

Explosion risk in coke, coal and sulphur storage

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ABSTRACT

The self-ignition of all kind of powdery substances is a topic studied over the years, especially if the dusty substance is coal or substances related with coal because it may be a cause of energetic materials and human losses. But it is important to note that this is not the only risk in industrial plants that generate or store solid substances. Every combustible powders are potentially explosive and they may cause serious consequences if all the necessary factors are developed. Due to this potentially risk, it is essential a good characterization and knowledge of all the parameters involved in those processes.

PALABRAS CLAVE: coal, coke, sulphur, explosibility, self-ignition.

1. INTRODUCTION

Although the most studied explosions are caused by combustible gases, explosions caused by dusts are as frequent and dangerous as the first ones. Moreover, the parameters involved on a dust explosion are more unknown than those involved on a gas explosion.

In order to a dust explosion occurs, it is necessary the occurrence of several factors: dust must be combustible, airborne and in the explosive range, its particle distribution should be capable of propagating a flame, the atmosphere in which the dust cloud is present must be capable of supporting combustion and an ignition source with sufficient energy to initiate flame propagation shall be present. [1]

The characterization of powdery substances is essential in any industrial plant in order to avoid dust explosion risks or to improve the measures to ensure that its effects are minimized. It is very important to be aware that all combustible dusts must develop an ignition if all the necessary factors are involved. [2] Those factors are known as explosion pentagon and they are: dust cloud, fuel, confinement, ignition source and oxygen source. [3]

Although all the combustible dusts might produce an explosion, depending on the explosive parameters of the dust, the consequent explosion might be more or less probable and its consequences more or less severe. A dust explosion may occur whether dust is deposited as a layer when it is dispersed as a cloud; this is the reason why it is necessary to know every parameter involved. Dust layers and clouds are considered separately because a dust cloud is itself an explosive atmosphere, while a dust layer represents a latent risk, a potential explosive atmosphere.

Dust layers are recognized as 'combustible dusts' if they can be ignited by a foreign ignition source and the local fire will propagate sufficiently after the outside source is taken away. [4] The danger of dust layers depends largely on the thickness of these: the greater thickness, the lower the minimum temperature required for that layer ignition. [5]

In order to study the prevention and protection necessities for all industrial plants, the characterization of dusts involved several parameters. Those characteristics are divided in five groups that are: general characteristics, ignition sensibility, explosion severity, thermal susceptibility and thermal stability.

Particle size and moisture are the main general factors affecting the explosibility of the combustible dusts. In relation to the particle size, it is considered as dust those substances that may be deposited by its own weight but may remain in suspension for a given time, usually when there is a fraction below 1 mm. In general, shapes with greater surface area (minor particle size) will propagate flame more readily and therefore be more hazardous. [6] [7] The moisture has a double effect on the explosibility of combustible substances, depending on the chemical composition of the substance; moderate moisture contents might inhibit or promote the explosion. [8]

The parameters involved on the ignition sensibility are those characteristics related with the ease of the substances to ignite in the presence of different sources of ignition. They are minimum ignition temperature (in layer and in cloud) [9], lower explosive limit and minimum ignition energy [10].

The group of explosion severity involves the characteristics that allow the explosion consequences evaluation. They are maximum explosion pressure, characteristic constant and limit oxygen concentration [11].

The thermal susceptibility is used in order to know the thermal behavior of solids and to determine their self-ignition tendency. The main parameters of this group are Maciejasz Index, flammable volatiles emission temperature, activation energy, characteristic oxidation temperature and the parameters determined by thermogravimetry and differential scanning calorimetry [12] [13].

Finally, it is significant to say the importance of the self-ignition risk on the storage and transport of these kind of substances. Self-ignition reactions of dusty substances are not completely well known but various theories are

developed. [14] What is well known is that self-ignition consequences might be catastrophic. This spontaneous combustion behavior is mainly determined by the self-ignition temperature, which is the parameter that describes the thermal stability of the substances.

Coal is one of the most studied combustible solids in these terms. Actually, an important alternative for coal is coke, and it not as well-known as coal. Moreover, the chemical composition of coal or coke greatly influences these parameters. This influence is largely viewed as the sulphur content of samples [15]. Due to these relations, and considering the high risk these substances involve, a detailed study about these parameters has been developed to coke, coal and sulphur samples.

2. MATERIALS AND METHOD

Three materials have been studied for this project: coke, coal and sulphur. All the samples have been crushed and screened before testing, collecting the fraction less than 0.180 mm for the tests, excepting the Self-ignition temperature test. In this test, samples were tested with higher particle size.

The tests developed to the three samples are divided in five tests groups and are detailed below.

General characteristics. Moisture and granulometry. The moisture was measured with a halogen analyser and the granulometric curves were determined by laser diffraction on dry way.

The ignition and explosion parameters determined for tested samples are mostly well known: 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).

Thermogravimetric analysis and differential scanning calorimetry provide the following parameters [8].

Thermogravimetric analysis (TG): In thermogravimetric analysis the weight of the samples is measured as a function of its temperature. The most significant parameters are: combustion induction temperature (IT) and maximum weight loss temperature (MLT) as shown in figure 1a.

Differential scanning calorimetry (DSC): The sample is placed in a crucible and heated at a regular rate, previously established. The difference in temperature between the sample and one of reference is measured and recorded against the temperature of the oven and the exchanges of heat in the sample determined and it is represented like in Figure 1b. The parameters used to characterize different substances are minimum temperature at which the exothermic reaction begins (initial temperature, IET), maximum temperature reached during the exothermic reaction (final temperature, FET) and temperature at which the fast exothermic reaction commences (change of slope temperature, CST).

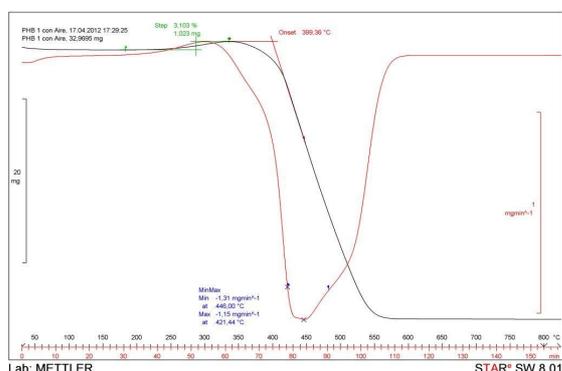


Figure 1a. Thermogravimetric analysis.

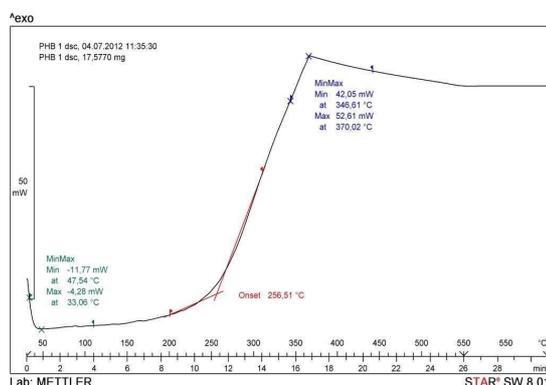


Figure 1b. Differential scanning calorimetry

Characteristic temperature (T_{character}): This temperature is determined by the thermogravimetry test adding an oxygen stream. The oxygen is an oxidant and because of its addition the sample has a sudden loss of weight. This loss happens at different characteristic temperature for each sample. Depending on this parameter samples can be classified by its self-ignition risk.

Activation energy (E_a): This parameter is used to evaluate the susceptibility of different solid samples, particularly coal. In order of its value, the self-ignition risk is classified.

Maciejasz Index (MI): It measures the required time (t) to produce a temperature increase of 65 K in the sample, when it is attacked with hydrogen peroxide. The Maciejasz index is calculated as $MI=100/t$. It determines the susceptibility to the self-combustion due to the oxidation of some compounds in the substance, for instance pyrites in coals. This method is frequently used for coals, especially when the sulfur content is high.

Ignition temperature of emitted volatile matter (TEV): A sample is progressively heated so that it can decompose. An ignition source is applied to the volatile matter of the sample and the appearance of flames is observed. It gives a good assessment for organic products that have flammable combustion products, which make the product more hazardous.

Electrical resistivity with the dust forming a layer (REC): it measures the electrical resistance through a dust layer. This test is performed to classify dusts as conductive or non-conductive.

Self-heating temperature (TSD): 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. The results reflect the dependence of self-ignition temperatures upon dust volume.

3. RESULTS AND DISCUSSION

General characteristics results show the first differences between the three samples and they are shown on Table 1.

Table 1. General characteristics.

Sample	Moisture (%)	Granulometry		
		d(0.1) µm	d(0.5) µm	d(0.9) µm
Coke	1.4	3.3	35.6	144.9
Coal	4.4	5.4	25.7	94.5
Sulphur	<0.1	6.1	25.7	94.5

The ignition sensitivity parameters also show these differences and they are shown on Table 2. It is important to note that the lower is the value of these parameters, the more sensible to ignition is the substance.

Table 2. Ignition sensitivity parameters.

Sample	MITI (°C)	MITc(°C)	LEL (g/m ³)	MIE (mJ)
Coke	350	610	125	>1000
Coal	370	530	20	200
Sulphur	It melts	210	2.5	<1

The MITI for the sulphur sample could not be determined because it melts before its ignition. The other parameters show lower values for this sample than for the coal and the coke, so this sample would ignite more easily than the others. The coke sample has higher values than the coal sample for all the parameters except MITI. Due to these values, the coal dust clouds will ignite with less severe conditions than the coke dust clouds, but if the dust is forming a layer, the coke would ignite at lower temperatures than the coal.

In relation to the explosion severity, it is shown that coke and coal have similar values, but both are very different from the sulphur sample as it is shown on Table 3.

Table 3. Explosion severity parameters.

Sample	Pmax (bar·g)	Kmax (bar·m/s)	Explosion class
Coke	6.9	126	St1
Coal	7.0	129	St1
Sulphur	5.3	214	St2

Samples may be classified in order to their Kmax value in four groups, from St0 to St1. The higher the group, the more explosion severity it has. According to this classification, only the sulphur sample bellows to St2 class, while coke and coal below to St1 class. So also in this case the sulphur sample has more dangerous characteristics than the other two samples.

In relation to the thermal susceptibility, the similarity between coke and coal is also shown with REC, LOC; MI and TEV as shown on Table 4. It is interesting to note that the three samples are no conductors because they have high REC values and also none of the three react exothermically with the hydrogen peroxide, so MI is less than 10 and they do not present special oxygen avidity.

Looking to TEV values, the sulphur sample is the only one that releases flammable volatiles at temperature lower than 400°C. The coke sample releases volatiles at 340°C but they are not flammable until the maximum temperature for this test, 400°C. The coal sample does not release any volatiles until 400°C.

The LOC is an important parameter because due to this value the inerting is developed. The sulphur sample needs a bigger decrease of the air oxygen to prevent its ignition than the other two samples.

Table 4. REC, LOC, MI and TEV values.

Sample	REC (Σ · m)	LOC (% V/V)	MI	TEV (°C)
Coke	$2.1 \cdot 10^9$	10	0	>400
Coal	$3.5 \cdot 10^{10}$	9	0	>400
Sulphur	$4.3 \cdot 10^{10}$	5	0	300

TG tests also show the different behavior of the sulphur, as observed in Figures 2a, 2b and 2c.

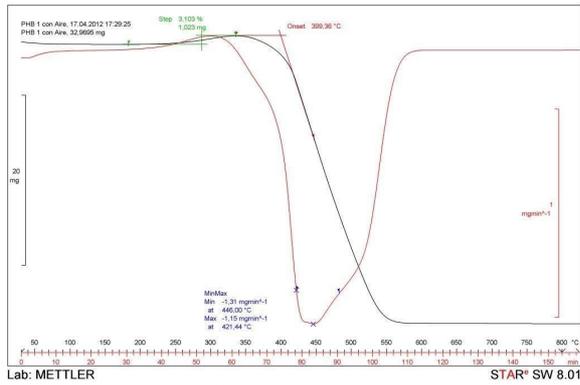


Figure 2a. TG coke

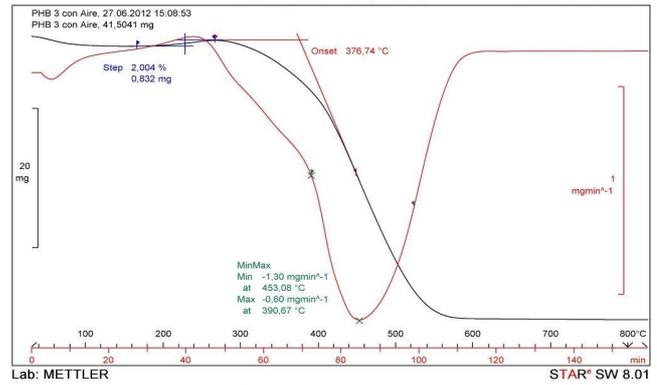


Figure 2b. TG coal

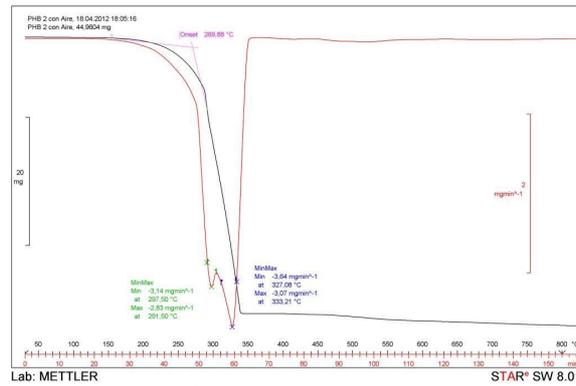


Figure 2c. TG sulphur

At DSC tests, sulphur sample presents an atypical calorimetric curve compared to solid combustibles, as shown in Figure 2, so the habitual evaluation procedure cannot be applied in this case.

Coke and coal samples follow the typical curve but quite different values (Figures 3a and 3b). Coke sample starts its exothermic reaction at lower temperature than coal sample and the maximum temperature it achieves is higher. But the most significant difference is the TCP value, because the lower this value, the higher the self-ignition risk. The temperature difference between both samples is 41°C, higher for coke sample than for coal sample. So it is shown that the coal sample shows a higher self-ignition risk than the coke sample.

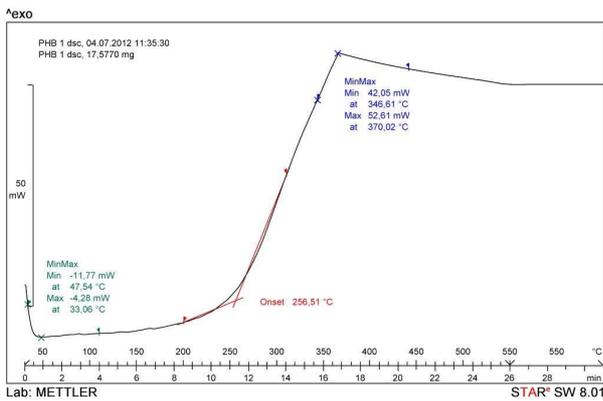


Figure 3a. Coke's calorimetric curve

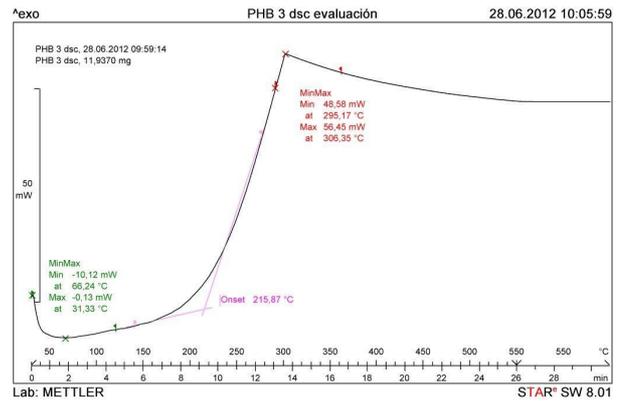


Figure 3b. Coal's calorimetric curve

A biaxial graphic is used for the E_a and $T_{charact}$ study. Figure 4 shows coke, coal and sulphur together with some other typical products. This graphic is divided in four regions according to the self-ignition risk. When the values for the sample studied are placed on the graph, it is shown that sulphur and coal samples are placed on the high risk zone and the coke sample is placed on the medium risk zone.

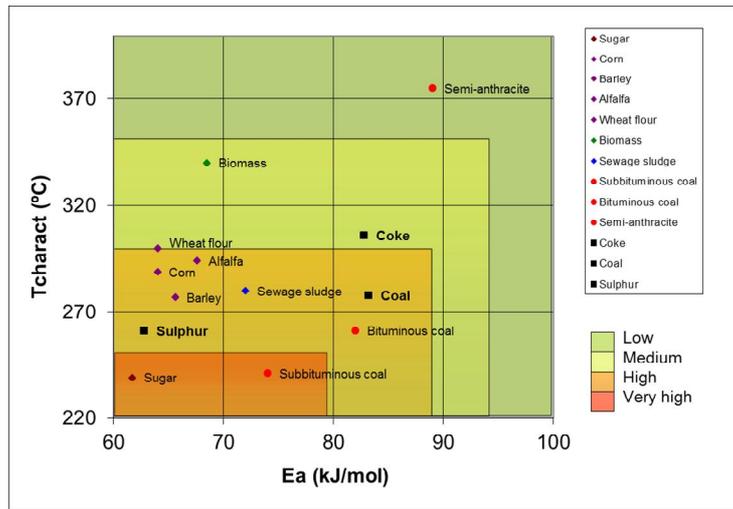


Figure 4. Ea vs Tcharact graphic.

In relation with the thermal stability, it could not be determined for sulphur sample because of its low melt point. In coal and coke samples, the Tsi values decrease with the increase of the volume tested, as shown in Figure 5.

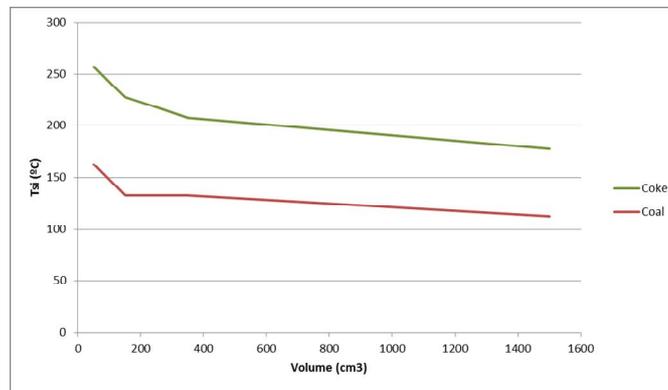


Figure 5. Self-ignition temperature vs volume graphic.

Due to the relation between Tsi and volume, it may be possible to extrapolate Tsi and induction time for higher volumes. With these extrapolations, it is determined that for a 1 m³ a coke sample would ignite at 76.5°C in 1.8 months, and for 0.1 m³ it would ignite at 107°C in 8 days. In the case of coal, a 1 m³ of sample would ignite at 40.1°C and a volume of 0.1 m³ would ignite at 61.5°C in 1.3 months.

Finally, the influence of the thickness of the dust layer on the MITI is determined and shown on Figure 6. The higher the thickness, lower the MITI. So when the dust accumulations are thicker it is more probable that ignition occurs, although it will take a longer period of time.

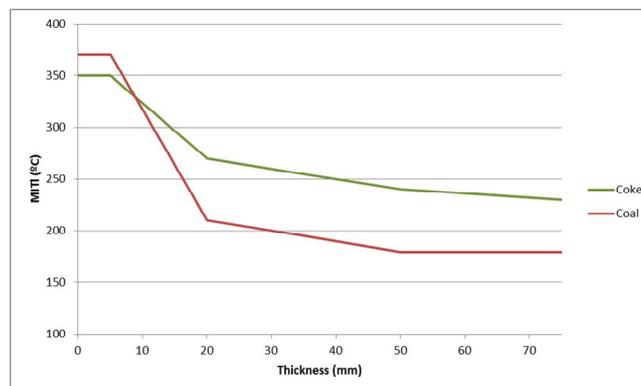


Figure 6. MITI vs thickness graphic.

4. CONCLUSIONS

The benefits of replacing coal with coke are actually well known and they are mainly due to the process by which coal is converted into coke. About explosibility, the characterization of both substances shows enough similarities. Nonetheless, the existing differences are important because of the parameters they involve, mainly self-ignition. The coal sample is situated into the high risk zone of the Tcharact vs Ea diagram, while the coke is situated into the medium risk zone. Furthermore, the self-ignition temperatures of the coal are higher than those of the coke, so the first one has a higher risk of such processes during storage.

In regard to the sulphur sample, in the determined parameters it is shown a large difference between this sample and the other two studied. In every studied parameter the sulphur samples has more dangerous parameters than the other two samples in terms of explosibility.

Through the MITI test for different thickness, it is shown that the cleanup plan is a very important prevention measure in any industrial plant. The MITI values decrease very quickly when the thickness of the dust layer increases. That is why in any industrial plant should be completely controlled dust deposits have thicknesses always negligible. Another important risk associated to this layer is that they may be placed on suspension and they can generate an explosive dust cloud potentially explosive. This risk of dust explosion should be carefully considered since accidents can be catastrophic.

Although these data show that sulphur is more dangerous than coke and coal, the final conclusion of this study is that the three substances are potentially dangerous since they can generate explosive atmospheres. Thus, in any industrial plant in which one of these substances is processed, generated or storage, it is essential to design and to maintain correctly prevention and protection measures to ensure safe operation.

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