



Determination of the risk of self-ignition of coals and biomass materials

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ARTICLE INFO

Article history:

Received 13 September 2011

Received in revised form

27 December 2011

Accepted 26 January 2012

Available online 7 February 2012

Keywords:

Self-ignition

Biomass

Coal

Frank–Kamenetskii

EN15188

ABSTRACT

The safe storage, processing and handling of coals and biomass resources requires their tendency to self-ignite be understood; fires caused by self-ignition have occurred on many occasions in ports and at industrial plants. This work provides information on the tendency of several types of coal and four types of biomass to self-ignite. Data were obtained using the isothermal oven procedure and analyzed using the Frank–Kamenetskii method and a scaling procedure, both contemplated in standard EN15188. The results obtained throw light on the optimum volumes and storage times of the studied materials. The results also validate the methodology followed for determining the risk of self-ignition.

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Introduction

Knowledge of the tendency of materials to self-ignite and explode is essential to plants that handle, store or process coals and biomass resources. It is thought that self-ignition might account for some 12% of the fires that occur in underground mines, and 6% of those that occur in the agri-food industry. Self-ignition not only involves fires but also explosions, which can occur when the dust originated in the handling of materials results in the formation of an explosive atmosphere [1–3]. The assessment of the exothermic reactions that take place within stored materials is therefore essential if accidents are to be prevented [4]. These reactions provide a source of ignition when the heat generated exceeds that which can be dissipated into the environment [5]. Critical conditions for self-heating in stored bulk materials can be determined by employing suitable laboratory-scale test methods [6], such as thermogravimetric analysis, differential thermal analysis, adiabatic calorimetry and isothermal oven tests [7–10]. Thermogravimetric analysis is one of the most commonly used [11], and can be performed under atmospheric, hyperbaric or pulse ignition conditions [12,13]. This requires only small quantities of sample material, and the results are highly repeatable. However, when the results are extrapolated, their dispersion increases beyond that seen with other methods, such as the isothermal oven test (although this is more

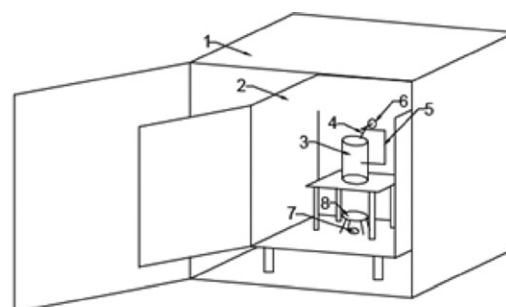
expensive since it requires longer experimental times and larger samples).

Following long and laborious experimental work by researchers worldwide, a standardized method was proposed for characterizing materials with respect to their spontaneous combustion; this is enshrined in European standard EN15188 [14]. The method involves the isothermal oven test to obtain the relationships between volumes, temperatures and storage times [15]. The results obtained can be analyzed using simple scaling procedures or methods based on the thermal explosion theory (which differ in their mathematical background) [16–18] to provide the correlation between the size of the characteristic dimension of a dust and its self-ignition temperature. Other simplified methods also exist to determine the susceptibility of materials to self-ignite [19], but their use is limited to defining the safety characteristics of the packaging that should be used when transporting them.

While self-ignition is a well-known problem in the mining industry, in biomass-based industries it is less well understood. In the present work, self-ignition in four types of biomass was examined: lycopodium, animal waste (pig manure), dry sludge and wheat. Lycopodium is a reference material used in dust explosion tests [20,21], yet little has been published regarding its self-heating and self-ignition. Neither have these phenomena been investigated in the other biomass materials examined, even though growing interest in the production of bioenergy has led to their being stored in large amounts. The data gathered in this work may be of use in the design of safer installations and storage facilities.

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- 1 Oven
- 2 Interior chamber
- 3 Basket with dust sample
- 4 Thermocouple for measuring ambient temperature
- 5 Thermocouple for measuring sample temperature
- 6 Air inlet
- 7 Air outlet
- 8 Deflector

Fig. 1. Photograph and diagram of the isothermal oven employed.

Materials and methods

The self-ignition behavior of different materials was determined using the method laid out in standard EN15118. Two series of samples were examined. Series 1 involved six kinds of coal (in the form of dust) from different countries, ranging from sub-bituminous to semi-anthracite types (Table 1). The selection of these coals was based on their involvement in fires during storage.

Tables 2 and 3 show the moisture, ash, volatile compound, CO₂, hydrogen and sulfur contents of the Series 1 coal samples.

Series 2 involved a reference bituminous coal and four organic products commonly used in industry: lycopodium, wheat, animal waste and dry sludge.

The EN15188 test method is based on heating different volumes of a test material to a constant temperature in an isothermal oven. The aim is to determine the self-ignition temperatures (SIT) of these different volumes, so that extrapolation of the results can identify maximum storage times and critical storage volumes. The oven has a volume of 90 l, large enough for an interior chamber to hold a sample of test material along with thermocouples for measuring its temperature and that of the surrounding air. The oven can be heated to 300 °C with a thermal stability of ±1%. The temperature is obtained using three type K thermocouples, two of them equidistant from the wall and the basket containing the sample, and the third placed at the geometric center of the sample. The oven also has two vents, one at the top and one at the bottom, to allow an air flow via natural convection (Fig. 1).

The basket containing the sample is made of a stainless steel mesh. This allows air to reach the sample.

The coal samples of Series 1 were tested over the temperature range 100–250 °C, using cuboid baskets of 17 cm³, 120 cm³, 240 cm³ and 1000 cm³ volume. The biomass materials and the additional coal samples of Series 2 were tested over the temperature range 100–200 °C, using cuboid baskets of 50 cm³, 150 cm³, 350 cm³ and 1500 cm³ volume. These different volumes were used in line with the conditions set out in standard EN15188.

Samples were heated using the natural (non-forced) convection current produced. The oven air and sample temperatures were recorded using a datalogger, as was the induction time (t_{ind}), i.e., that required for the sample to increase in temperature to 60 K above the oven temperature [14].

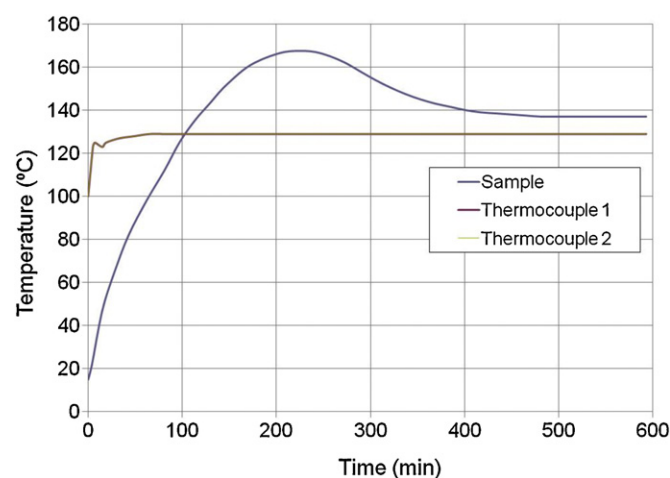


Fig. 2. No self-ignition at 130 °C.

The SITs were calculated using the equation:

$$SIT = \frac{T_{ni} + T_i}{2} \quad (1)$$

where SIT is the mean for the minimum oven temperature at which the self-ignition of a particular volume of the test material occurs (T_i) and the maximum temperature at which self-ignition does not occur (T_{ni}) (the latter determined by three confirmatory tests). These minimum and maximum temperatures were measured in two consecutive tests in which the difference between them was ≤5 K.

Example

Figs. 2 and 3 show the temperature records for tests involving a 150 cm³ sample, with self-ignition clearly occurring at 135 °C but not at 130 °C. Therefore, the $SIT = (130 + 135)/2 = 132.5$ °C.

The results obtained with the Series 1 coal samples were analyzed using the Frank–Kamenetskii (FK) method [17B]. The results for two samples of coal, belonging to different ranks for the sake of comparison (IMV-2 and IMV-6), were also examined using a simple scaling model, also recommended by standard EN15188. FK analysis allows the correlation between the sample volume obtained from r (the characteristic linear dimension of the dust sample or

Table 1
Coal types examined and their origin.

Sample	Category	Company	Coal mine	Mining area	Locality	Country
IMV-1	Sub-bituminous	SAMCA	Sierra de Arcos	Ariño-Andorra	Teruel	Spain
IMV-2	Sub-bituminous	Aragón Minero	María y Regina	Ariño-Andorra	Teruel	Spain
IMV-3	Bituminous	HUNOSA	San Nicolás	Caudal	Asturias	Spain
IMV-6	Semi-anthracite	H.V.L.	Sta. Lucía	Ciñera-Matallana	León	Spain
IMV-7	Bituminous	HBL	Remaux	Lorraine	Moselle	France
IMV-8	Bituminous	Daw Mill Colliery	Daw Mill	Warwickshire Thick	Arley	UK

Table 2
Composition of the Series 1 coal samples.

Sample	Moisture content (%)	Ash content (%)	Volatile compound content (%)	CO ₂ (%)	Carbon content (%)	Hydrogen content (%)
IMV-1	7.65	27.05	29.35	0.19	44.90	4.00
IMV-2	17.50	12.45	30.15	0.03	50.57	5.23
IMV-3	0.80	21.55	23.25	1.56	68.15	4.17
IMV-6	1.00	33.65	9.20	2.65	57.36	2.72
IMV-7	1.40	6.35	30.45	–	78.77	4.76
IMV-8	3.90	29.20	24.80	–	51.94	3.63

Table 3
Composition of the Series 1 coal samples.

Sample	Sulfate sulfur content (%)	Pyritic sulfur content (%)	Organic sulfur content (%)	Total sulfur content (%)
IMV-1	0.34	4.13	2.52	6.69
IMV-2	0.51	1.48	3.31	5.30
IMV-3	<0.01	0.21	0.43	0.64
IMV-6	< 0.01	1.19	0.69	1.88
IMV-7	< 0.01	0.15	0.61	0.76
IMV-8	0.12	0.34	0.87	1.33

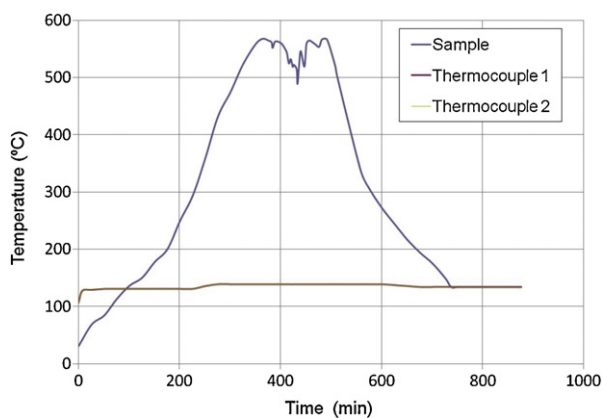


Fig. 3. Self-ignition at 135 °C.

the shortest distance from the center of the sample to its surface) and the SIT to be determined via the following equation:

$$\ln \left(\frac{\delta_{cr} \cdot SIT^2}{r^2} \right) = \ln \left(\frac{\rho \cdot H_0}{\lambda} \cdot \frac{E}{R} \cdot k_0 \right) - \frac{E}{R \cdot SIT} \quad (2)$$

where δ_{cr} is the critical FK value (in m), ρ the bulk density (in kg m^{-3}), H_0 the gross calorific value (in J kg^{-1}), λ the thermal conductivity (in $\text{W K}^{-1} \text{m}^{-1}$), k_0 the frequency factor, E the apparent activation energy (J mol^{-1}), and R is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$).

All calculations were made using a purpose-designed ESTUFA computer program involving a spreadsheet embedded with macros allowing automated FK analysis via Eq. (2). It also provided ignition curves tracing the frontier between ignition and non-ignition, and afforded the critical dimensions of the materials at different temperatures.

Two samples from Series 2 (bituminous coal and lycopodium) were used to compare the results returned by the scaling and FK methods. Based on the results obtained, on the experience gained with the coals of Series 1, and the results of other researchers [22,23], the results for the remaining Series 2 samples were analyzed using the scaling method alone. Naturally, the use of this or the FK method remains the user's choice. Standard EN15188 indicates that further methods can be used, although the scaling method is the most commonly employed and therefore usually the most suitable for comparing the results of different studies.

The results were analyzed by plotting $\log(\text{volume sample/surface area of the bottom of the sample})$ (i.e., V/A in m) against $1/\text{SIT}$ (SIT in K), interpolating a line that provides information on the critical temperatures for different stored volumes. Graphs of $\log(V/A)$ against $\log t_{ind}$ (in h) (where t_{ind} is the induction time) were plotted to provide information on the critical storage times for specific volumes.

Results and discussion

FK analysis of the Series 1 sample results

Table 4 shows the SIT results for the Series 1 samples obtained using the FK method.

Fig. 4 shows the curves obtained for coals of different rank. The medium rank sub-bituminous coals (IMV-1 and IMV-2) returned steeper slopes than the higher rank bituminous (IMV-3 and IMV-7) or semi-anthracite (IMV-6) coals. However, the bituminous coal IMV-8, a high rank coal, showed behavior similar to that of the lower rank coals. This could be a consequence of its carbon content, which is quite similar to that of sub-bituminous coals.

The FK method also determined the critical dimension of the samples (the shortest distance from their center to their surface)

Table 4
Self-ignition temperatures (°C), of the Series 1 coal samples.

Basket volume (cm ³)	IMV-1	IMV-2	IMV-3	IMV-6	IMV-7	IMV-8
17	140	140	180	220	160	140
120	120	120	160	200	140	120
240	120	120	150	190	130	120
1000	110	110	140	170	120	110

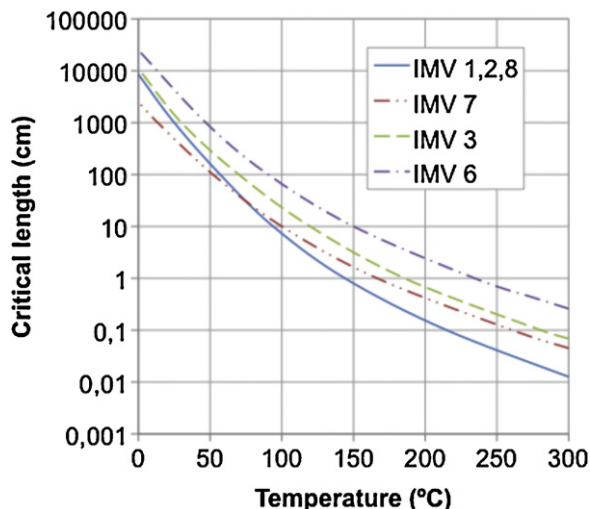


Fig. 4. Curves achieved using the FK method for the Series 1 coal samples.

Table 5
Critical dimensions for the Series 1 coal samples.

Sample	Crit. Dim. (m) at 20 °C	Crit. Dim. (m) at 30 °C	Crit. Dim. (m) at 50 °C
IMV-1	175	57	7
IMV-2	175	57	7
IMV-3	291	115	21
IMV-6	532	230	50
IMV-7	673	353	109
IMV-8	175	57	7

Table 6
Self-ignition temperatures (°C) for Series 1 samples IMV-2 and IMV-6.

Basket volume (cm ³)	IMV-2	IMV-6
50	119.2	203.7
150	112.3	188.5
400	107.1	178.0

(Table 5). The higher the temperature, the smaller the sample volume needed to achieve self-ignition.

Scaling analysis of the results for two Series 1 samples

Scaling analysis was also used to examine the self-ignition behavior of the Series 1 coal samples IMV-2 and IMV-6. Table 6 shows the results obtained; note that the larger the sample the lower the self-ignition temperature.

Scaling analysis determines the SIT via an Arrhenius-type graph (log[V/A] vs. 1/T). Samples of different volume V and area A are associated with different temperatures T. The curve in Fig. 5 represents the threshold above which ignition occurs.

Fig. 6 shows the induction times t_{ind} necessary for self-ignition to occur. For example, a cuboid volume of 1 m³ of sample IMV-6 (semi-anthracite from León) would self-ignite at temperatures above 117 °C. If it were to remain at 117 °C, self-ignition would occur in 2.3 days. For sample IMV-2 (sub-bituminous coal from

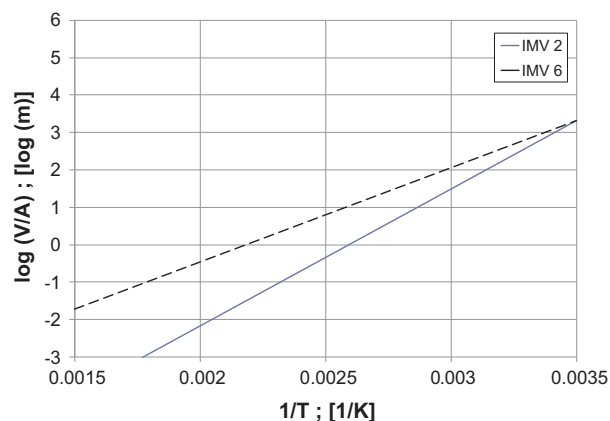


Fig. 5. Arrhenius-type self-ignition diagram.

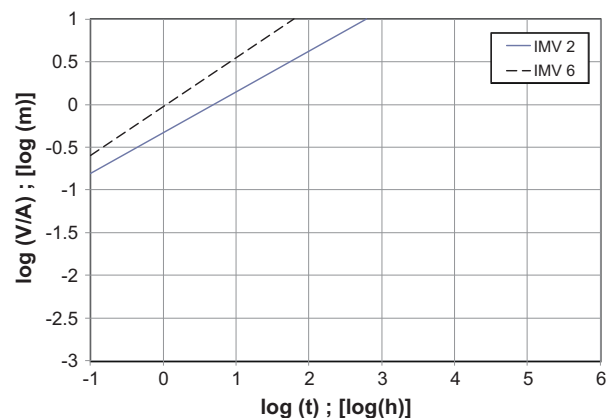


Fig. 6. Induction times of Series 1 samples IMV-2 and IMV-6 determined by the scaling analysis method.

Teruel), the self-ignition temperature for 1 m³ of coal would be 74.8 °C, and the induction time would be 23.4 days if the SIT were maintained.

Comparison of the scaling method with the FK method for two Series 2 samples

For the sake of comparison, the scaling and FK methods were used to analyze the SIT results for the bituminous coal and lycopodium (Table 7).

The scaling method predicts the self-ignition of 1 m³ of lycopodium to occur at 46.3 °C after 40 days, while the FK method predicts 46.8 °C and 40 days. At 50 °C, 0.6 m³ of lycopodium would self-ignite in 27.1 days according to the scaling method, and a 0.7 m³ sample would do so in 28.3 days according to the FK method. Thus, the two methods show good agreement. Indeed, the differences between them are of the same magnitude as the error of the temperature readings (i.e., the sensitivity of the thermocouple) and, being ≤5 K, are less than the difference between the minimum and maximum temperatures recorded in consecutive tests. Thus, in

Table 7
Comparison of the scaling method with the Frank–Kamenetskii for lycopodium and bituminous coal.

Scaling method			FK method		
Volume (m ³)	Temperature (°C)	Time (days)	Volume (m ³)	Temperature (°C)	Time (days)
<i>Lycopodium</i>					
1.0	46.3	40.0	1.0	46.8	40.0
0.6	50.0	27.1	0.7	50.0	28.3
4.2	35.6	100.0	4.3	36.3	100.0
<i>Bituminous coal</i>					
1.0	95.6	4.8	1.0	96.0	4.8
>100	50.0	168.0	>100	50.0	183.0
>100	56.0	100.0	>100	57.0	100.0

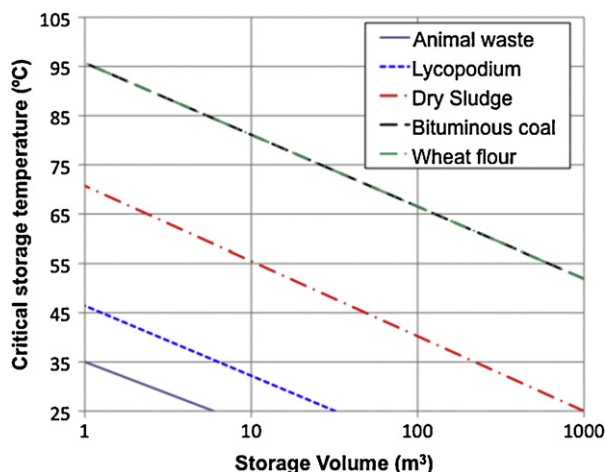


Fig. 7. Critical storage temperatures vs. storage volumes for Series 2 samples.

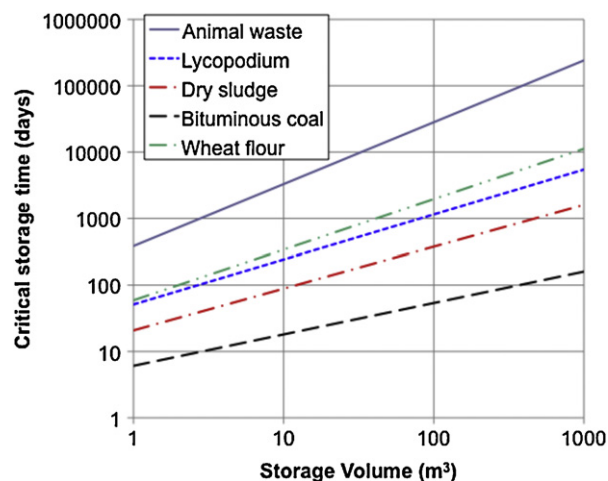


Fig. 8. Critical storage times vs. storage volumes.

terms of the quality of results, neither method is better than other; scaling analysis is, however, easier to perform.

Based on this experience, and that of other researchers, the remaining Series 2 sample results were examined using the scaling method alone.

Scaling analysis of the Series 2 sample results

Table 8 shows the SITs and induction times for the Series 2 materials.

The SITs of all of these materials became lower as the volume of material increased, a consequence of heat dissipation becoming ever more difficult. The induction time increased with the sample volume.

A clear trend was seen for all the materials of Series 1 and 2: the SIT fell as the storage volume increased. Further, all would require considerable time to ignite if the temperature were held at the corresponding SIT.

Fig. 7 shows the results obtained for the different biomass materials. It should be noted that the wheat dust and bituminous coal had the same SIT, yet the induction times observed for these materials were quite different, the bituminous coal igniting before the wheat dust. This might be explained by the different chemical composition of the samples, in particular with respect to the content of volatile compounds emitted during heating, the different physical properties of these materials, and their capacity to dissipate heat.

Fig. 8 shows the induction times for the series 2 samples.

Figs. 7 and 8 show that small storage volumes of animal waste can self-ignite at low temperatures, while the wheat dust would cause no such problems at volumes of even 100 m³; for the ignition temperature to be reached (65 °C according to the present work) some 30 years might be needed if the temperature were maintained at the SIT.

A certain spread of results should be expected for the slopes relating V/A with SIT when different laboratories perform such tests, a consequence of the use of different ovens. A margin of uncertainty should therefore be contemplated around the values reported here until all particular test details are normalized (through the additional work of other groups), including the type of oven to be used and the amount of air passing through it.

When planning tests it is recommended that preliminary work be undertaken with small quantities of samples to observe behaviors such as increase in volume, the emission of gases, the appearance of rapid reactions or flames, etc., and to glean information on the range of heating temperatures to be employed. The main drawback of the method is that full tests require rather large quantities be available and may take a long time. Thus, other preliminary tests involving thermogravimetric or scanning differential calorimetric techniques (which require smaller samples and take less time to complete) are advisable in order to gain information on the oxidation properties of samples. Tests involving the isothermal oven can then be performed to determine critical volumes and induction times.

Scaling analysis is probably the simplest option for analyzing the results of experimentally determined SITs, although the FK method could also be used. The latter is based on the thermal explosion theory and assumes an infinite heat transfer coefficient at the boundary surface between the environment and the sample. The drawback is that this is only valid for large sample sizes. Although the FK method is more sophisticated than the empirical $\log(V/A)-1/SIT$ plot, it can only deal with volumes of simple shape, and certain thermal boundary conditions cannot be contemplated, e.g., when the heat flux is not equal to zero. To help overcome this, Thomas [17,18] proposed a correction of the critical FK parameter (δ_{cr}) for finite heat transfer coefficient values.

Table 8
Self-ignition temperatures and induction times for the Series 2 samples.

Basket volume (cm ³)	Lycopodium		Bituminous coal		Animal waste		Dry sludge		Wheat dust	
	SIT (°C)	t (min)	SIT (°C)	t (min)	SIT (°C)	t (min)	SIT (°C)	t (min)	SIT (°C)	t (min)
50	145	64	185	51	145	36	170	51	187.5	44
150	130	155	175	73	130	71	155	63	177.5	92
350	120	276	165	156	115	400	145	109	167.5	196
1500	105	629	150	238	100	411	130	381	152.5	462

For solid materials stored in metallic silos or in piles in the open air, the FK method might, however, be the most advisable. It has been shown experimentally that this method provides good predictions of self-ignition for coal stored in the open air [24]. Its use can be extended to storage in metallic deposits given the latter's high capacity to transmit heat. However, when a test material is to be stored in a concrete silo it may be better to use the Thomas correction (also suggested in standard EN15188) since concrete provides a tougher barrier to the transfer of heat, perhaps leading to heat build-up within the stored material. However, this proposal needs to be tested.

Conclusions

The literature contains very few studies on the self-ignition of biomass resources. The isothermal oven method provided sufficient quantitative information to determine the self-ignition behavior of the present samples. Although there are other methods, for the evaluation of the results, the simplest option is probably to use scaling analysis. The information obtained in this work may be of use to those who need to provide solutions (e.g., changing the particle size, compaction, provision of ventilation, cleaning, reduction of stored volumes, optimization of storage time, installation of protection systems, etc.) to the risks of self-ignition in the design and management of storage installations.

Acknowledgments

This work was partially funded by the European Coal and Steel Community and the Interministerial Commission of Science and Technology (European Project 7220-AC/009 and CICYT Project AGL2009-13181-C02-01).

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