Characterization of spontaneous combustion tendency of dried sewage sludge

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Abstract

The general purpose of this study was the determination of the safety conditions to avoid the presence of explosive atmospheres in the wastewater industry. Eight Spanish plants located in Madrid, Barcelona and Málaga were considered and several sludge samples were taken in different seasons. The base for the assessment of the spontaneous ignition behaviour of dust accumulations is the experimental determination of the self-ignition temperature under isothermal conditions. Self-ignition temperatures at four volumes were obtained for one sample of sewage sludge, allowing their extrapolation to large storage facilities. A simple test method, based also on an isothermal study of samples, is the UN classification of substances liable to spontaneous combustion. Two different samples were so tested, obtaining unlike results if transported in packages of different volumes. By means of thermogravimetric techniques it is possible to analyse the thermal susceptibility of dried sewage sludge. Apparent activation energy can be obtained from the rate of weight loss. It is also applied to the study of self-ignition susceptibility by modifying test conditions when oxygen stream is introduced. As a consequence of this oxidant contribution, sample behaviour can be very different during testing and a step drop or sudden loss of weight is observed at a characteristic temperature for every substance, associated to a rapid combustion. Plotting both the activation energy and the characteristic temperature, a map of self-ignition risk was obtained for 10 samples, showing different risk levels for samples taken in different locations and at different seasons. A prediction of the self-ignition risk level can be also determined.

Keywords: *spontaneous combustion, sludge, self-ignition, flammability*

1. Introduction

The volume of wastewater produced worldwide has increased dramatically due to the large global population growth and industrialization. (Eurostat, 2013) Dried sewage sludge is a product of high interest in the near future due to the different potential uses, including its use as a fuel. (Fodor & Klemes, 2012) (Rulkens, 2008). However, some cautions must be considered since dusts show high risk of self-ignition, and are explosive as a dust–air mixture.

In 2006 the explosion of the sewage treatment plant in Besós, Barcelona, killed a worker and injured two others seriously (Europa Press, 2006). In this plant, sludge from purification of wastewater is subjected to a dehydration treatment using centrifuges and subsequent drying and pelletization. The explosion was caused by unknown causes in the machinery of sludge drying.

In the particular case of the wastewater treatment there are present risks of explosive atmospheres in different phases of the process due to the digestion gases generated in the treatment of wastewater that can form explosive gas-air mixtures. The dry sludge solids generate dust and being a fuel product, can also generate explosive dust clouds.

Chemical properties of sewage sludge are related to ignition parameters and the ignition risk may be reduced by means of preventive measures (Nifuku, et al., 2005). It is well known that the main influent parameter on ignition risk is the particle size: the smaller the particle size, the greater ignition hazard (Eckhoff, 2009)

During the process of thermal drying, sewage sludge humidity sharply diminishes below 10% or even less, so that storage of sludge is facilitated for long periods. However, the drier the product, the larger quantities of fines are produced and the ignition risks associated to the powdered products generated in the process greatly increase (Rulkens, 2008).

Flammability and explosibility properties of sewage sludge samples from different origins in Spain collected at different seasons were determined by measuring ignition and explosion parameters: Minimum ignition temperature with the dust forming a cloud (MITc) or deposited in a layer (MITl), Lower explosive limit (LEL), Minimum ignition energy (MIE), Maximum explosion pressure (Pmax), Characteristic constant (Kmax), Limiting oxygen concentration (LOC) (Fernández Áñez, et al. 2013)

Self-heating and self-ignition risks associated with dusts have been evaluated for agricultural materials by Ramírez, et al. (2009), due to the importance of the characterization of those materials to avoid these risks. Several experimental techniques can be used to characterize the thermal behaviour of materials, taking into account that the thermal behaviour of sewage sludge presents several differences with other well-studied materials as coal, as the weight loss during sludge combustion takes place not in one step as for coal but in two (Otero, et al., 2002). Due to this differences several studies were conducted showing that due to the devolatilization of sewage sludge, in the co-combustion of coal and sewage sludge, the activation energy may decrease with the addition of sewage sludge (Folgueras, et al., 2003). Furthermore, the devolatilization of materials depends on several parameters, being the main one the presence of hydrogen inside the structure of the samples. (Arenillas, et al., 2003).

These relations and the variability of these parameters on sewage sludge have been studied. In addition, the risk of self-ignition during the transport of sewage sludge has been also studied following the procedure for classification of dangerous goods for transportation developed by the United Nations. (United Nations, 2009)

2. Experimental methodology

Ten samples have been collected in eight wastewater treatment plants belonging to three regions in Spain: Catalonia, Madrid and Málaga, The origin of the samples collected, together with their moisture contents and average particle sizes are detailed on Table 1 and their chemical composition is detailed on Table 2. Carbon (C), hydrogen (H) and nitrogen (N) were measured as percentages following EN 15104:2011 standard and sulphur (S) contents was determined following the A method of ASTM D4239 standard. Oxygen content (O) has been determined as the complementary part of these values, taking into account that the sum of these five elements has to represent one hundred percent.

Table 1. Collected samples

Sample	Origin	Apparent moisture (%)	d50 (μm)
SEW-1	Barcelona	7.3	67.9
SEW-2	Barcelona	7.0	339.5
SEW-3	Barcelona	12.1	100.4
SEW-4	Madrid	6.2	382.2
SEW-5	Madrid	6.5	397.2
SEW-6	Madrid	7.2	385.9
SEW-7	Madrid	6.2	382.5
SEW-8	Malaga	6.9	27.3
SEW-9	Barcelona	4.1	74.4
SEW-10	Madrid	8.3	286.3

Table 2. Chemical composition

Sample	C (%)	H (%)	N (%)	S (%)	O (%)
SEW-1	37.43	4.91	3.01	0.61	21.84
SEW-2	28.48	3.56	2.96	0.84	16.06
SEW-3	33.72	4.94	5.00	1.63	10.81
SEW-4	34.72	4.70	4.46	1.24	10.08
SEW-5	35.76	4.74	4.52	1.31	8.67
SEW-6	31.90	4.77	5.01	1.21	15.41
SEW-7	31.73	4.69	4.89	1.14	15.75
SEW-8	36.13	5.19	4.51	4.90	12.17
SEW-9	38.30	6.33	3.72	1.08	12.07
SEW-10	33.40	6.24	4.37	1.23	13.06

Among possible ignition sources are exothermic reactions, including self-ignition of dusts. A number of experimental techniques can be used to characterize the thermal susceptibility of bulk solids and their thermal stability

2.1 Classification of substances liable to spontaneous combustion

Transportation or storage of large quantities of products showing thermal susceptibility can lead to self-ignition. The classification of substances liable to spontaneous combustion according to the recommendations on the transport of dangerous goods comes from ONU N2+N4 tests (United Nations, 2009), so that substances classified as Division 4.2 are considered as liable to undergo dangerous self-heating processes. Tests are performed to determine if substances reach ignition in sample cubes of 25 mm or 100 mm side when heated at temperatures of 100 ºC, 120 ºC and 140 ºC. The classification criterion is based on the self-ignition temperature of charcoal, which is 50 ºC for a sample cube of 27 m^3.

2.2 Thermal susceptibility

Thermal susceptibility is the term used to group the diverse parameters that allow the study of the thermal behaviour of solids and to determine their spontaneous combustion tendency (Querol, et al., 2000). Parameters included in this group are the following: Maciejasz Index (MI) as a measure of reactivity and avidity for oxygen when sample is attacked with oxygen peroxide, Temperature of emission of flammable volatiles (TEV) as a sort of flash point for solids, Thermogravimetry test (TG), Differential Scanning Calorimetry (DSC), Activation energy (Ea) and Characteristic oxidation temperature (Tcharact.). The meaning and the experimental procedures for these parameters are described in detail by Ramírez, et al. (2009)

2.3 Thermal stability

The thermal stability of a material is based on the determination of self-ignition temperatures in samples of different volumes in an isothermal oven that reproduces environmental temperatures. Self-Ignition Temperature (SIT) is the temperature at which a given volume of dust will ignite. The experimental basis for describing the self-ignition behavior of a given dust is the determination of the self-ignition temperatures of differently-sized bulk volumes of the dust by isothermal hot storage experiments (storage at constant ambient temperatures) in commercially available drying ovens. Plotting volume/sources ratios against the reciprocal of the temperature, it is possible to characterise the self-ignition behaviour of dust deposits and piles. The results reflect the dependence of self-ignition temperatures upon dust volume.

3. Results and discussion

3.1 Transport classification

To determine if the material is susceptible to self-heating, a cubic sample container of 100 mm side is introduced in an oven at 140 ° C and held for 24 hours, recording the sample temperature. If no ignition is observed and the temperature does not exceed 200 °C, the material is not classified in Class 4.2. If there is ignition or the temperature exceeds 200 ° C, the test is repeated with a sample cube of 25 mm side. If there is ignition or exceeds 200 °C, is assigned a packing group II of Division 4.2. If there is no ignition, the test is repeated using the cubic cell of 100 mm side within the oven set to 120 º C. If no ignition is observed, the material is considered exempt if shipped in packages of less than 3 m^3. If there is ignition the test is repeated with the cell 100 mm side with oven at 100 °C. If there is no ignition, it is considered exempt if shipped in packages of less than 450 litres. If there is ignition a packing group III of Division 4.2 is assigned. Table 3 shows the results obtained for two samples, which were selected by their different origin, one from Madrid and the other from Barcelona. As can be seen, both samples are identically classified.

Table 3. ONU N.4. Division 4.2.test

Sample	Self-heating in a 100 mm cube at 140 ºC	Self-heating in a 25 mm cube at 140 ºC	Self-heating in a 100 mm cube at 120 ºC	Self-heating in a 100 mm cube at 120 ºC	Classification
SEW-2	Yes	No	No	-	Exempted if transported in packages ≤ 3 m^3
SEW-7	Yes	No	No	-	Exempted if transported in packages ≤ 3 m^3

Thermogravimetry tests were done to evaluate the thermal susceptibility of sewage sludge. Two different criteria based on two parameters, activation energy and characteristic temperature, were used.

3.2 Evaluation of susceptibility: activation energy (Ea)

Following a conventional thermogravimetry test, the apparent activation energy of the sample is calculated at the point of maximum weight loss by means of a simple mathematical model applied to a set of points around that of maximum weight loss in a suitable representation of the recorded test points. The activation energy is related to the rate of weight loss, leading to the estimate of an "apparent activation energy" from the slope of least-squares line fitted to the selected test data. Thermodynamic and mathematical basis of Cumming's equation, based on first order reaction characteristic equations, simplifies and provides the estimate and use of this activation energy, turning it into a typical parameter of the sample representing the easiness for the reaction to take place.

3.3 Evaluation of susceptibility: oxidation temperature (Tcharact)

Thermogravimetric technique is applied to the study of self-ignition susceptibility by modifying test conditions when oxygen stream is introduced. As a consequence of this oxidant contribution, sample behaviour can be very different during testing and a step or sudden loss of weight is observed, associated to a rapid combustion and produced at a characteristic temperature in every substance. Thus, from this unique value of the "characteristic temperature" powdered substances can be easily classified.

Table 4 shows the obtained values for the determination of the thermal susceptibility of sludge.

Table 4. Evaluation of thermal susceptibility

Sample	Temperature of flammable volatiles TEV	Maciejasz Index MI	Activation energy Ea	Characteristic oxidation temperature Tcharact
SEW-1	380	0	70.7	309
SEW-2	340	29	72.0	281
SEW-3	310	0	67.8	262
SEW-4	360	10	68.5	266
SEW-5	330	3	69.0	264
SEW-6	320	0	53.3	277
SEW-7	320	0	69.0	267
SEW-8	260	0	66.6	203
SEW-9	330	8	66.1	224
SEW-10	310	25	66.8	218

The determined activation energies and characteristic temperatures of oxidation in oxygen flow are plotted in Figure 1 as an experimental comparative graph. This kind of graphs was previously used for other materials, such as agricultural products and also different types of coals, allowing the definition of four regions depending on the ease of the oxidation process.

Cut-off values defining the different regions in this plot were taken considering the clustering observed in various typical samples previously studied, including different rank coals

As can be seen, one sample is placed in the *medium risk zone*, six samples in the *high risk zone* and three samples in the *very high risk zone*. All the samples located in the medium and high risk zones have H contents below 5 %, while samples in the very high risk zone have H contents higher than 5%.

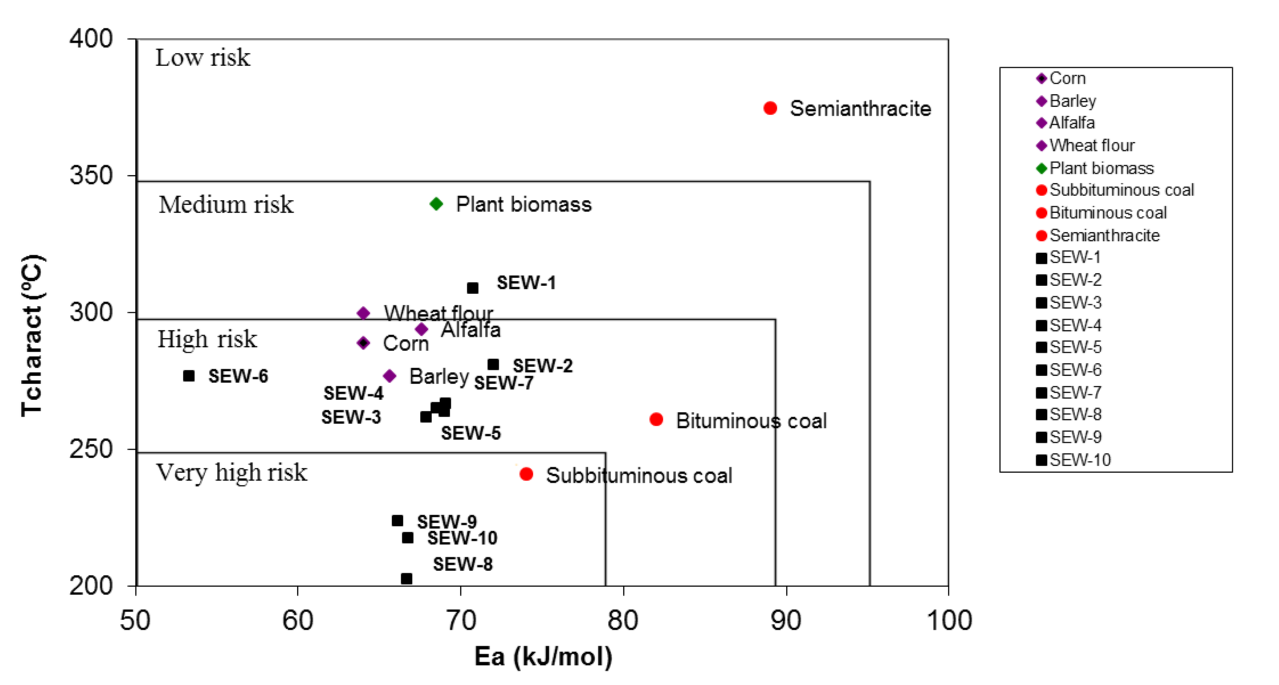

Figure 1. Spontaneous combustion tendency of sewage sludge

3.4 Self-ignition temperatures

A more detailed testing has been done for sample SEW-10 in order to determine its self-ignition temperature. Using four different volumes of sample, ranging from 50 cm^3 to 1500 cm^3 and subjecting the samples to increasing oven temperatures, both the lower temperature leading to an ignition and the higher temperature without ignition can be determined, so that the self-ignition temperature can be defined as the medium value among those temperatures, Table 5 shows the results.

Table 5. Self-ignition temperature test

Sample Volume (cm^3)	**Lower temperature leading to ignition (ºC)**	**Higher temperature without ignition (ºC)**	**Self ignition temperature (SIT) (ºC)**
1500	125	120	122.5
350	140	135	137.5
150	145	140	142.5
50	155	150	152:5

Figures 2 and 3 represent the size of the sample versus the inverse of temperature and versus time. Extrapolating these results it can be deduced that a volume of 1 m^3 will reach self-ignition at 76 °C after 4.4 months; for 10 m^3, the temperature would drop to 62 ºC, but the required time would increase to 3 years.

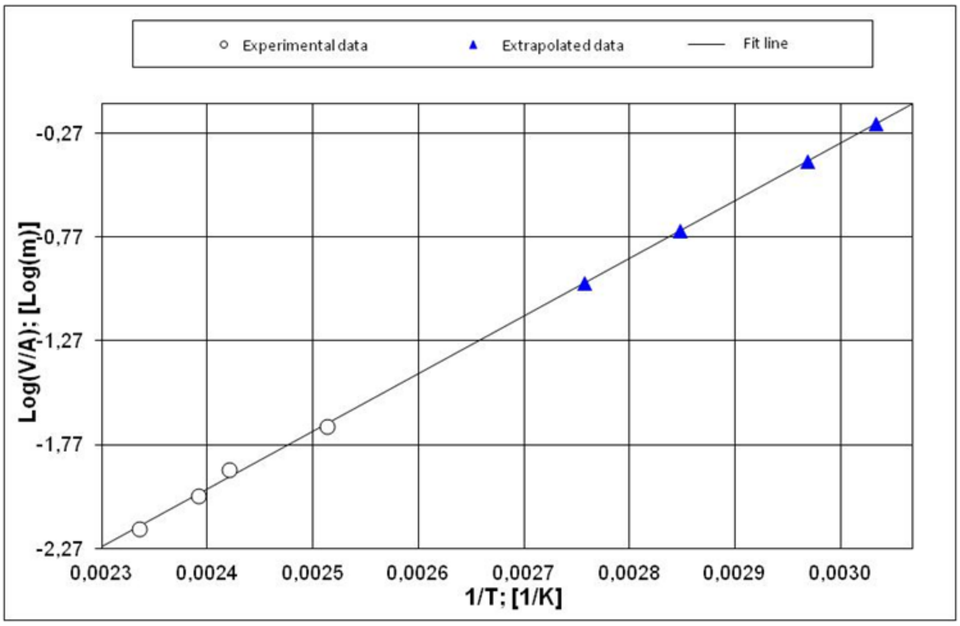

Figure 2. Extrapolation of SIT. Temperature [1/T] versus size [Log (V/A)]

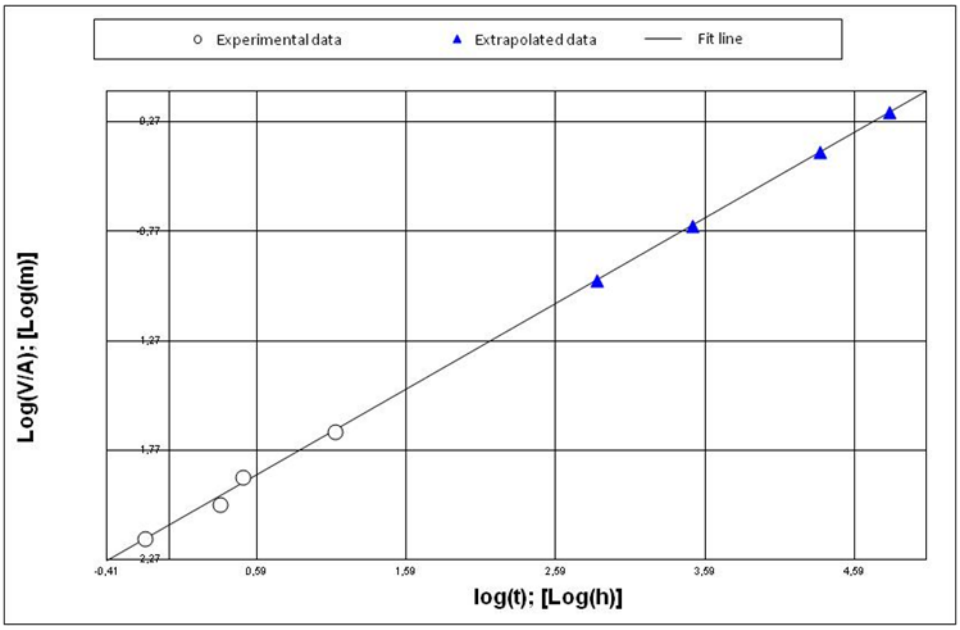

Figure 3. Extrapolation of SIT. Time [log (t)] versus size [Log (V/A)]

4. Conclusions

It is observed that in the studied samples, the higher the hydrogen content, the higher spontaneous combustion tendency of sewage sludge. The three samples that are located inside the very high risk zone are those three with hydrogen contents over 5 %. This location proved that the hydrogen concentration of sewage sludge produces the same effect as the release of volatiles during devolatilisation previously observed in other organic materials, such as different types of coals. For different rank coals, a higher spontaneous combustion risk is observed when volatile contents are higher, as it is the case of subbituminous coals.

This relation is not observed in the other direction for sewage sludge, since the sample that is located in the medium risk (SEW-1) is not the sample with less hydrogen content. This suggests that the hydrogen content is not the only parameter causing this differentiation. This sample is the one with the lowest sulphur content and the highest oxygen content, which may be the cause of this differentiation.

Transport classification tests did not produce a distinction between samples from different origins, but they belonged to the same spontaneous combustion risk zone, so these tests should be done in the future for samples falling in different regions of the risk plot.

The knowledge of ignition properties of sewage sludge will improve the design of prevention and protection measures to decrease the hazards associated with the management, transport and storage of dusts. As a general rule, prevention measures similar to those extensively used for coals would be applicable to sludge.

Some parameters can be controlled during normal operation of plants. It is recommended to avoid the accumulation of large amounts of dust in industrial facilities, since they can promote the initiation of self-heating processes and also they mean always an increase in the risk of dust explosions. This goal can be also obtained by adding certain percentages of inert materials.

A continuous monitoring of temperatures, or even better, of CO emissions from dust accumulations will allow the early detection of self-heating processes, providing more time for the protective measures to act properly.

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