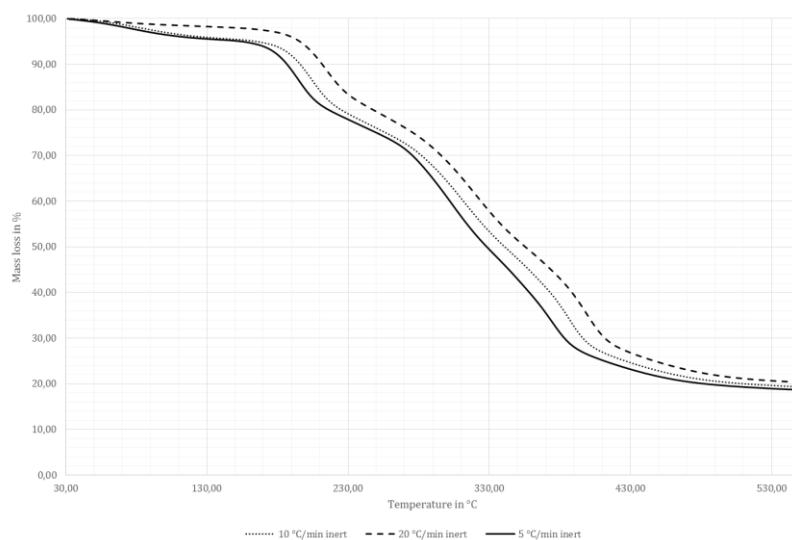


Figure 4: TGA thermogram of milk powder under inert atmosphere.

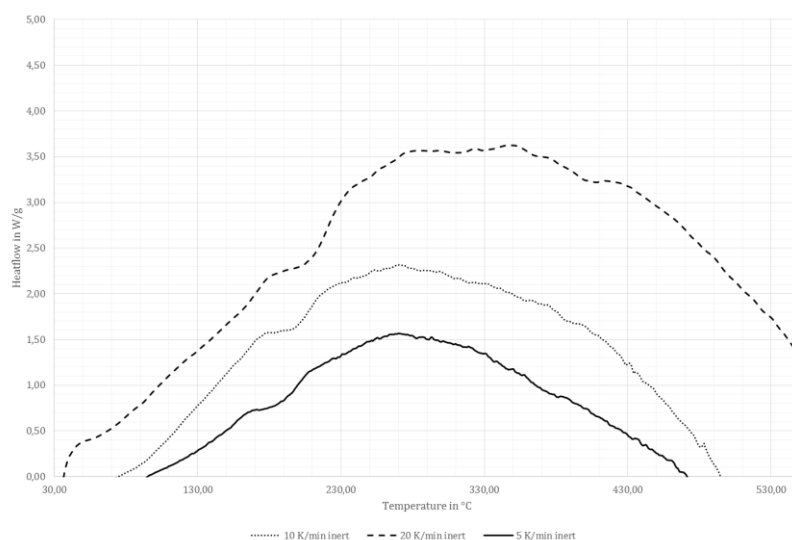


Figure 5: DSC thermogram of milk powder under inert atmosphere.

FT-IR ANALYSIS

By means of coupled Fourier-transformed infrared spectroscopy (FT-IR), the gaseous reaction products from the TGA were investigated by a separate measurement under air conditions and with a heating rate of 20 K/min. The measurements showed under this experimental conditions that mainly the reaction products carbon dioxide and water are released in the first reaction step. Only in the second decomposition reaction, at about 300 °C, carbon monoxide could be firstly detected. In the third decomposition reaction, which was probably identified as an oxidative decomposition, respectively carbonization a clear release of carbon monoxide can be observed.

KINETIC ANALYSIS

Based on the generated data from the thermal analysis, it is possible to obtain an estimation of the present kinetics of the thermal decomposition of the milk powder. By using the method of Flynn-Wall-Ozawa it is possible to assess the activation energy of a decomposition reaction under the application of the mass loss. The method allows an analysis of the kinetics under non-isothermal conditions in the thermal analysis, which takes place according to a constant heating rate, cf. (Flynn und Wall 1966; Ozawa 1992; Sewry und Brown 2002). The activation energy can be determined by plotting the natural logarithm of the heating rate β versus the corresponding inverse temperature at a certain conversion. Using the results from the TGA, the entire reaction sequence was analysed. **Figure 6** shows the course of the activation energy as a function of the conversion in mass-%. The individual decomposition reactions can be seen in the plot. By means of averaging, a representative activation energy could be determined for each decomposition reaction. Because of the residue in the crucible under an inert atmosphere and due to a constant mass loss, further evaluation was not possible. The following activation energies and frequency factors which could be determined are shown in **Table 1**.

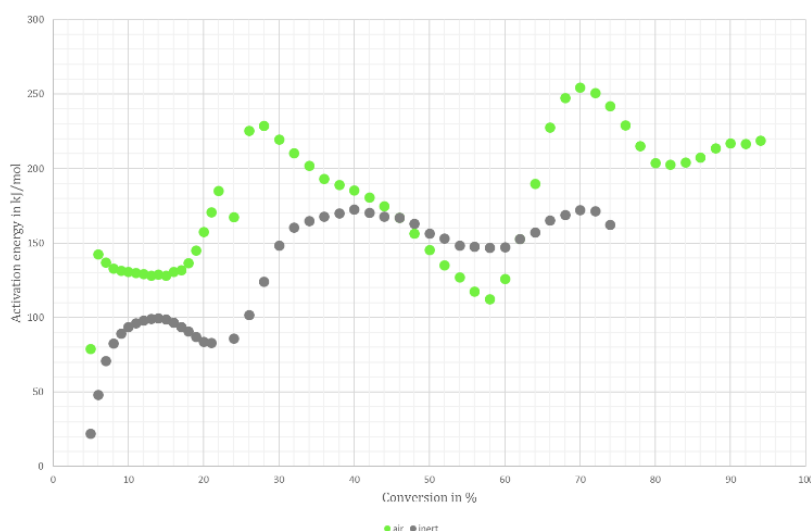


Figure 6: Plot of the activation energy of the decomposition process under air and inert atmosphere.

Table 1: Calculated activation energies and frequency factors.

	air			inert		
	E_A	k_0	R^2	E_A	k_0	R^2
	$\frac{kJ}{mol}$	$\frac{1}{s}$	-	$\frac{kJ}{mol}$	$\frac{1}{s}$	-
Reaction 1	133,59	$1,39 \cdot 10^{16}$	0,969	84,45	$8,57 \cdot 10^9$	0,961
Reaction 2	178,35	$5,98 \cdot 10^{20}$	0,997	156,55	$4,37 \cdot 10^{14}$	0,974
Reaction 3	206,93	$2,89 \cdot 10^{17}$	0,997	157,78	$3,13 \cdot 10^{12}$	0,999

HAZARD OF SELF-HEATING

With the help of the estimated kinetic parameters of the self-heating process - which can make a potential hazard regarding fire and explosion protection tangible - can be determined. Based on the theory of heat explosion, according to Frank-Kamenetskii, it is possible to calculate thermally critical states in a reaction system, cf. (Frank-Kamenetzki 1959). For this, however, a theoretical model is necessary. Due to the possibilities described at the beginning of the contribution, plate-like and spherical deposits were assumed. By means of the given critical Kamenetskii parameters of the both possible geometries, the critical layer thickness or the critical diameter of a product deposit in the spray drying tower can be calculated. Furthermore, a time to the maximum reaction rate can be calculated before the assumed deposition takes a critical state and inflammation occurs. Thus, the time under a given operating temperature can be estimated until a potential ignition source is present in the spray drying process. However, assumptions must also be made, which can lead to deviations from reality. For example, a zero-order reaction is assumed. Equation (1) describes the calculation of the critical Kamenetskii parameters based on (Steen 2009).

$$\delta_c = \frac{E_A \cdot r^2 \cdot \rho \cdot H_0 \cdot k_0}{\lambda \cdot R \cdot T_U^2} \cdot e^{-\left(\frac{E_A}{R \cdot T_U}\right)} \quad (1)$$

E_A = Activation energy; ρ = Bulk density; H_0 = Heat of reaction; k_0 = Frequency factor; λ = Thermal conductivity;

R = Universal gas constant; T_U = Ambient temperature

By changing and applying the critical Kamenetskii parameters from **Table 2**, the critical diameter r can be calculated.

Table 2: Critical values of the Frank-Kamenetskii parameter for different deposit forms (Bowes 1984; Steen 2000).

Geometry of the deposit	δ_c for $Bi = \infty$
Sphere	3,32
Plate	0,88

The critical layer thickness assuming the activation energy of the first decomposition reaction, a plate and an operating temperature of 80 °C is 23.2 mm. In the case of a spherical deposit, however, the critical diameter is about 45 mm. The values of the layer thickness decrease with increasing temperature. Although the first decomposition reaction did not show a marked heat release, it can be regarded as an initial step in self-heating, so that a consideration of this reaction is a worst case, although only a browning of the milk powder and a slight temperature increase can be expected. Furthermore, it is possible to predict an ignition time under typical operating parameters. Equations (2) and (3) are used for this purpose.

$$t_{wex} = \varrho \cdot \frac{\rho \cdot c_p \cdot r^2}{\lambda} \quad (2)$$

c_p = Specific heat capacity

Equation (2) allows to calculate the theoretical time to be calculated until the inflammation of a defined milk powder deposition. ϱ describes the dimensionless ignition temperature, which can be calculated using equation (3), cf. (Babrauskas 2003).

$$\varrho = \frac{1}{a + b \left(\frac{\delta}{\delta_c}\right) - c \left(\frac{\delta}{\delta_c}\right)^{-\frac{1}{2}}} \quad (3)$$

The parameters a, b and c are dependent on the chosen geometry and must be taken from the literature. Thus, the time to maximum reaction rate is about 3 hours, assuming a plate-shaped deposit with a layer thickness of 50 mm, the kinetics from the first decomposition reaction and an ambient temperature of 80 °C. The second and third decomposition steps were detected as oxidative reactions. In comparison to the real process, the air flow through the sample in the crucible is poorer, which can cause a deviation.

CONCLUSION

Thermal analysis, such as TGA or DSC measurements, are recognised methods which make it possible to investigate the thermal behaviour of substances. The procedures have many advantages. Thus, the tests can be carried out without great effort and the small sample quantity which is required is not particularly costly. Furthermore, valuable insights of the thermal stability and decomposition of substances are obtained. It is also shown that it is possible to generate kinetic data from the thermal analysis. However, this is merely an estimation, but these kinetic data subsequently permit a calculation of critical process parameters, e.g. the critical layer thickness of a milk powder deposit in drying processes, or the time to the maximum reaction rate of a milk powder deposit for the initial reaction of the self-heating. Due to the low sample quantities, slight influences can already lead to a deviation in the results, cf. (Steinbach 1995). A supplementary analysis of the gaseous decomposition products provides important insights for the safety concept in the case of drying plants, because fire detection in spray dryers is usually carried out by means of carbon monoxide detection, cf. (Vingerhoets et al. 2016).

Furthermore, the question arises whether the process conditions can be simulated as realistically as possible by means of TGA and DSC measurements. Material and system parameters, such as moisture, particle size and composition can cause systematic errors in the safety assessment. In principle, there is a discrepancy between the two determining factors of safety and economy, so that no real conditions can often be created and checked. Therefore, approximations, possible deviations and systematic errors must be accepted. The ignition of the milk powder is a critical condition, which caused a massive increase in the risk of fire and explosion. A glowing fire can act as an effective ignition source but the ignition temperature itself cannot be directly predicted by the shown analyses. For this purpose, the self-ignition behaviour must be determined by further safety-relevant investigations. As further investigations, usually hot storage tests in accordance with DIN EN 15188 are recommended for this problem. In principle, a scale-up, as shown in **Figure 7**, should also be carried out in the case of safety-relevant investigations, like the process developing concept.

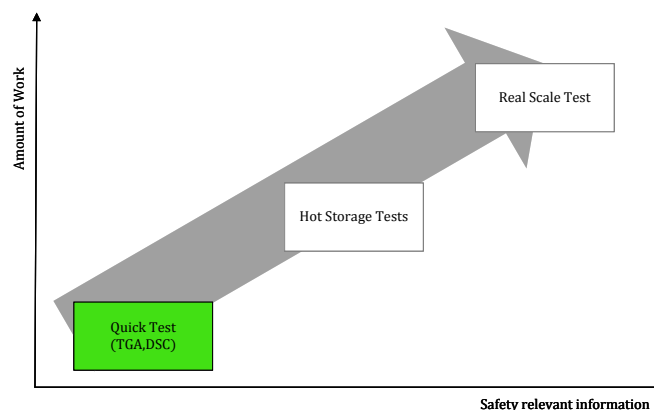


Figure 7: Schematic representation of the information obtained from a safety-relevant analysis.

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