

PROCESS OPTIMIZATION OF SAMPLING AND DETERMINING THE UNCERTAINTY ASSOCIATED WITH THE PROPERTIES OF SOLID FUELS FOR COCOMBUSTION

OPTIMIZACIÓN DEL PROCESO DE MUESTREO Y DETERMINACIÓN DE LA INCERTIDUMBRE ASOCIADA A LAS PROPIEDADES DE COMBUSTIBLES SÓLIDOS PARA COCOMBUSTION

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ABSTRACT: This paper presents the process used to determine the statistical uncertainty associated with eight different properties of solid fuels for co-combustion tests of moisture and ash. Provides a map of sampling to determine the sample sizes in the light of the uncertainties that are considered acceptable. The values obtained show that despite the heterogeneity of the fuel itself, a well-planned campaign of samples can extrapolate the properties of the samples from the entire lot with an uncertainty controlled and quantified.

KEYWORDS: co-combustion, sampling, uncertainty.

RESUMEN: En este trabajo se presenta el proceso empleado para la determinación estadística de la incertidumbre asociada a diversas propiedades de ocho combustibles sólidos para co-combustión a partir de los ensayos de humedad y cenizas. Se establece un mapa de muestreo que permite determinar los tamaños muestrales en función de las incertidumbres que se consideren aceptables. Los valores obtenidos permiten afirmar que a pesar de la heterogeneidad propia de dichos combustibles, una campaña de muestreos bien planificada permite extrapolar las propiedades obtenidas de las muestras a la totalidad del lote analizado con una incertidumbre controlada y cuantificada.

PALABRAS CLAVE: co-combustión, muestreo, incertidumbre.

1. INTRODUCTION

In today's society, air pollution has become an issue of particular interest, the Kyoto Protocol

sets limits on emissions of greenhouse gases [1]. Measures to assess and reduce emissions appear as a priority. Co-combustion is an alternative technique in which the fossil fuel used in a boiler

is replaced by biomass. This option achieves the benefit of the environmental advantages of biomass burning instead of the use of fossil fuels like coal. The technologies employed in co-combustion are direct co-combustion, indirect co-combustion and co-combustion in parallel [2]. In the direct co-combustion type, the biomass is introduced into the boiler. The two fuels are burned together. Indirect co-combustion requires the biomass to be processed prior to an independent device of external combustion or gasification. Then, products generated by each process and fuel are introduced into the boiler. These systems reduce the problems that may arise in the boiler by using a fuel other than that for which it was designed. In parallel co-combustion the biomass is burned in a separate boiler. The main advantages of co-combustion highlighted by different authors [2-7] are: Reduction of the percentage of CO₂ emitted into the atmosphere per Joule produced, because the CO₂ emissions related to biomass burning are considered to be neutral. Reduced emissions of SO₂, as a result of the low sulfur content of biomass and a positive effect on NO_x emissions. Reduction of the dependence on fossil fuels by using local agricultural and forest waste. An increase in operation flexibility with respect to plants that burn only biomass. The major drawbacks are the cost of additional facilities and potential negative effects of biomass burning, such as decreased performance, increased corrosion and increased fouling [2]. The intrinsic heterogeneity of the biomass increases the complexity to define systems that allow an objective knowledge of their technical characteristics. The types of biomass are analyzed in the study of diverse backgrounds, variable presentation and packaging of different forms. There are extensive published data [8-11] on different sampling methods to provide answers to the problems associated with the materials on which this work is based. A sampling theory should be suitable to answer the questions of how to select a sample and how much material must be taken [8]. It is often necessary to obtain small samples from large lots. These great reductions require a careful sampling and sample reduction. Some of the most important factors to consider working with solid materials are the phenomena of

segregation and stratification (fig 1) [10]. A good sampling method should be able to get a representative sample without the influence of these phenomena. In order to know their technical characteristics, a study method was designed. In this method each material with different origins, appearance or packaging, is considered as a lot.

The moisture content and ash of solid biomass are chosen for the study; moisture as a feature related to the material and processes for storage, as well as environmental conditions and ashes as a feature associated with the material.

The objectives of this work are find out the values of moisture and ash contents of each lot tested, as well as the uncertainty associated with the number of samples. Once the above parameters are known, the minimum number of samples required for an error and a given level of reliability will be determined. Moisture content influences the low heating value, which affects the performance of the device, and the ashes are critical to the effects of fouling and corrosion of heat exchangers [2, 12-14].

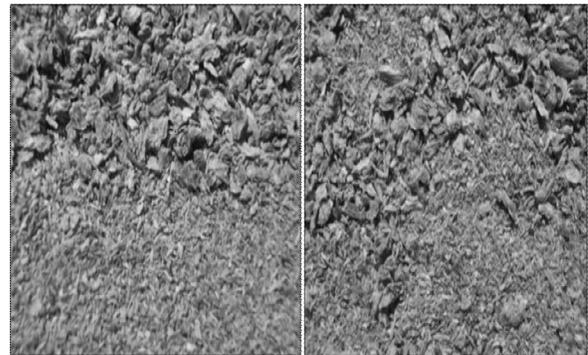


Figure 1. Different segregation states for the same sample. The left picture shows a high degree of segregation. The image on the right shows the opposite case

2. METHODOLOGY

2.1 Materials

Materials from agriculture and forestry were selected for the study, covering a broad spectrum of solid biomass which could be used as fuel in

processes of co-combustion. The materials of agricultural origin were stored in big-bags. The materials of forest origin pellets were stored in sacks.

The materials of agricultural origin selected were: pine kernel shell, almond shells, hazelnut shell and crush olive stones. The materials of forest origin were selected as follows: Pellets of pine, oak pellets, brasic pellets and poplar pellet.

2.2 Sampling

Samples of various materials were obtained through a tube sampler design. The tube sampler used was built with the intention of being able to use the types and presentations of biomass and bulk pellets which are studied in this work. This design also takes into account that these materials were supplied in sacks or pallets of big-bag. It is considered that the nominal

maximum size "d" of the material sampled is 0.02 m [15], so the tube sampler should have an increased ability to collect no less than [16]:

$$V_{\min} = 0.05 \cdot d = 0.05 \cdot 20 = 1 \text{ dm}^3 = 10^{-3} \cdot \text{m}^3$$

The tube sampler is composed of three parts (see fig 2). The first part is the outer tube which presents a series of six holes; each rotated 30 degrees to the previous hole. The holes are 80x30mm and the greatest dimension is in the direction of the axis. The second piece is the inner tube which can be rotated within the outer tube which enables the holes to be closed while the tube is inserted in the sample, and then opened when the device is in the correct position for collecting the sample. The third piece is joined onto the tip of the outer tube to facilitate the penetration of the device in the sack of material under study. This cone is removable for easy cleaning of the instrument. The design of this instrument is based on the standard [17] and the work of Pierre Gy [16].

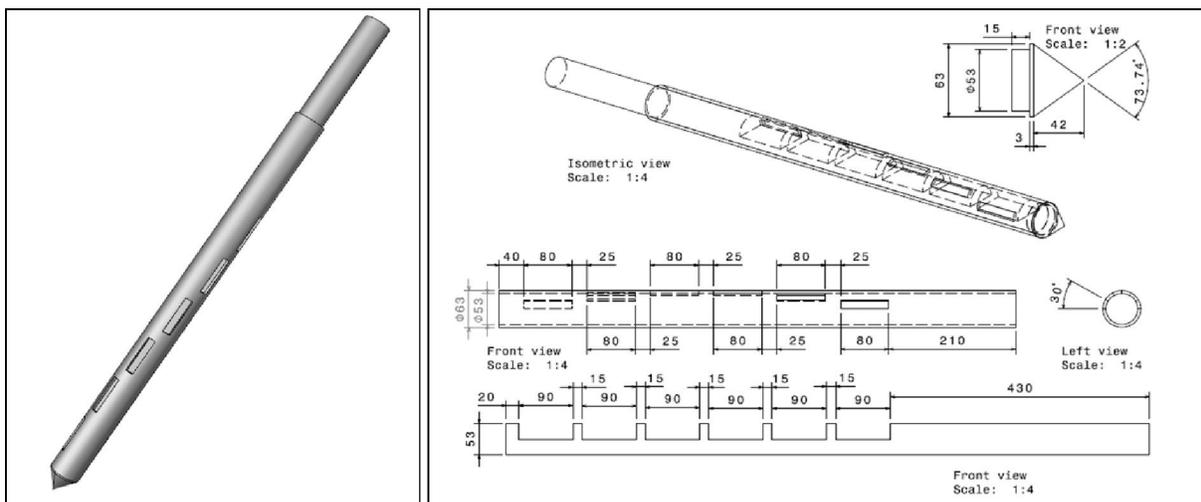


Figure 2. 3D picture and drawing of the tube sampler

2.2.1 Procedure for lots in big-bag

9 samples of approximately 10^{-3} m^3 volume were extracted [17]. The upper surface of the big-bag, which is circular, is divided into 8 equal circles. Samples were removed from each circular sector by introducing a tube sampler at 2/3 from the centre. The sample n° 9 was removed from the centre of the big-bag.

2.2.2 Procedure for lots in bags of pellets

Samples of about 10^{-3} m^3 volume of each of the 5 bags were selected using a table of random numbers [17]. Samples were obtained by firstly introducing the tube sampler from a corner of the bag to the opposite corner below and secondly from opposite corners in the other direction. The two samples from each bag were mixed and

stored in the same bottle, thereby obtaining five bottles of each sample material.

In the case of pellets of pine and oak the process was analogous but samples from the same bag were not mixed, therefore ten sample bottles were obtained. The bottles used to store the samples are made of polypropylene, wide-necked with a lid and screw top and therefore air tight.

2.3 Reduction of the samples

For samples that were subjected to laboratory tests, it was necessary to reduce their size; the process was the same for all samples.

1. The selected samples were completely ground in a RETSCH SM-100 grinder, using a 6 mm nominal square step sieve. This filter was chosen because there are studies that indicate that for cocombustión this particle size is sufficient even with pulverized coal [18, 19]. The olive stone samples do not receive this treatment because they are already crushed when delivered. The ground samples were stored back in the original bottles.

2. The sample is divided in similar parts using a slotted box, called a Boerner divider, which separates them into smaller samples. In Table 1 rounded average weights of the samples selected for analysis of each material are shown. Once a sample is selected, it is separated by half. One part is subjected to testing in order to determine the moisture content and the other is stored.

Table 1. Rounded average weight of the samples

MATERIAL	WEIGHT OF LABORATORY SAMPLE	
	Moisture	Ashes
Hazelnut Shell (Hs.)	$21.7 \cdot 10^{-3}$ kg	$8.5 \cdot 10^{-3}$ kg
Pine nut Shell (Pns.)	$17.9 \cdot 10^{-3}$ kg	$6.8 \cdot 10^{-3}$ kg
Almond Shell (As.)	$23.9 \cdot 10^{-3}$ kg	$9.2 \cdot 10^{-3}$ kg
Grinded olive stones (Gos.)	$18.1 \cdot 10^{-3}$ kg	$7.8 \cdot 10^{-3}$ kg
Poplar pellets (Pp.)	$14.0 \cdot 10^{-3}$ kg	$8.2 \cdot 10^{-3}$ kg
Brásica pellets (Bp.)	$13.9 \cdot 10^{-3}$ kg	$3.1 \cdot 10^{-3}$ kg
Oak pellets (Op.)	$21.7 \cdot 10^{-3}$ kg	$8.8 \cdot 10^{-3}$ kg
Pine pellets (Pin)	$19.0 \cdot 10^{-3}$ kg	$10.1 \cdot 10^{-3}$ kg

3. The determination of moisture content was carried out. Dry samples were returned to the bag from which the sample for the ash test was

obtained. Before testing, the sample was ground in a mill with IKA MF 10.2, with an impact grinding head, producing a particle size less than $3 \cdot 10^{-3}$ m, to determine the ash content.

4. The sample obtained in the previous step is divided into two parts, one of which is sealed in a bag, and the other used to determine the ash content.

3. TESTS

3.1 Moisture

The method used is oven drying (Nabertherm) of the wet sample obtained by the reduction procedure described above. Aluminium trays with an interior diameter of 0.093 m which have no corrosion phenomena and no moisture adsorption, are used.

The samples are weighed using the “Great Series VXI-110” scales with 0.100 kg maximum and precision of 10^{-8} kg. The empty tray is weighed. Then the sample is uniformly distributed over the surface of the tray with about 10^{-3} kg/ 10^{-4} m². The weighed samples of each material are simultaneously introduced in the oven at a temperature of 105°C. The time spent on stabilising these conditions is 180 minutes to ensure constant mass. Moisture content on wet basis (M_{ar}) is obtained by the following expression [20].

$$M_{ar} = \frac{(m_2 - m_3) - (m_4 - m_5) + m_6}{(m_2 - m_1)} \cdot 100 \quad (1)$$

Where the different m_i (10^{-3} kg) indicate:

m_1 : Empty tray.

m_2 : Tray and sample before drying.

m_3 : Tray and sample after drying.

m_4 : Reference tray at room temperature before drying.

m_5 : Tray after drying when reference is still hot.

m_6 : Moisture packing where applicable.

3.2 Ashes

The ash are known as the inorganic mass residue which remains after combustion of a biofuel sample at a controlled temperature of $550 \pm 10^\circ\text{C}$

in air oven until the constant mass is established [21]. To set up the tests, crucibles with composition SiO_2 and Al_2O_3 were used as recipients. Their properties are chemical stability, low mechanical strength expansion at high temperature and thermal shock resistance [22]. The sample covers the surface of the container in a proportion equal to, or less than, $10^{-4} \text{ kg}/10^{-4} \text{ m}^2$, the smallest amount tested is 10^{-3} kg . To weigh the samples, scales with precision of 10^{-8} kg were used. The sample was grinded and passed through the 3 MF 3 mm sieve. Before starting the tests, the crucibles were placed in the oven at $550 \pm 10^\circ\text{C}$ for 60 min. The sample was introduced into the crucible and uniformly distributed over the bottom surface. The dry sample and crucible were weighed and then put into the oven when cold in order to start the test. A heating rate of $5^\circ\text{C}/\text{min}$ to 250°C was programmed. Once finished, the temperature was kept at 250°C for 60 min to evaporate the volatiles. With the same heating rate, the temperature increases to $550 \pm 10^\circ\text{C}$ and is maintained for 360 min. The ash content in dry basis, A_d , is calculated by [21].

$$A_d = \frac{(m_3 - m_1)}{(m_2 - m_1)} \cdot 100 \quad (2)$$

Where the different m_i (10^{-3} kg) indicate:

m_1 : empty crucible.

m_2 : crucible and sample.

m_3 : crucible and ash.

4. STATISTICAL TREATMENT

Lots of a large number of unspecified random units, with unit masses more or less uniform (with a tolerance of approximately 20%) and assumed to be independent of each other can be considered as zero-dimensional objects. Using the sampling procedure described, a sample of the total lot or package of material, L , is chosen. M_L is the mass of the lot and M_m is the mass of the sample ($M_m \leq M_L$). F_i denotes the minimum fragment or sampling unit, and N_F the number of fragments that form the lot. Each F_i has a probability P_i of being included in the sample. If the sampling procedure is suitable, the value of concentration of component A in the sample, a_m , is a good estimate of a_L (good estimate refers to

minimizing some error criteria). Ultimately, the goal is to estimate the value of unknown concentration a_L of component A . A is the critical component that is often described by their concentration or percentage a . In a zero-dimensional lot, a sample may consist of fragments F_i independently selected previously. This type of sampling, known as simple random sampling, verifies that the probability $P_i = P = 1/N_F$ is constant. Another type of sampling, which is also very common, is one in which groups of neighbouring fragments are removed from the lot, G_n . In this second case the probability that a group be included in the sample, P_n , is the one which remains constant: $P = P_n = 1/N_G$, where N_G is the number of groups that comprise the lot L . Under the assumption that the sampling procedure is correct, the sampling error, SE , can be expressed as the sum of two components: the fundamental error, FE , and the segregation and grouping error, SGE . Moreover, as these two errors are independent, the following relationship between their variances $\sigma^2(SE) = \sigma^2(FE) + \sigma^2(SGE)$ is verified.

4.1 Definition of fundamental error FE

The fundamental error is related to the constitution heterogeneity, CH_L , and occurs when the sampling units of the lot that are withdrawn, L , are fragments F_i . These units have also been collected after a properly-designed and undertaken sampling process. The FE is never be zero, but it is the minimum sampling error that can be made. The constitutional heterogeneity is an intrinsic property of the lot, a material property, and is calculated as an average of squared errors:

$$CH_L = \frac{1}{N_F} \sum_{i=1}^{N_F} \left(\frac{a_i - a_L}{a_L} \right)^2 \quad (3)$$

Where a_i is the concentration of component A in an F_i fragment and $(a_i - a_L)/a_L$ is a random variable, called sampling error, which represents the deviation of the concentration of components in the fraction F_i , as a proportion of the total concentration of lot L . The variance of the fundamental error can be expressed as:

$$\sigma^2(FE) = \left(\frac{1}{M_m} - \frac{1}{M_L} \right) \times HI_L \quad (4)$$

where $HI_L = CH_L \cdot M_L / N_F$ is the heterogeneity invariant. Taking into account the expression of HI_L and knowing that $M_L = M_i \cdot N_F$, then:

$$HI_L = \frac{1}{N_F} \sum_{i=1}^{N_F} \left(\frac{a_i - a_L}{a_L} \right)^2 \frac{M_L}{N_F} = \frac{1}{N_F} \sum_{i=1}^{N_F} \left(\frac{a_i - a_L}{a_L} \right)^2 M_i \quad (5)$$

$$\sigma^2(FE) = \left(\frac{1}{M_m} - \frac{1}{M_L} \right) \times \frac{1}{N_F} \sum_{i=1}^{N_F} \left(\frac{a_i - a_L}{a_L} \right)^2 M_i \quad (6)$$

In view of the above expressions, it is easy to deduce that $\sigma^2(FE)$ is zero if, and only if, some of the following two conditions holds: the sample is the whole lot, $M_m = M_L$, or the material is completely homogeneous, which means that: $a_i = a_L$, $\forall i=1, 2, \dots, N_F$.

4.2 Definition of the segregation and grouping error SGE

The grouping and segregation error is related to the distribution heterogeneity, which, like the above mentioned, occurs when the elements F_i of the sample are not chosen independently with equal probability, but the F_i elements are selected from the G_n groups. These groups have the same probability of being selected, $P_n = P = 1/N_G$.

$$DH_L = \frac{1}{N_G} \sum_{n=1}^{N_G} \left(\frac{a_n - a_L}{a_L} \right)^2 \quad (7)$$

with a_n the concentration of component A in a G_n group. There is a relationship between the constitution and the distribution heterogeneity:

$$DH_L = CH_L \frac{1+YZ}{1+Y} \quad (8)$$

Y and Z are nondimensional parameters which characterize the size of groups and distribution of components in the lot, respectively. Since $Y \geq 0$ and $0 \leq Z \leq 1$ then, $0 \leq DH_L \leq CH_L$ is assured.

4.3 Bounding the variance of sampling error:

Even when the sample is well-chosen, there are still two types of error: the fundamental error,

caused by the constitutional heterogeneity, and the segregation and grouping error, caused by the distribution heterogeneity. The sampling error is then: $SE = FE + SGE$.

Since both errors are independent, the variance of the sampling error can be expressed as the sum of the variances: $\sigma^2(SE) = \sigma^2(FE) + \sigma^2(SGE)$. The variance of the grouping and segregation error cannot be calculated, but as the relationship: $0 \leq \sigma^2(SGE) \leq \sigma^2(FE)$ is verified, we can deduce that: $\sigma^2(FE) \leq \sigma^2(SE) \leq 2\sigma^2(FE)$. Assuming that the sampling error follows a normal distribution, i.e.: $SE \sim N(0, \sigma(SE))$, we can ensure with a confidence level of 95%:

$$|SE| \leq 1,96 \sigma(SE) \leq 1,96 \sqrt{2} \sigma(FE) = 1,96 \sqrt{2} \sqrt{\left(\frac{1}{M_m} - \frac{1}{M_L} \right) HI_L} \quad (9)$$

Finally, assuming that $M_m \ll M_L$, it is easy to show:

$$|SE| \leq 1,96 \sqrt{\frac{2HI_L}{M_m}} \quad (10)$$

The following conclusions can be inferred from the above equation, with a confidence level of 95%:

1. If the mass of the sample is constant, the sampling error has an upper bound of a maximum sampling error given by:

$$|SE| \leq SE_{\max} = 1,96 \sqrt{\frac{2HI_L}{M_m}} \quad (11)$$

2. If we set a maximum sampling error, the mass of the sample should be:

$$M_m \geq 7,68 \frac{HI_L}{SE_{\max}^2} \quad (12)$$

3. Regardless of the material, a direct relationship between increases in the maximum error of sampling and the mass of the sample is observed:

$$SE_{\max}(1 - \Delta_{SE}) = 1,96 \sqrt{\frac{2HI_L}{M_m(1 + \Delta_M)}} \Rightarrow \Delta_{SE} = 1 - \sqrt{\frac{1}{1 + \Delta_M}} \quad (13)$$

For example, an increase of 50% mass reduction of the sample represents a maximum sampling error of 18.35%.

4. By setting a maximum error and considering a constant sample mass, we can ask wonder about what is the effect of the fragment size F_i on the sampling error. Logic suggests that using a single piece of mass $M_i=M_m$ is not the same as doing it with a number k , $k \in N$, $k>1$ of fragments of mass $M_i= M_m/k$. In fact, it can be shown that by increasing the number of elements included in the sample, even when M_m remains constant, the maximum value of the sampling error is reduced. This result is a consequence of the heterogeneity invariant, HI_L , which is a function of the number of fragments that constitute the sample and varies according to the type of material, but it is not the function of the mass sample M_m . Thus, if we divide each fragment into k , smaller fragments then $M'_i =M_i/k$, $N'_F=k \times N_F$. Using the HI_L expression and assuming that the concentration of the new fragments, a'_i is similar to that of the original fragment $a'_i \approx a$, then the heterogeneity invariant in the new fragment is calculated as:

$$HI'_L = \frac{1}{N'_F} \sum_{i=1}^{N'_F} \left(\frac{a'_i - a_L}{a_L} \right)^2 M'_i \approx \frac{1}{k \times N_F} \sum_{i=1}^{k \times N_F} \left(\frac{a_i - a_L}{a_L} \right)^2 M_i = \frac{1}{k \times N_F} \sum_{i=1}^{N_F} \left(\frac{a_i - a_L}{a_L} \right)^2 M_i = \frac{1}{k} \times HI_L \quad (14)$$

So, the sampling error has an upper limit calculated as:

$$|SE'| \leq 1,96 \sqrt{\frac{2HI'_L}{M_m}} \approx \frac{1}{\sqrt{k}} SE_{\max} \quad (15)$$

and it can be seen that when k tends to infinity, the sampling error tends to zero.

4.4 Application to biomass data

Following [23], HI_L can be estimated from a sample obtained by simple random sampling, provided that the number of fragments in the sample, N_m , is big enough:

$$HI_L \approx HI_m = \frac{1}{N_m} \sum_{i=1}^{N_m} \left(\frac{a_i - a_m}{a_m} \right)^2 M_i \quad (16)$$

where a_m , the concentration of component in the sample, is obtained by averaging the concentrations of the extracts:

$$a_m = \frac{1}{N_m} \sum_{i=1}^{N_m} a_i \quad (17)$$

For the calculations shown below, the mass of the fragment is assumed as a dimensionless unit of mass $M_i=1$, so that the mass sample is represented as sampling units N_m .

Table 2. Values of moisture and ash in % for each material tested

Material	Property	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
Hs	Moisture	12.264	12.054	11.961	12.189	11.875	12.075	11.997	12.038	11.933	
	Ashes	1.181	0.998	1.064	1.088	1.017	1.129	1.138	1.306	1.0553	
Pns	Moisture	12.062	12.101	12.184	12.418	12.207	12.695	12.700	12.683	12154	
	Ashes	1.430	1.438	1.378	1.277	1.333	1.252	1.263	1.248	1.243	
As	Moisture	12.621	12.631	12.562	12.628	12.532	12.588	12.642	12.643	12.498	
	Ashes	0.982	1.233	1.784	1.428	0.972	1.025	1.351	0.918	0.855	
Gos	Moisture	12.628	12.658	12.811	12.393	12.416	12.623	12.698	12.763	12.594	
	Ashes	0.546	0.573	0.556	0.515	0.525	0.531	0.575	0.544	0.591	
Pp	Moisture	8.024	8.044	7.700	7.816	8.016					
	Ashes	2725	3.054	3.203	2.856	3.039					
Bp	Moisture	10.301	9.906	10.344	10.004	10.070					
	Ashes	9.925	9.775	9.402	9.809	9.745					
Op	Moisture	7.568	7.515	7.479	7.742	7594	7.549	7.182	7.301	7.674	7.452
	Ashes	0.761	0.780	0.768	0.766	0.763	0.806	0.811	0.799	0.796	0.751
Pin	Moisture	7.349	7.208	7.605	7.448	7.287	7.365	7.062	7.694	7.411	7.347
	Ashes	0.520	0.523	0.475	0.524	0.530	0.523	0.516	0,493	0.529	0.522

5. RESULTS

Table 2, shows the values of moisture in % and ash for each material tested.

The medium, maximum, and minimum value of moisture and ash content in %, are shown respectively in figure 3.

The moisture value observed in hazelnut shell, pine nut, almond and olive stones, is similar. These materials were presented in big-bag. The pellets presented in sacks, also have humidity values, with the exception of brassica pellets, which contain a higher percentage of humidity. The high ash content in the brassica pellets is significant. The results also show a significant uniformity in the average values of the ashes of hazelnut shells (1.10%), pinion (1.32%) and almond (1.17%). The lowest ash percentage is found in oak, olive stones and pine pellets. These values make these pellets best suited for burning in boilers. In poplar pellets, a high ash value, was found. Figure 4 illustrates the values of the variances of moisture and ash for the materials studied.

By analyzing the value of the variances of moisture and ash obtained for the different materials, we can conclude that the sampling plans should take into account what the properties to be studied are, as well as their accuracy and reliability. For example, materials like olive stone, pellets of pine and oak have a very low variance for the ashes, but, on the other hand, have significant values for the moisture content. It can also be seen that the values obtained for the variances of moisture and ash, indicate that there are independent variables. A surprising case is that of almond shell and pine, which show very contrasting values of variance for the two properties. This fact requires different sampling plans, if we want to obtain the same accuracy and reliability in the results. As the moisture of the material depends on its own characteristics and external actions to which it was subjected, a greater value for their variances was expected, than the variances associated with the ashes. This hypothesis was confirmed in only five of the materials.

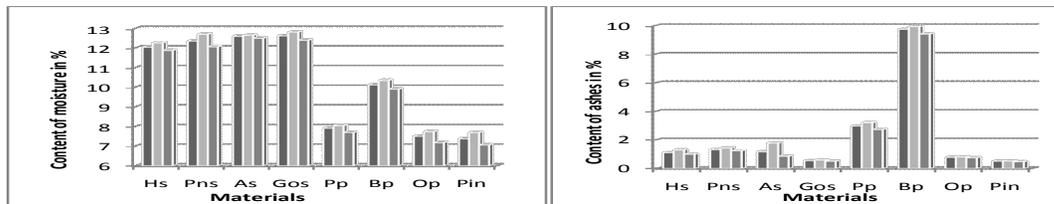


Figure 3. Medium, minimum and maximum values (%) of moisture content and ash

Table 3. Values for the intrinsic heterogeneity of moisture and ash concentrations observed in different biomass materials

	HI_L	
	Moisture	Ashes
Hs	$9.21 \cdot 10^{-05}$	$6.46 \cdot 10^{-03}$
Pns	$4.28 \cdot 10^{-04}$	$3.20 \cdot 10^{-03}$
As	$1.55 \cdot 10^{-05}$	$5.97 \cdot 10^{-02}$
Gos	$1.11 \cdot 10^{-04}$	$1.86 \cdot 10^{-03}$
Pp	$3.02 \cdot 10^{-04}$	$3.14 \cdot 10^{-03}$
Bp	$2.81 \cdot 10^{-04}$	$3.25 \cdot 10^{-04}$
Op	$4.40 \cdot 10^{-04}$	$6.71 \cdot 10^{-04}$
Pin	$5.44 \cdot 10^{-04}$	$1.05 \cdot 10^{-03}$

By applying the statistical treatment described above to the sample data, the values of HI_L shown in Table 3 are obtained.

With these values, it can be deduced that the maximum sampling error for a fixed sample mass and the mass of a minimum sample size has a fixed sampling error. These results are given in Tables 4 and 5, for data of humidity, and Tables 6 and 7 for details of ashes. With these Tables, it is possible to determine the maximum permissible error for a sample size, which is necessary for the determination of moisture and ash respectively (Tables 4 and 6), or alternatively, for a predetermined sample size, the maximum error made can be determined.

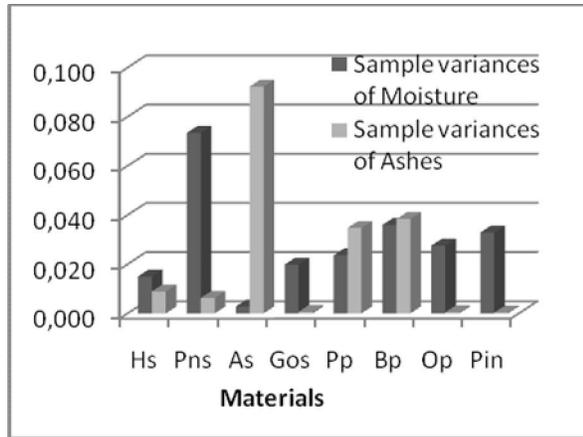


Figure 4. Variances of moisture and ash

The sampling errors have a certain correlation with the results of variance in Figure 4. Those materials with large sample variance will, in general, have a higher sampling error. In the case of the correlation between the moisture sampling error (Tables 4-7) and sample variance (Fig. 4) it is 0.69. In the case of ash, the correlation increases to 0.85. Then, it can be deduced that the sample variance is a more qualitative than quantitative indication of the sampling errors,

but in no case, can be estimated. The perfect correlation (1.00) exists between the coefficient of variation (sample standard deviation between sample mean) and the sampling error.

6. CONCLUSIONS

In determining properties of a lot, a sampling plan for each property to be studied should be designed and the sampling error that is made with the chosen sampling process should be determined. This is crucial in order to discover the subsequent propagation of error in future calculations with the set property value. In particular, biomass fuels, despite being heterogeneous materials, with an appropriate sampling procedure, the experimental error associated with different properties, can be reasonably limited. In other words, we can say that, despite the heterogeneity of the fuel itself, a well-planned campaign of samples can extrapolate the properties of the samples from the entire lot with a controlled, analyzed and quantified uncertainty.

Table 4. Moisture. Minimum sample mass, expressed as N_m sampling units, sampling error for a determined maximum sampling error

		Minimum Simple size for a determined maximum sampling error							
		Hs	Pns	As	Gos	Pp	Bp	Op	Pin
HI_L		$9.21 \cdot 10^{-05}$	$4.28 \cdot 10^{-04}$	$1.55 \cdot 10^{-05}$	$1.11 \cdot 10^{-04}$	$3.02 \cdot 10^{-04}$	$2.81 \cdot 10^{-04}$	$4.40 \cdot 10^{-04}$	$5.44 \cdot 10^{-04}$
Maximum error	0.001	707.66	3286.59	119.00	850.23	2317.20	2160.77	3382.87	4180.88
	0.005	28.31	131.46	4.76	34.01	92.69	86.43	135.31	167.24
	0.01	7.08	32.87	1.19	8.50	23.17	21.61	33.83	41.81
	0.05	0.28	1.31	0.05	0.34	0.93	0.86	1.35	1.67

Table 5. Moisture maximum sampling error for a simple mass, expressed as N_m sampling determined units

		Maximum error for the simple size							
		Hs	Pns	As	Gos	Pp	Bp	Op	Pin
HI_L		$9.21 \cdot 10^{-05}$	$4.28 \cdot 10^{-04}$	$1.55 \cdot 10^{-05}$	$1.11 \cdot 10^{-04}$	$3.02 \cdot 10^{-04}$	$2.81 \cdot 10^{-04}$	$4.40 \cdot 10^{-04}$	$5.44 \cdot 10^{-04}$
Sample size	1	$2.66 \cdot 10^{-02}$	$5.73 \cdot 10^{-02}$	$1.09 \cdot 10^{-02}$	$2.92 \cdot 10^{-02}$	$4.81 \cdot 10^{-02}$	$4.65 \cdot 10^{-02}$	$5.82 \cdot 10^{-02}$	$6.47 \cdot 10^{-02}$
	10	$8.41 \cdot 10^{-03}$	$1.81 \cdot 10^{-02}$	$3.45 \cdot 10^{-03}$	$9.22 \cdot 10^{-03}$	$1.52 \cdot 10^{-02}$	$1.47 \cdot 10^{-02}$	$1.84 \cdot 10^{-02}$	$2.04 \cdot 10^{-02}$
	100	$2.66 \cdot 10^{-03}$	$5.73 \cdot 10^{-03}$	$1.09 \cdot 10^{-03}$	$2.92 \cdot 10^{-03}$	$4.81 \cdot 10^{-03}$	$4.65 \cdot 10^{-03}$	$5.82 \cdot 10^{-03}$	$6.47 \cdot 10^{-03}$
	200	$1.88 \cdot 10^{-03}$	$4.05 \cdot 10^{-03}$	$7.71 \cdot 10^{-04}$	$2.06 \cdot 10^{-03}$	$3.40 \cdot 10^{-03}$	$3.29 \cdot 10^{-03}$	$4.11 \cdot 10^{-03}$	$4.57 \cdot 10^{-03}$

Table 6. Ashes. Minimum sample mass, expressed as N_m sampling units, sampling error for a determined maximum sampling error

		Minimum Simple size for a determined maximum sampling error							
		Hs	Pns	As	Gos	Pp	Bp	Op	Pin
HI_L		$6.46 \cdot 10^{-03}$	$3.20 \cdot 10^{-03}$	$5.97 \cdot 10^{-02}$	$1.86 \cdot 10^{-03}$	$3.14 \cdot 10^{-03}$	$3.25 \cdot 10^{-04}$	$6.71 \cdot 10^{-04}$	$1.05 \cdot 10^{-03}$
Maximum error	0.001	49636.02	24610.14	458536.03	14276.25	24128.00	2493.56	10594.04	8080.74
	0.005	1985.44	984.41	18341.44	571.05	965.12	99.74	423.76	323.23
	0.01	496.36	246.10	4585.36	142.76	241.28	24.94	105.94	80.81
	0.05	19.85	9.84	183.41	5.71	9.65	1.00	4.24	3.23

Table 7. Ashes maximum sampling error for a simple mass, expressed as N_m sampling determined units

		Maximum error for the simple size							
		Hs	Pns	As	Gos	Pp	Bp	Op	Pin
HI_L		$6.46 \cdot 10^{-03}$	$3.20 \cdot 10^{-03}$	$5.97 \cdot 10^{-02}$	$1.86 \cdot 10^{-03}$	$3.14 \cdot 10^{-03}$	$3.25 \cdot 10^{-04}$	$6.71 \cdot 10^{-04}$	$1.05 \cdot 10^{-03}$
Sample size	1	$2.23 \cdot 10^{-01}$	$1.57 \cdot 10^{-01}$	$6.77 \cdot 10^{-01}$	$1.19 \cdot 10^{-01}$	$1.55 \cdot 10^{-01}$	$4.99 \cdot 10^{-02}$	$7.18 \cdot 10^{-02}$	$8.99 \cdot 10^{-02}$
	10	$7.05 \cdot 10^{-02}$	$4.96 \cdot 10^{-02}$	$2.14 \cdot 10^{-01}$	$3.78 \cdot 10^{-02}$	$4.91 \cdot 10^{-02}$	$1.58 \cdot 10^{-02}$	$2.27 \cdot 10^{-02}$	$2.84 \cdot 10^{-02}$
	100	$2.23 \cdot 10^{-02}$	$1.57 \cdot 10^{-02}$	$6.77 \cdot 10^{-02}$	$1.19 \cdot 10^{-02}$	$1.55 \cdot 10^{-02}$	$4.99 \cdot 10^{-03}$	$7.18 \cdot 10^{-03}$	$8.99 \cdot 10^{-03}$
	200	$1.58 \cdot 10^{-02}$	$1.11 \cdot 10^{-02}$	$4.79 \cdot 10^{-02}$	$8.45 \cdot 10^{-03}$	$1.10 \cdot 10^{-02}$	$3.53 \cdot 10^{-03}$	$5.08 \cdot 10^{-03}$	$6.36 \cdot 10^{-03}$

In this work, it can be seen that, despite the fact that the sample variance of a property of a material is an indication of the level of heterogeneity, this does not accurately quantify the error committed. To do this, a determination of the statistical uncertainty associated with this property, which allows us to quantify this error precisely, is necessary.

Eight biomass fuels and a map of sampling to determine the sample sizes in the light of the uncertainties which are considered acceptable and vice versa have been established. These techniques, the sampling procedure and statistical determination, can be extrapolated to any solid material in granular form with approximately homogeneous sizes.

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