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A METHODOLOGICAL APPROACH TO THE SPONTANEOUS COMBUSTION OF AGRICULTURAL DUSTS

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1. INTRODUCTION

The most common operations in industries where combustible dusts are produced or handled are grinding, drying, pneumatic transport, filtering, and storage in silos. Unfortunately, these operations all too often give rise to fires or explosions with catastrophic consequences. Spontaneous combustion must be considered to be a potential ignition source for a dust explosion every time that a large mass of combustible dust comes in contact with air.

In this paper we present a methodological approach to the characterization of combustible dusts with respect to self-heating and give results for certain agricultural dusts.

Our method includes the use of modeling and various laboratory tests such as Thermal Differential Analysis coupled with Thermo-Gravimetric Analysis (DTA-TGA), Isothermal Oven Tests, and Adiabatic Calorimetry. The objective of these tests is not only to rank the various dusts by order of reactivity but to determine under what conditions a given dust will pose a threat of spontaneous combustion.

2. HAZARDS OF COMBUSTIBLE DUST STORAGE OR DEPOSITS

Combustible dusts are found in industry as finished products or process intermediates created voluntarily by milling or involuntarily by abraison of larger sized solids, such as feed pellets or as a by-product of the raw materials (wheat dust). Fire in a storage unit or in a dust layer can be started by an external ignition source or by self-heating. Combustion of dust can occur with or without flames depending on the local ventilation conditions and diffusion and may create hot oxygen-poor zones where flammable gases can be produced by pyrolysis or partial oxidation. When dust layers are blown into suspension, a dust explosion can occur if there is a sufficient ignition source present. An extremely dangerous situation is present if the dust is put into suspension after having undergone spontaneous combustion because the ignition source is within. Figure 1 summarizes some of the hazards associated with agricultural dusts.

3. SELF-HEATING OF AGRICULTURAL DUSTS

The physical mechanism of self-ignition can be understood by a simple energy balance. Combustible (and fermentable) materials can undergo reactions even at room temperature. Though the amount of heat produced is not very great, if it is not dissipated to the surroundings, the temperature will rise. As the temperature rises, the oxidation accelerates. If a steady state is not achieved between the heat produced and the heat dissipated to the surroundings, the temperature will continue to climb until ignition occurs.

As for the process of heat dissipation, many agro products and virtually all dusts are excellent thermal insulators. As the size of the dust deposit or storage volume increases, the thermal insulation becomes more efficient. It thus becomes apparent that self-ignition in large volumes is more likely than in small ones.

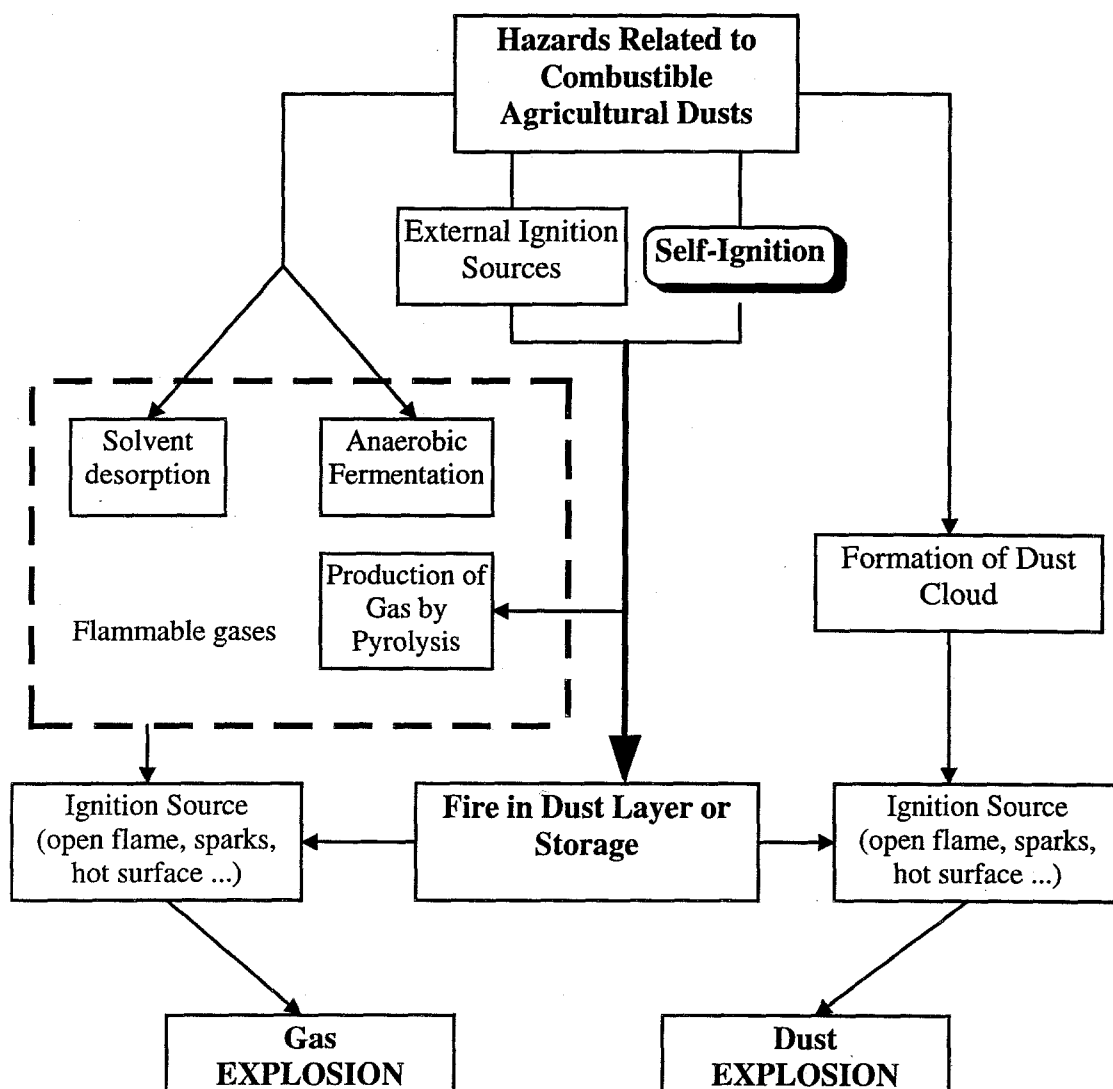


Figure 1. Hazards of Combustible Agricultural Dusts

Self-ignition can develop at any starting temperature. At low starting temperatures, the heat production rate is low and self-ignition occurs only after a long induction time, from several days to many months, in large storage volumes. At high temperatures (such as can be found in dryers), the reaction rate is much faster; spontaneous combustion can take place in stagnating dust deposits and the induction time is much shorter, from minutes to hours.

Between ambient temperature and 80 °C, reactions other than chemical oxidation, such as physical or biological processes, can be responsible for rapidly heating the material up to 80 °C.

- The biological processes that lead to a rapid heating of agricultural products are essentially the respiration of living micro-organisms and biological oxidation under aerobic conditions. The latter mechanism is strongly related to moisture content; below a certain level, biological activity does not take place. Normal storage conditions however are such that the moisture content is below this level for product quality.

- As for all dusts, an equilibrium exists between the moisture content of the dust and the surrounding atmosphere depending on the temperature and the relative humidity of the air. When a dust is too dry (overdrying for example) with respect to its equilibrium point, it will have a tendency to pick up moisture from the surrounding air liberating the heat of condensation of the water. Typically, a 1% gain in moisture content leads to a 20°C adiabatic rise in temperature of the substrate.

Above 80°C it is chemical oxidation that takes over and leads to self-ignition. However, since chemical oxidation follows the Arrhenius equation (an exponential law), the rate at which heat is produced is much greater at 80 °C than at room temperature.

To have spontaneous combustion, several conditions must be present at the same time:

1. The substance must be combustible.
2. The combustible substance must have a sufficiently high surface area on which oxygen can react. In many industrial applications, the nature of the combustible dust and its particle size are dictated by the process. But for some agro products, highly reactive oil from the plant can be dispersed on a porous support.
3. Oxygen must be present. The rate of heat production is a function of the partial pressure of oxygen in the atmosphere. Below a certain limit, the heat production is not sufficient to produce spontaneous combustion.
4. The temperature of the substance or the surroundings must be high enough so that the rate of oxidation is sufficient (heat production).
5. The storage or deposit configuration must be such that the heat is retained. In practical situations, dusts are very good heat insulators and heat transfer is governed by the storage or deposit size.
6. The residence time of the dust in a given storage or deposit configuration must be long enough to allow spontaneous combustion to take place.

In order to avoid spontaneous combustion, one of these six conditions must be eliminated.

As a conceptual tool, we can construct a "self-ignition hexagon" analogous to the fire triangle (fuel, oxygen, ignition), representing the six main conditions that are needed to obtain self-ignition:

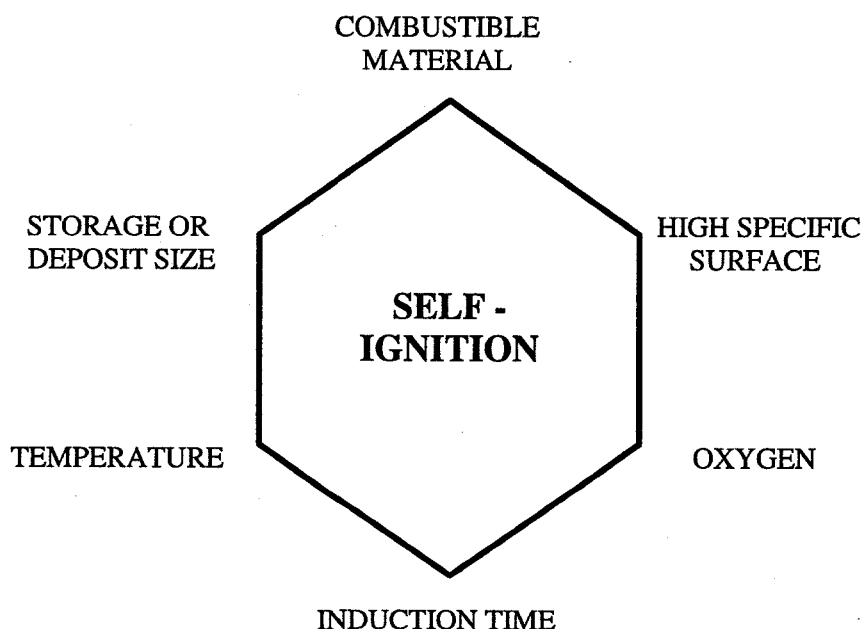


Figure 2. Self-Ignition Hexagon

4. METHODOLOGICAL APPROACH TO THE DANGERS OF SELF-HEATING OF COMBUSTIBLE DUSTS IN DEPOSITS AND IN STORAGE UNITS

The procedure to identify, characterize, and extrapolate the risks related to deposits and storage of combustible dusts is summarized in figure 3 and is comprised of the following steps :

a) Physico-chemical characterization of the dust (particle size distribution, elementary analysis, moisture content, etc.)

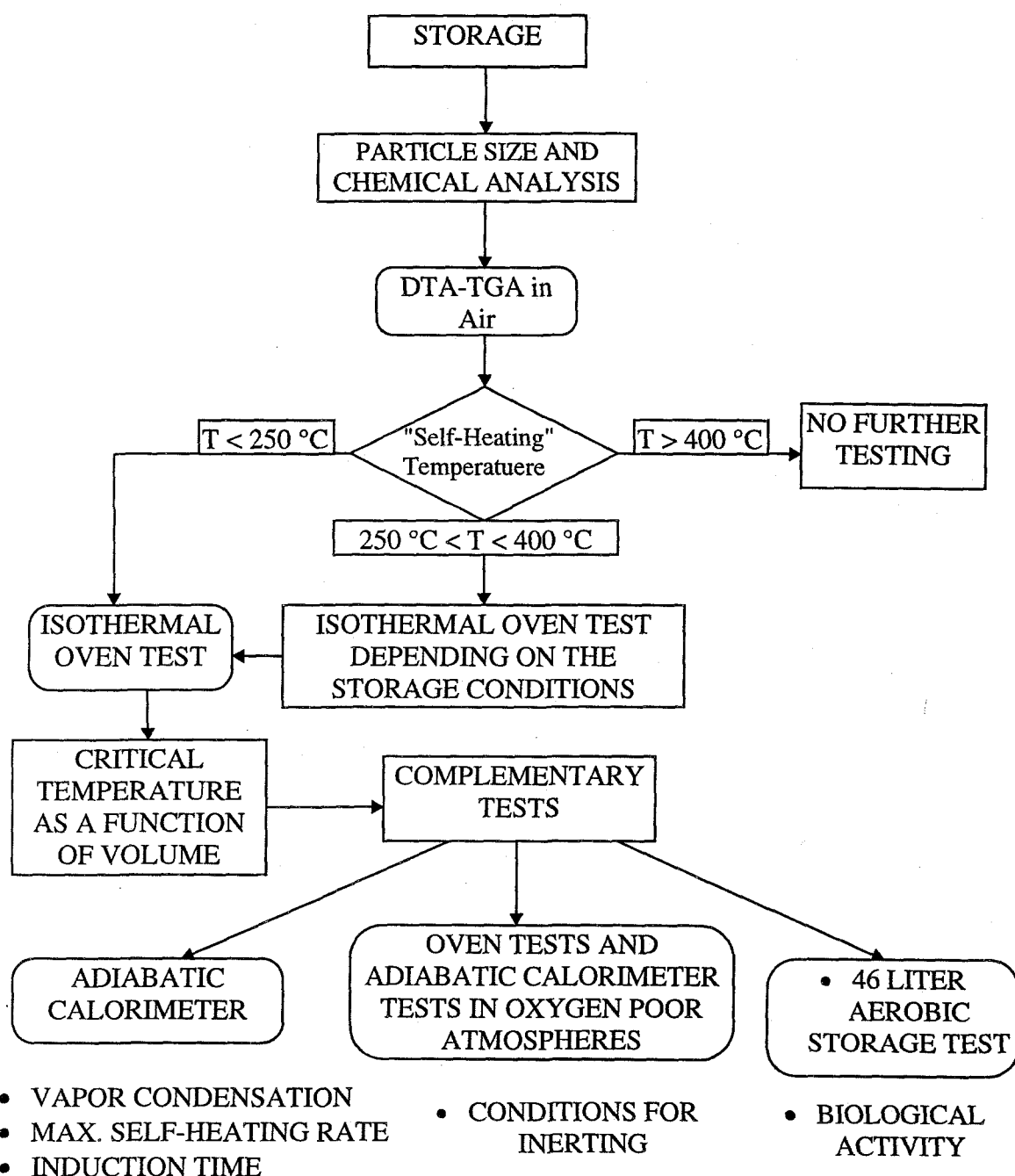


Figure 3. METHODOLOGY FOR THE EVALUATION OF SELF-IGNITION IN AGRICULTURAL DUSTS

b) Differential Thermal Analysis (DTA) coupled with a Thermo-Gravimetric Analysis (TGA) makes it then possible to rank the combustible dusts by order of risk based on their "self-heating temperature". Normally, three categories of dusts can be distinguished:

1. The least reactive dusts give a "self-heating temperature" greater than 400 °C and need no further testing,
2. The moderately reactive dusts give a "self-heating temperature" between 250 °C and 400 °C and undergo complementary testing if warranted by the actual industrial conditions (drying temperature, silo dimensions, storage temperature etc.)
3. Reactive dusts give a "self-heating temperature" less than 250 °C and undergo further testing. Very reactive dusts give a "self-ignition temperature" less than 200 °C.

This ranking scheme has been developed at INERIS based on over a thousand tests on all kinds of combustible dusts.

c) Dusts able to ferment are subjected to aerobic storage testing in order to determine the temperature rise to expect from biological reactions.

d) An adiabatic calorimeter is used to determine :

- the rate of oxidation as a function of temperature which enables us to estimate the induction time before ignition as a function of initial storage temperature
- the temperature rise due to the capacity of the sample to absorb moisture from the air,

e) Isothermal oven tests are made to estimate the critical temperature as a function of storage or deposit volume.

f) Tests are carried out under oxygen-poor atmospheres in order to help set the maximum permissible oxygen concentration during inerting operations.

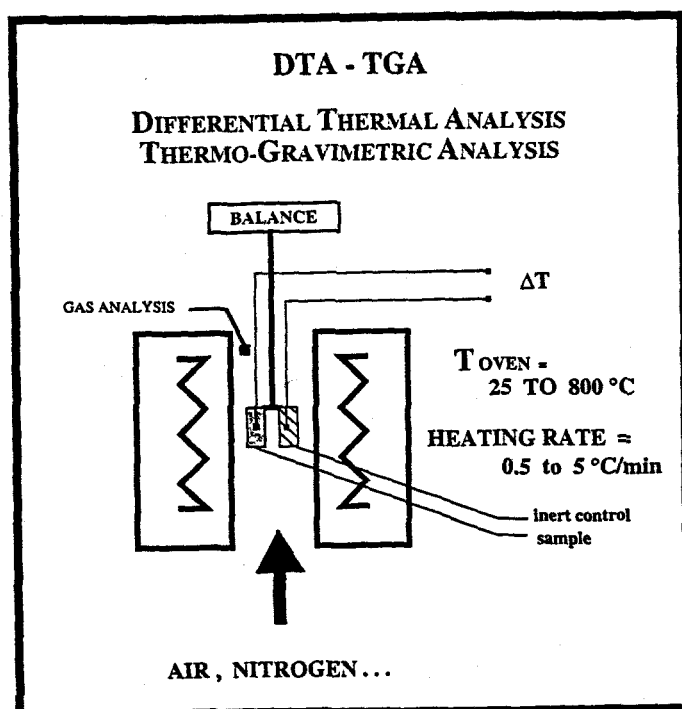


Figure 4. Coupled DTA - TGA Apparatus

4.1. Characterization of the Reactivity of Combustible Dusts by Thermal Analysis

The basic test used at INERIS to characterize the oxy-reactivity of dusts is Differential Thermal Analysis (DTA) coupled with a Thermo-Gravimetric Analysis (TGA) (Figure 4). The sample size is from 1 to 6 grams depending on its density.

The weight of the sample placed in an oven heated at a fixed rate (5°C/min) is measured by an electronic balance as a function of time and recorded by a personal computer. The temperature of the sample and that of an inert reference substance are recorded as well. Air pre-heated to oven temperature flows through the oven to maintain an oxidizing atmosphere. In these conditions, by comparing the temperatures of the sample and the inert reference substance ($\Delta\Theta$ temperature difference), it is possible to identify endothermic or exothermic phenomena that may take place as a function of temperature.

Figure 5 shows the results of a rape dust. An endothermic peak is observed at 100°C due to the evaporation of water accompanied by a 8% weight loss. A measurable exothermic oxidation is detected at about 180 °C and accelerates slowly up to the runaway point at 216°C where the sample burns freely. At the end of the experiment, there is an unburnt residue of about 12%.

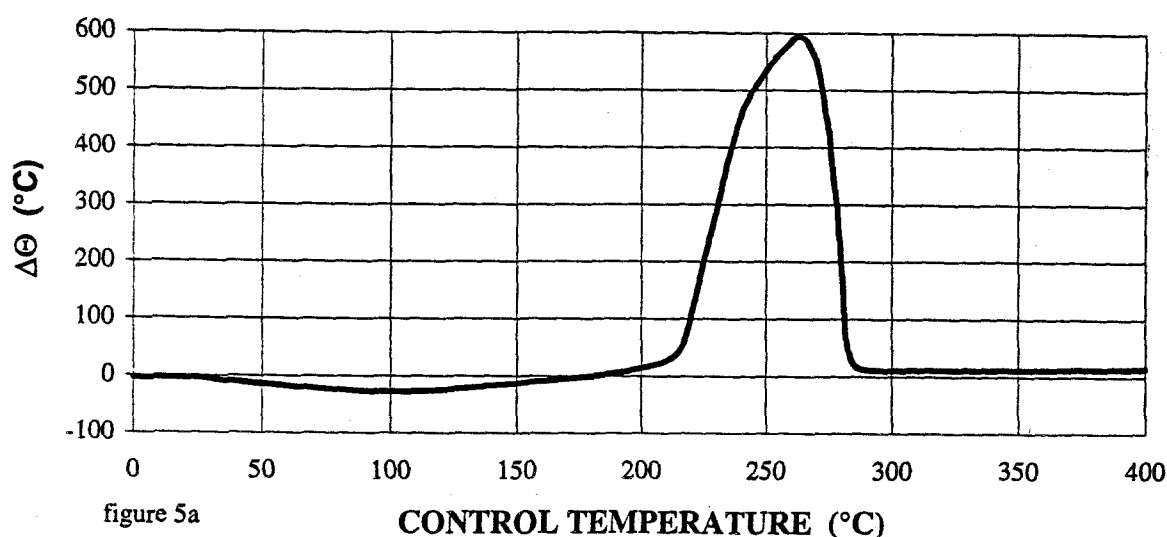


figure 5a

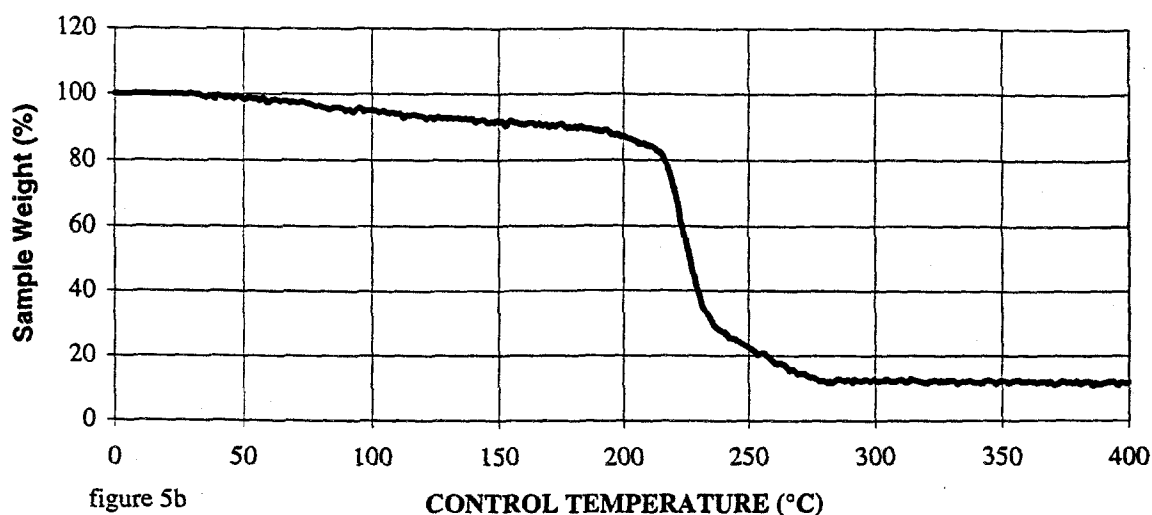


figure 5b

Figures 5a and 5b. DTA and TGA Results on Rape Dust Respectively

To facilitate the analysis of the results, we can tabulate several characteristic temperatures taken from the figures :

- the temperature at the beginning of the rapid weight loss
- the temperature corresponding to the start of the exothermic reaction (usually $\Delta\Theta = 0^\circ\text{C}$)
- the temperature at thermal runaway ($\Delta\Theta = 50^\circ\text{C}$) taken to be the "self-heating temperature" for this particular test.

These parameters are tabulated in Table 1 for several agricultural dusts :

TABLE 1 Characteristic Temperatures from DTA - TGA Experiments on Agricultural Dusts

Samples	Temperature at the beginning of rapid weight loss	Temperature at the beginning of exothermic reaction $\Delta\Theta = 0^\circ\text{C}$	Thermal runaway temperature $\Delta\Theta = 50^\circ\text{C}$
Rape dust	216 °C	180 °C	216 °C
Sunflower dust n°1	200 °C	157 °C	212 °C
Sunflower dust n°2	190 °C	110 °C	180 °C
Wheat dust	239 °C	187 °C	240 °C
Alfalfa dust	200 °C	150 °C	215 °C
Corn dust	230 °C	200 °C	233 °C

The self-heating temperature of a given combustible dust is not a unique temperature but depends on many factors such as the form and dimension of the storage or deposit, the nature of the heat source, the heating rate, etc.

This method does however make it possible to make a preliminary ranking of dusts by order of risk to self-heating. Further, it is sufficiently reproducible and reliable to differentiate substances that pose a real danger from those that don't.

One can see that the sunflower dust n°2 is the most reactive dust and that there is a significant difference in reactivity with the other sunflower dust taken from another installation. We would classify all of these dusts as very to fairly oxy-reactive and further testing should be carried out based on the environment in which they are found in the industrial facility.

4.2. Determination of the Critical Self-Heating Temperature by Isothermal Storage Tests

This method consists of the determination of the critical self-heating temperature of a combustible dust as a function of sample volume (for full discussion of experiment, theory, and restrictions see

Bowes). The dust is placed in cubical cages whose sides are made out of a sieve material sufficiently fine to contain the sample but large enough not to interfere with the diffusion of oxygen. The cage is placed in an air circulating oven pre-set to the desired temperature. A thermocouple placed at the center of the sample in the cage allows one to determine whether the sample comes to thermal equilibrium with the oven or if there is spontaneous combustion. The test is repeated at an oven temperature higher or lower, depending on the previous results in order to determine the minimum temperature for spontaneous combustion for that particular volume. This temperature is called the critical temperature.

The critical temperatures for different storage volumes can be fit to a lumped parameter equation based on Frank-Kamenetskii's thermal explosion theory.

$$\ln (\delta c T^2/r^2) = M - N/T \quad (1)$$

- δc is a form factor (≈ 2.6 for cubes)
- T is the ambient temperature [K]
- r is the characteristic dimension [m] of the storage volume ; it is the half-edge length of a cube. (basically this is the distance between the most thermally insulated part of the storage volume and the external surface of the volume where heat is carried away from the system).
- M and N are constants (independent of temperature and storage size) for a given dust that depend on its oxy-reactivity, heat capacity, particle size, thermal conductivity, density, activation energy, heat of reaction ...

The values of M and N are found by a least squares fit of the experimental results to equation 1.

After determining the values of M and N for a particular dust, we can rearrange equation 1 to extrapolate the critical characteristic dimension as a function of temperature:

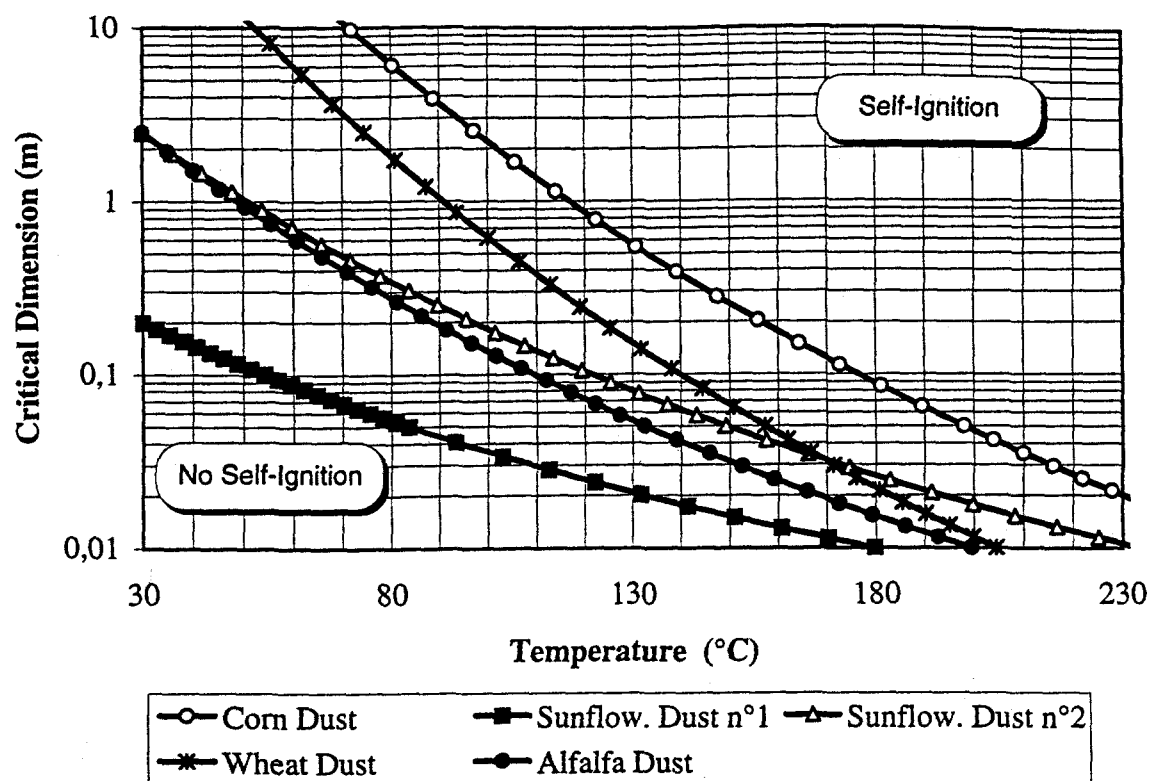
$$r = \sqrt{\delta c T \exp (M/2 + N/2T)} \quad (2)$$

Other form factors can be used to fit the real industrial configuration (cylinders, layers ...). The curves that we obtain from the experimental data given in Table 2 are presented in figure 6 for selected Agricultural dusts.

TABLE 2. Critical temperatures as a Function of Volume for Selected Agricultural Dusts.

Dust \ Volume	8 cm ³	120 cm ³	340 cm ³	1 000 cm ³
Alfalfa dust	200 °C	156 °C	148 °C	
Wheat Dust	204 °C	176 °C	169 °C	156 °C
Rape Dust	193 °C	152 °C	142 °C	128 °C
Sunflower Dust n° 1	236 °C	177 °C	163 °C	154 °C
Sunflower Dust n° 2	178 °C	120 °C	105 °C	81 °C
Corn Dust	256 °C	222 °C	215 °C	195 °C

Figure 6. Extrapolation of the Critical Dimension as a Function of Temperature for Cubic Volumes of Selected Agricultural Dusts. The critical dimension is the half-edge length.



It can be seen from these curves that there is little risk of spontaneous combustion for the wheat or corn dusts tested at low or relatively high temperatures. The alfalfa and sunflower N° 2 dusts are more reactive and may pose a threat of self-ignition in large volumes at low temperatures or in dryers if large deposits are allowed to form. However, if mechanisms other than chemical oxidation heat the product up to 65 °C, such as biological activity or condensation we can have self-ignition problems in moderate sized storage units. Sunflower dust N°2 is very reactive in all cases.

A more detailed analysis than given here is needed to treat borderline cases or fix safe temperatures for dryers.

4.3. Adiabatic Calorimeter Tests

The adiabatic calorimeter used at INERIS is shown schematically in figure 7. The principal of the method consists of maintaining the dust sample under adiabatic conditions while being traversed by a small flow of air preheated to the same temperature as the sample. The sample holder is submerged in an oil bath. When there is a temperature rise in the sample the oil bath is heated immediately and automatically to maintain the oil bath at the same temperature as the sample. In this way, all of the heat generated by the oxidation goes to heat up the sample. The air flow rate must be large enough to provide oxygen for the reaction but also must be small enough not to take any significant quantities of heat away from the system.

The volume of the glass sample holder is about 20 cm³. The temperature of the sample is recorded as a function of time. The rate of self-heating, which is directly proportional to the reaction rate, is simply the slope of the temperature-time curve. We can measure self-heating rates from 0.03 to 3 K/min.

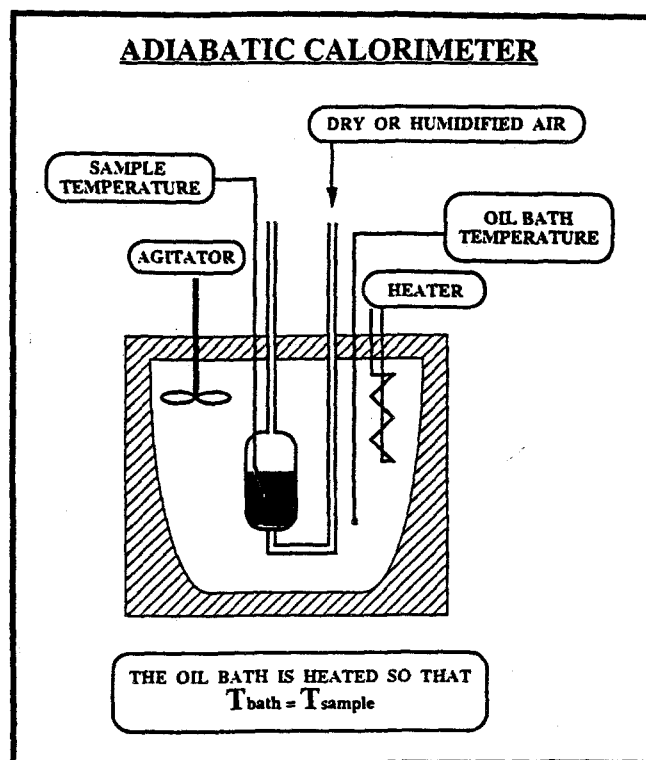


Figure 7. Schematic Representation of a Fow Adiabatic Calorimeter

To characterize chemical oxidation, the predried sample is traversed by a flow of dry air and the self-heating rate is governed by the Arrhenius equation :

$$dT/dt = A \exp (-E/RT)$$

The results can be put on an Arrhenius diagram where we plot the logarithm of the self-heating rate as a function of inverse absolute temperature. From the slope and the intercept, we can calculate the activation energy and the preexponential factor given in the Arrhenius equation.

Under adiabatic conditions, the self-heating rate is at its maximum because by definition, there are no heat losses to the surroundings. We can then use the Arrhenius equation to estimate the minimum time necessary for spontaneous combustion to take place (induction time) :

$$\text{Induction time} = \int \frac{dT}{A \exp (-E / RT)}$$

Knowing A and E, we can extrapolate the calorimeter results to calculate the induction time as a function of the initial storage temperature at temperatures lower than those studied experimentally. For example, when we store a combustible dust at a given temperature, there is no danger of self-ignition if the storage time is not longer than the induction time corresponding to that temperature.

In figure 8 estimates are presented for the induction time for two samples of alfalfa coming from two different industrial facilities. At 20°C, the induction times are estimated to be three weeks for one product and seven weeks for the other. They are significantly shortened however if the storage temperature is above 50°C.

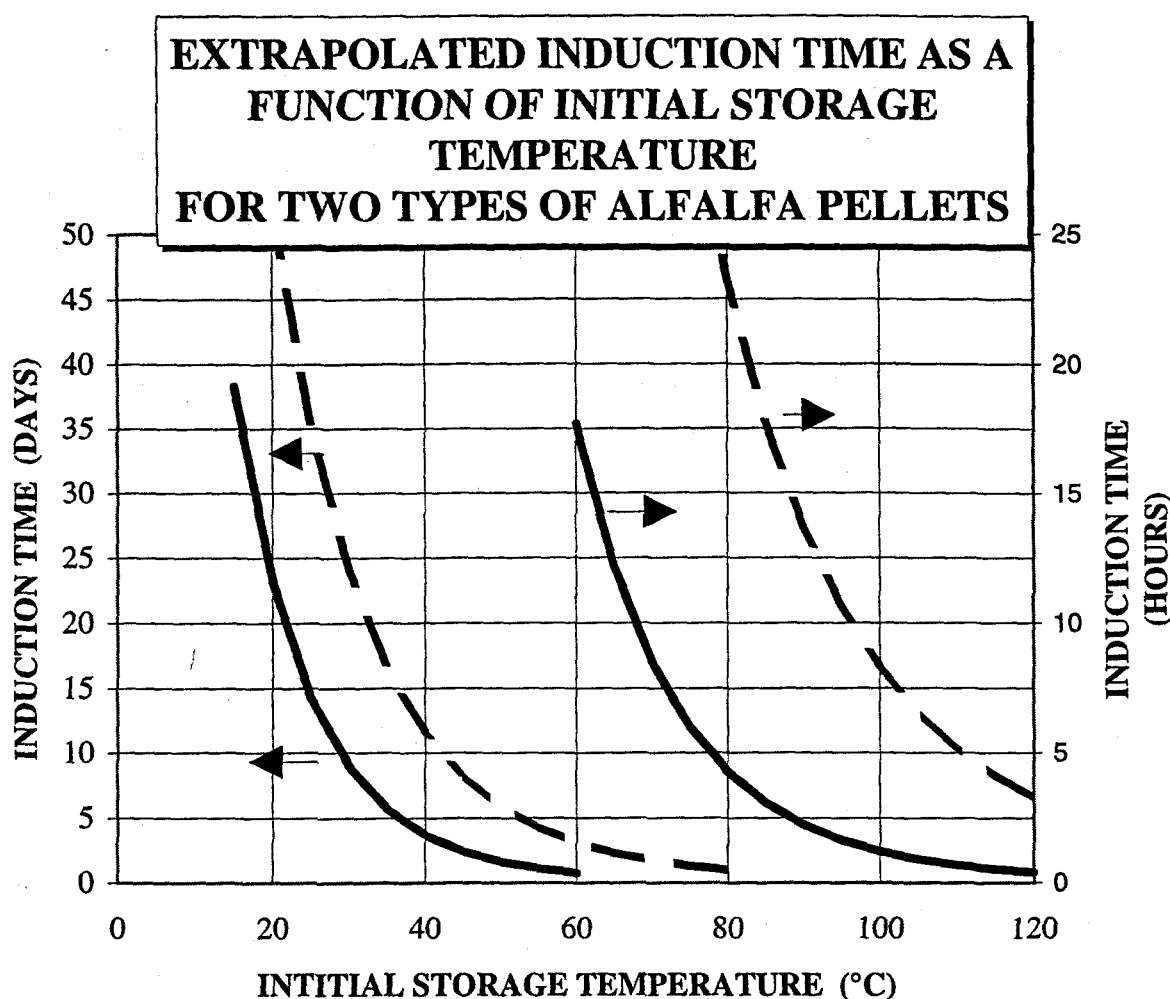


Figure 8. An Estimation of the Induction Time Before Self-Ignition for Two Alfalfa Samples Based on Adiabatic Calorimeter Results

The adiabatic calorimeter is also used to provide data on the kinetics of vapor condensation from atmospheric humidity. In this case, the predried sample is traversed by air saturated with humidity at 40°C. The temperature rise and the rate of temperature rise are determined starting at 40°C.

Generally, the test shows that for a 1 % gain in moisture content of the dust sample by condensation, the temperature rises 20 °C (release of the heat of condensation). Depending on the sample and its level of drying, temperature rises of 20 to 30 °C have been observed within 30 to 90 minutes.

It is apparent that this heating mechanism is very fast compared to oxidation at these temperatures.

4.4. Biological Oxidation

The respiratory activity of microorganisms is an exothermic phenomenon that produces heat and CO₂ which develops in an oxidizing atmosphere(aerobic). We can see that schematically from the oxidation of hexose :



The two types of active microorganisms are the mesophiles which develop optimally up to 40 - 50°C and the thermophiles which are active up to 70°C. Above 70-80°C, the population drops rapidly and the exothermic effects stop. In a confined environment, as soon as the level of CO₂ reaches 10 % the respiratory phenomenon is blocked and the heat production falls.

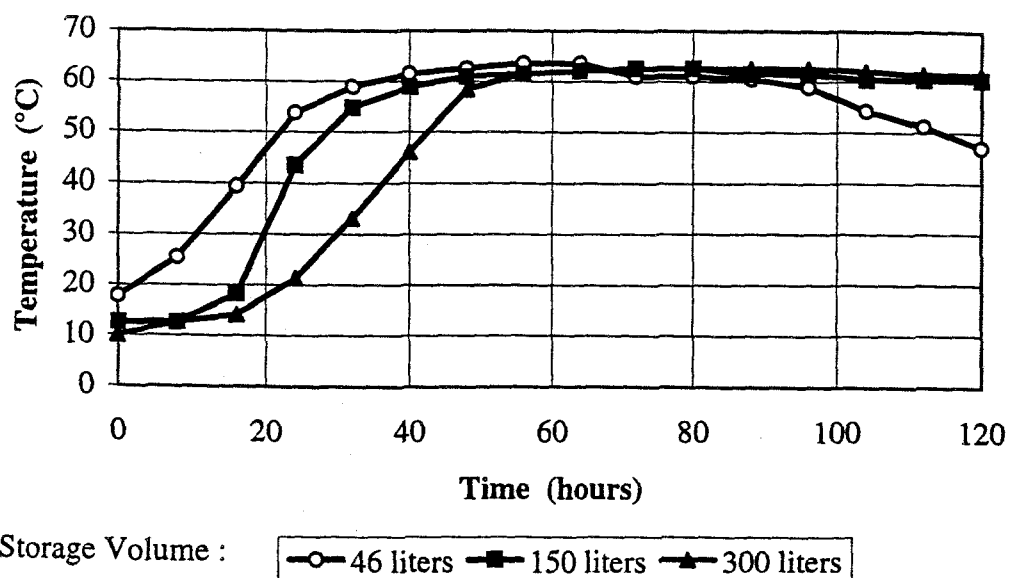
An experimental procedure has been developed to study this type of biological activity.

Substances that can ferment are placed in cubic cages whose sides are made out of a metallic screen that is fine enough to hold the sample but allows the passage of air. The cage is then placed in an oven preset to the desired temperature, 35 °C. The temperature at the center of the sample is recorded as a function of time as well as the composition of the gas phase (CO, CO₂, O₂) at the center of the storage. This is done by aspiration of the gas through tubes at a rate of 10 l/hour using a gas chromatograph for analysis.

An example of the behavior of sunflower seeds is given below (Burghart and Lodel).

In the first series of experiments, sunflower seeds with a 27 % moisture level were tested in volumes of 46, 150 and 300 liters to determine whether the storage volume had an influence on the heating process. The results shown in figure 9 show that the maximum temperature reached in all three cases was about 63 °C, attained after 24 to 48 hours. However it can be seen that the smaller volume heats up more quickly than the larger volumes, perhaps due to oxygen diffusion. These results show that in a storage unit, the maximum temperature reached is independent of volume. We can suppose that a storage unit undergoing biological activity will have an effective storage temperature equal to that which is given by the laboratory test even if the surrounding temperature and the initial storage temperature are 20 °C.

Figure 9 . Evolution of the Temperature as a Function of Time for an Aerobic Storage Test on Sunflower Seeds at 27 % Moisture.



In a second series of experiments, tests were conducted in the 46 liter volume on samples with varying moisture content (obtained by adding water). The results (Table 3) show that the heating effect is a function of the moisture content, and that above 25%, the maximum temperature reached did not vary.

Table 3. Aerobic Storage Tests on Sunflower Seeds as a Function of Moisture

Moisture in Sunflower Seeds	Oven Temperature	Maximum Temperature Reached	Maximum CO2 Concentration	Minimum O2 Concentration
8 %	35 °C	32 °C	0.5 %	17.0 %
14.6 %	35 °C	49 °C	1.3 %	16.7 %
24.8 %	35 °C	63 °C	5.4 %	15.0 %
33.0 %	35 °C	63 °C	17.3 %	7.4 %

In cases where it may be possible for the agricultural product to pick up moisture, this test should be conducted to determine the maximum level of moisture that does not lead to self-heating and the maximum temperature reached for use in determining the probable storage temperature.

5. INTERPRETATION OF RESULTS AND CONCLUSION

The interpretation of the results is made based on the self ignition hexagon.

For a given combustible dust or agricultural product (thus given specific surface area), we can estimate:

- the reactivity of the dust to determine whether further testing is necessary (DTA-TGA)
- the temperature rise due to biological activity (aerobic storage test)
- the temperature rise due to water vapor condensation (adiabatic calorimeter test with saturated air)

These two temperature rises must be taken into account along with the process temperatures (storage, drying, ambient, ... temperatures) to determine which temperature should be taken as the probable storage temperature to be used in the following two relationships.

- the relationship between storage or deposit size and the critical temperature (isothermal oven tests)
- the relationship between induction time and temperature (adiabatic calorimeter test with dry air)

(These two relationships are relevant to chemical oxidation and can be established as a function of oxygen concentration in the atmosphere if needed)

There is a high probability of spontaneous combustion if the last two relationships show that the probable relevant temperature is greater than the critical temperatures.

This method of characterization has been successfully used at INERIS in numerous investigations and safety audits to explain and prevent fires by spontaneous combustion in agro-industries and to help in planning early detection systems.

The results presented here also show that there are large differences in reactivity of the "same" agricultural dust, depending on its origine.

Bibliography

Bowes, P.C., 1984. " Self-Heating: Evaluating and Controlling the Hazards" . Elsevier Science Publishers B.V. Amsterdam, The Netherlands.

Burghart, R. and Lodel, R. "Les Incendies de Séchoirs en Tournesol", Revue Générale de Sécurité, N° 95, pp.41 (1990).

Carson, D. and Lodel. R. "Inflammation Spontanée des Poussières", Face au Risque, N° 320, pp. 25 (1996).

Frank-Kamenetskii, D.A., 1969. 3Diffusion and Heat Exchange in Chemical Kinetics". 2nd Edition Translated, J.P. Appleton, Plenum Press.