NOVE METODE ODREĐIVANJA INICIJALNE TEMPERATURE GASA U VEZI SA EMISIJAMA PRI SAGOREVANJU

NEW METHODOLOGY FOR DETERMINATE INITIAL TEMPERATURE OF GAS RELATED TO COMBUSTION EMISSIONS

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Detekcija početnog procesa sagorevanja predstavlja ključni faktor u industrijskoj bezbednosti, zbog toga što može da spreči ozbiljne nezgode. Razvijene su različite metode za detektovanje procesa samogrevanja, jer bi to mogao da bude prvi korak u procesu samozapaljenja, između ostalog i detekcija putem metoda u vezi sa emisijom gasa, što je bio cilj ove studije. Ovim postupkom je testirano šest različitih uzoraka i pored toga što se ova metoda ispitivanja pokazala stabilnom, jednačina vrednovanja temperature nije odgovarala očekivanim rezultatima. Da bi se ova metoda poboljšala, razvijen je novi pristup vrednovanju. Uzorci su ispitivani u različitim granulometrijama, tako da je metoda primenjena na četrnaest uzoraka šest različitih tipova i uočene su razlike u početnoj temperaturi emisije gasa. Takođe je upoređena početna temperatura emisije CO i CO2. U većini uzoraka emisija CO je nastala pre CO2, ali u nekim uzorcima sitnih čestica postojala je emisija CO2 zbog toga što granulometrija utiče na vazduh koji se nalazi između čestica. Rezultati su upoređeni sa originalnim postupkom vrednovanja i sa još dve metode: metodom tačke infleksije i ekološkom standardom metodom. U svim slučajevima novi postupak daje bolju aproksimaciju, budući da uzima u obzir nagib krive na njenom samom početku.

Ključne reči: *self-heating; combustion gasses; industrial safety; biomass; coal*

Detection of incipient combustion process is a key factor in industrial safety as it can prevent severe accidents. Different methods to detect self-heating processes have been developed, as it might be the first step of self-ignition process, including the detection through gas emission methodology whose improvement is the aim of this study. Six different samples were tested using this procedure and, besides the test method turned to be stable, the temperature evaluation equation did not match the expected results. In order to improve the method, a new evaluation approach has been developed. The samples were tested in different granulometries so the method was applied to fourteen samples of six different types, so differences were seen in the initial temperature of gas emission. It was also compared the CO and CO2 initial emission temperature. In most of the samples the emission of CO was produced before CO2, but in some fine particle samples the CO2 was emitted before because the granulometry affects to the air available between the particles. The results were compared to the original evaluation procedure, and two more methods: the inflection point method and the environmental standard method. In all cases, the new procedure provides a better approximation as it considers the slope of the curve in its very beginning.

Key words: *Self-heating; combustion gasses; industrial safety; biomass; coal*

1 Introduction

Several industrial accidents have occurred in the past years due to self-ignition processes [1] during transport or storage activities. Self-ignition, also known as spontaneous ignition, is a process

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in which the substance begins its combustion in the absence of external ignition sources such as hot surfaces, sparks, etc. This process first stage is self-heating process, in which the substance starts its oxidation and releases heating because of the exothermic reaction, and as the temperature increases, so it does the oxidation velocity. It means that a deep understanding of the self-heating process is an important factor in order to avoid accidents related to spontaneous ignition.

Because of that, different methodologies to study self-heating process have been developed, such as thermogravimetric analysis (TGA) [2], differential scanning calorimetry (DSC) [3], heat release rate (HRR) [4], etc. All of them aims to measure the very beginning of the process defining the onset temperature, the maximum specific heat, etc. This study focusses on the combustion-related gas emission and aims to define the initial temperature at which the carbon monoxide (CO) and dioxide (CO_2) emissions highly increase as it means the oxidation velocity has increased, and so the heating.

Some studies have measured other gases in order to define the process in a more accurate way, but their amount is not so significant as carbon monoxide and dioxide, and their emission start at the very beginning of the combustion process [5] [6].

Fernandez Anez et al. [7], first defined the method to detect self-heating by measuring the gases, so this is the procedure used to develop this study, but also trying to improve it incorporating a new evaluation method that uses a graphical approximation.

2 Materials and Methods

2.1 Samples and screening

Six different materials have been used in this study as it aims to be applicable to several substances. The samples used were charcoal, biomasses (agricultural and forestry) and dog food. The samples were milled using a blade mill and sieved through 1 mm sieve in order to define possible differences due to the particle size. The charcoals samples were milled twice and sieved using 1 mm and 75 μm sieves, in order to obtain three different fractions. Table 1 shows the samples' identification, its particle size and the moisture content.

The moisture content was determined using a halogen analyzer, repeating the test three times per sample when the standard deviation was lower than 0,15% and ten times when grater. The final result is the average of the three (or ten) tests. The test was carried out using a Mettler Toledo HB43-S halogen analyzer.

Table 1: Sample screening

Sample	*Identification*	*Particle size*	*Moisture*
Pine shaving	PS-1	Coarse	6,23 %
	PS-2	< 1mm	
Wheat straw	WS-1	Coarse	6,56 %
	WS-2	< 1mm	
Charcoal 1	CC1-1	Coarse	6,06 %
	CC1-2	< 1mm	
	CC1-3	< 75 μm	
Charcoal 2	CC2-1	Coarse	4,70 %
	CC2-2	< 1mm	
	CC2-3	< 75 μm	
Dog food	DF-1	Coarse	7,00 %
	DF-2	< 1mm	
Olive pellets	OP-1	Coarse	7,00 %
	OP-2	< 1mm	

2.2 Thermogravimetric Analysis (TGA)

TGA is a thermal analysis which measures the weight by a constant record while a heating rate is applied. The test begins at 30 ºC and ends at 800 ºC with a heating rate of 5 K/min, and with air flow applied, so the weight decreases along the time because of the oxidation reactions that takes place. The results can be plotted in a graph in which the combustion reaction is clearly shown after the moisture release (water evaporation) [8]. The first derivative of the curve (DTG) must be calculated in order to obtain two main parameters: the combustion induction temperature (IT), that is the temperature at which the oxidation velocity accelerates and the proper combustion begins and the maximum weight loss temperature (MLT), that determines the end of the devolatilization process and the beginning of the char oxidation as it represents the volatile matter yield. The IT can be determined as the last point before the mass decreases significantly, and usually is calculated as the intersection point of two lines as can be shown in Figure 1. The TGA allows the calculation of the activation energy (E_a) of the combustion process using Cumming's equation [9].

As this study aims to evaluate the initial step of self-heating process, the very beginning of the combustion reaction needs to be calculated. Moisture of the samples is known, so if this percentage is subtracted from the mass at the first part of the test, the remaining mass corresponds to the combustion reaction, so the initial combustion temperature (ICT) can be determined as the temperature at which the moisture percentage is removed from the total mass. Figure 1 shows the TGA graph and the parameters mentioned above. The test was carried out using a TG-DSC Mettler Toledo TG-50 analyzer.

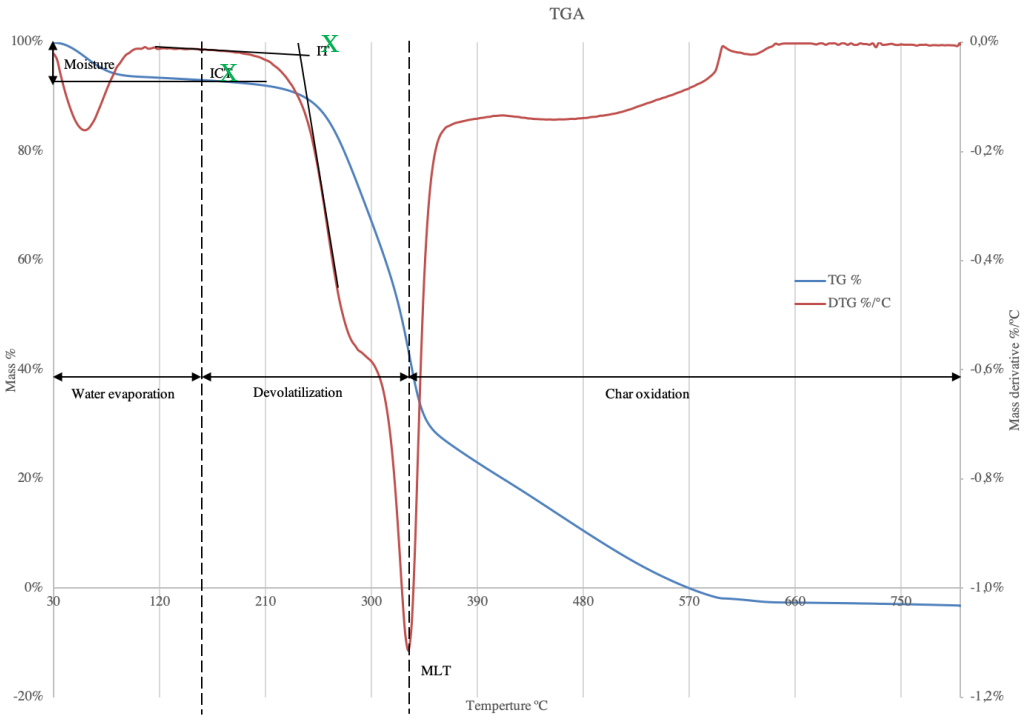

Figure 1: TGA graph

2.3 Gas emission analysis

Gas emissions test has been carried out following the procedure defined by Fernandez Anez et al. [7], in which the sample is placed inside a 1 L cubic basket with a thermocouple inside, and the basket is introduced inside a sealed container provided by plastic tube with a Mohr wrench to open or close it. The plastic tube is connected to a suction pump that fills tedlar bags when the circuit is opened. The sealed container is placed inside an isothermal preheated, and when the sample reaches the desirable temperature, the circuit is opened and the tedlar bags are filled. Once the gasses are collected, the bags are connected to a gas analyzer and the amount of carbon monoxide and dioxide. In this study, gasses were collected every 20 ºC, from 40 ºC to 200 ºC. Rosemount Analytical NGA-2000 analyzer was used to measure the amount of CO (ppm) and CO_2 (%).

In order to evaluate the initial temperature for gas emissions, the following procedure was used. The relative percentages for each temperature interval, are calculated as defined in the previous methodology using the following equations:

$$RD = (e_{Ti}\text{-}e_{Tf}) / e_{Ti} \; ; \; RP = 100 \cdot (RD / \Sigma RD_i) \qquad (1)$$

Where RD is the relative difference for each temperature interval, e_{Ti} is the emission amount at the initial temperature of the interval, e_{Tf} is the emission amount at the final temperature of the interval, and RP is the relative percentage for each temperature interval.

Once that the relative percentages are calculated, the first one greater than 20% represents the critical interval. Two moving average lines are calculated: the first one using the points below the critical interval, and the second one using the points above the critical interval (including itself). The intersection point between those lines represents the initial gas-emission temperature (IET). The saturation points (those whose RP is lower than 2%) are removed before calculating the moving average lines, as those points represents the saturation of the gas emission signal. Figure 2 represents the procedure mentioned above.

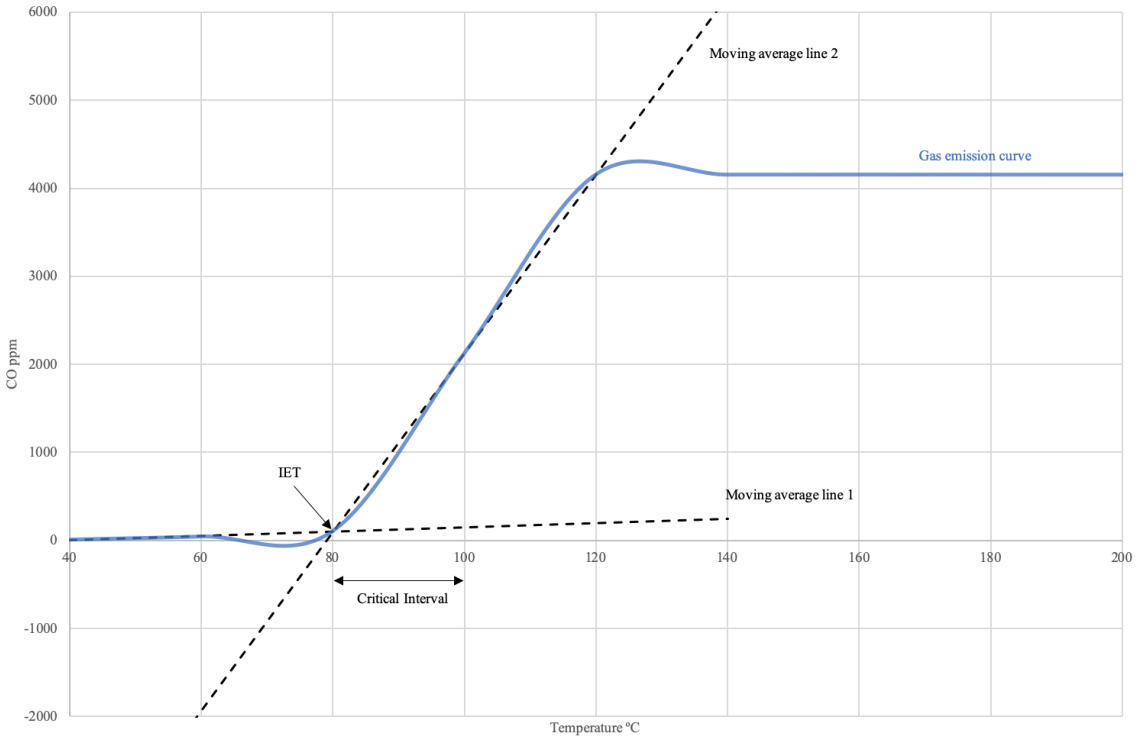

Figure 2: Gas emission evaluation

3 Results and Discussion

The Table 2 shows the results of the thermal analysis for each sample. Even if the evaluation of the IET will be compared only to the ICT, it is still relevant to consider the other parameters such as MLT, IT and E_a in order to have a global idea of the thermal behavior of the sample and the combustion process that takes place.

The data recorded from the gas analysis was evaluated as described previously, and table 3 shows the critical interval and the IET for CO and CO_2 emissions.

The IET values are greater than the critical intervals (which indeed corresponds to the previous methodology). This result is due to the fact that the critical intervals method only takes into account a great enough increase, while the IET considers the shape of the curve and calculates the very beginning of the slope. Also, the new methodology shows different IET for the same sample when they are prepared in different granulometries, and an earlier CO emission than CO_2. Both results approach this method to the real combustion process as it is known that monoxide emissions begin before dioxide, and finer particles heat before coarse ones.

Table 2: TGA results

	MLT [ºC]	*IT* [ºC]	E_a [kJ/mol]	*ICT* [ºC]
PS	330	257	66,56	100
WS	309	255	67,86	150
CC1	310	346	86,33	89
CC2	465	362	84,17	110
DF	279	255	65,86	128
OP	289	244	66,31	130

Table 3: Gas emission evaluation

	CO Critical Interval [ºC]	*CO IET* [ºC]	*CO_2 Critical Interval* [ºC]	*CO_2 IET* [ºC]
PS-1	80-100	138,9	60-80	171,1
PS-2	60-80	87,7	60-80	104,7
WS-1	60-80	78,9	60-80	89,2
WS-2	40-60	80,1	40-60	79,8
CC1-1	80-100	103,9	100-120	120,4
CC1-2	60-80	87,1	60-80	113,4
CC1-3	60-80	74,6	40-60	75,12
CC2-1	80-100	108,4	100-120	133,6
CC2-2	40-60	83,5	60-80	87,8
CC2-3	40-60	79	60-80	125
DF-1	40-60	106,5	40-60	82,1
DF-2	40-60	96,6	40-60	67,8
OP-1	60-80	126,4	100-120	141,9
OP-2	60-80	103,4	60-80	112,6

In order to define the validity of the new methodology, the IET has been compared to the ICT and the relative error (ε_r) was calculated. The IET used was the arithmetic average of the sample, for CO emissions as they began before CO2, and represent better the beginning of the combustion which is the parameter defined by the ICT. Also, there are studies stating that CO has a really important role in order to detect spontaneous heating processes [4]. The results are collected in Table 4.

Table 4: IET vs ICT

	CO IET Average [ºC]	*ICT* [ºC]	ε_r *[%]*
PS	113,3	100	12%
WS	79,5	150	89%
CC1	88,5	89	1%
CC2	90,3	110	22%
DF	101,5	128	26%
OP	114,9	130	13%

The detection using IET gives lower temperatures than the real beginning of the combustion in every sample but the pine shaving, even so the method appears to be stable for most of the samples, but not for the wheat straw whose relative error is 89%.

4 Conclusions

The new methodology for incipient detection of gas emissions seems to be stable enough and gives a result close to the real combustion parameter, which means that it really can be used for early detection. The relative error when comparing IET and ICT was acceptable meaning that the IET can estimate the ICT with not great error. The fact that the method did not work at all for the wheat straw sample may be due to the composition of the sample, it may be related to the moisture or the ligno-cellulosic and cellulosic molecules of the sample. Further studies need to be carried out in order to define new parameters that make the method useful in all samples.

While the interval method only attempted to give wide information about the beginning of the process, the new methodology can be used to define safety measures applicable to storage and transport activities, as it is more precise and less tight.

In order to define a complete method, further studies need to be carried out, such as test using different volumes and defining the heat transfer mechanisms that takes place during the process, and different samples in order to make a statistic study for the new method.

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