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DEVELOPMENT OF BIOMASS FAST PROXIMATE ANALYSIS BY THERMOGRAVIMETRIC SCALE

B. Velázquez- Martí[1], J. Gaibor-Chávez[2] I. Z. Niño-Ruiz[2], E. Cortés-Rojas[2]

1) Departamento de Ingeniería Rural y Agroalimentaria. Universitat Politècnica de Valencia. Camino de Vera s/n, 46022 Valencia (España)

2) Grupo de Biomasa. Centro de Investigación de Ambiente, Departamento de Investigación. Universidad Estatal de Bolívar. Guaranda (Ecuador)

Abstract

EN norms set the methods for determining the ash and volatile content in biomass. These establish the use of a muffle to heat the samples at temperatures of 550ºC and 900ºC respectively, with a minimum analysis time of 4h as standard method. The objective of this work was to reduce significantly the analysis times, making very short heating periods using a thermogravimetric scale (TGA), and to apply an equation to the residual weight to obtain the weight of ash, volatiles and fixed carbon in biomass samples. We analyzed the factors: the temperature ramp, atmosphere and airflow in the determination. In this work new validated methods were developed with an analysis time of 10-20 min.

Keywords: biomass, biofuel, pruning residues, energy wood

INTRODUCTION

The use of thermogravimetric scales in the characterization of biomass is a technique that is widely used in laboratories [1-2]. The thermogravimetric analysis evaluates the loss of weight of a sample when the temperature is increased in a controlled atmosphere. This can be an oxidizing atmosphere (air) or an inert atmosphere (Nitrogen or Helium).

Current equipment allows setting the method of each experiment. A method of analysis fixes the ramp of temperature increase (R K/min), which can be performed in one or several stages or segments, intercalating constant temperature periods [3]. On the other hand, each method allows to fix an injection of a gas flow on the sample in each segment. This programming capability of the different stages of the process allows to devise more versatile and fast methods than those established in the norms for the proximate analysis of biomass, whose objective is to determine the amount of ash, volatile and fixed carbon [4].

EN-ISO 18122: 2015 [5] establishes the method for the determination of ash in solid biofuels. This standard method was developed by the Technical Committee CEN/TC 335 of the European Committee for Standardization. The sample requires a minimum mass of 1 g which must be pre-dried in an oven at 105°C for 1 h. Once dried, the sample is introduced into the muffle, where temperature is uniformly raised to 250°C for a period of between 30 min and 50 min (i.e. with a rise between 4.5°C/min and 7.5°C/min). Then, this temperature is maintained for 60 min to allow volatiles being evaporated before ignition. Subsequently the temperature in the oven is continuously raised to 550±10°C for a period of 30 min, or an elevation of 10°C/min, and this temperature is maintained for at least 120 min. By counting the time required in the different segments, the minimum test duration for ash determination is 40 + 60 + 30 + 120 = 250 min.

EN-ISO 18123:2015 [6] establishes the method for the determination of volatile matter in solid biofuels. This was also developed by the Technical Committee CEN/TC 335 of the European Committee for Standardization. According to the established procedure, the sample of at least 1 g in a ceramic crucible with a lid, without contact with ambient air, is heated to 900 ºC ± 10ºC for 7 min. The percentage of volatile matter is calculated from the mass loss of the test portion after deduction of the mass loss due to moisture. The disadvantage of the application of this method in muffle is the control of the increase of temperature and the withdrawal of the sample at 900ºC. To remove the sample it is necessary to wait for muffle cooling, which can distort the measurement.

The objective of this work was to analyze the factors: the velocity of temperature increase, atmosphere and airflow in the determination of content of ash, volatile, and fixed carbon in biomass samples by means of thermogravimetric balance (TGA) to reduce the time of analysis in the laboratory. Some investigations have proposed methods of proximate analysis with TGA. Torcuato et al. (2017) [7] found, using a series of thermogravimetric methodologies, that heating rate and particle size are important factors to be taken into account, whereas temperature and carrier gas (type and flow rate) are critical to enable the proper quantification of volatiles and fixed carbon. In their experiments, the best condition was achieved by applying 600ºC and CO2 as carrier gas (instead of N_2). It is the highlight of the proposal method regarding the conditions often applied for this purpose. Furthermore, this method has proved to be advantageous in three important aspects: A single measurement is enough for quantification of all properties, it can be performed in a short time (1 h 27 min) in comparison with methods performed in a muffle furnace, and it can be applied for different kinds of biomasses, from lignocellulosic to residue. However García et al. (2013) [8] had proposed a 25 min-last thermogravimetric method as a tool to determine biomass sample's proximate analysis data (moisture, ash, volatile matter and fixed carbon contents) just by direct measure of weight changes on each sample's TG chart. We in this work have taken up the idea of García et al. (2013), but started from the hypothesis that if the sample is subjected to rapid similar temperature increases the residual weights are constant, and these are related to the residual weights obtained when the sample is subjected to slow heating processes, obtaining from them the percentage of ash, volatile and fixed carbon. This is demonstrated in this paper, our purpose being to reduce the test to 10-15 min.

MATERIALS AND METHODS

Initially ash and volatile tests were performed according to EN-ISO 18122:2015 [5] and EN-ISO 18123:2015 [6] respectively, using a muffle. The values obtained served as reference for the validation of the methods developed with TGA.

The experimental design shown in Table 1 was followed. In the experimental design, 4 factors were evaluated: On one hand, temperature increasing speed (ramp factor) at two levels, one at 25ºC/min and the other at 50ºC/min; On the other hand, atmosphere and flow factor were evaluated, also at two levels, 0 and 20 ml/s with airflow and nitrogen flow. Maximum temperature reached 550°C for ash determination, and 900°C for volatile determination. Before each test, the sample was dried in oven at 105°C following the indications of the norm ISO-EN 18134-3:2017 [9].

Evaluated materials were residual wood of the pruning of *Euphorbia lancifolia*, cultivated in the province of Bolivar in Ecuador. This is a species of special relevance in terms of its use as biomass in Ecuador as well as its medicinal applications [10-11]. This plant provides a large amount of residue, and has a great propagation capacity, with a very fast growth, both of the stem and of the branches after pruning [12-13].

The mass of each sample placed in the TGA ranged from 5 to 7 mg. Samples with different percentages of wood and leaf were evaluated: 100% wood, 90% wood-10% leaf, 80% wood-20% leaves, 70% wood-30% leaves, 60% wood-40% leaves, 50% wood -50% leaves, 100% leaves. This is very convenient because when pruning residues are used as biofuel, these residues present different percentages of leaves [14-16]. For this reason this analysis was performed.

In standard tests performed in muffle, according to EN-ISO 18122:2015 [5], the ash content was calculated according to equation (1), where m_1 is the mass of the crucible, its lid and sample before heating, in grams,; m_2 is the mass of the crucible, its lid and sample after heating, in grams,; m_{crisol} is the mass of the empty crucible and its lid, in grams.

$$\%Ash = \frac{m_2 - m_{crisol}}{m_1 - m_{crisol}} \cdot 100 \quad (1)$$

In standard tests performed in muffle, according to EN-ISO 18123:2015 [6], the content of volatile matter in each experiment was calculated according to equation (2), where m_1 is the mass of the crucible, its lid and the sample, in grams, before heating; m_2 is the mass of the crucible, its lid and the sample, in grams, after heating; m_{crisol} is the mass of the empty crucible and its lid, in grams.

$$\%volatile = \frac{m_1 - m_2}{m_1 - m_{crisol}} \cdot 100 \quad (2)$$

Fixed carbon content is obtained by difference, applying equation (3).

$$\%fixed\_carbon = 100 - \%volatile - \%Ash \quad (3)$$

To evaluate if there were influences of the factors studied (temperature, flow, atmosphere type and maximum temperature) in the calculated ash and volatiles, an analysis of variance with a 95% confidence level was performed.

For the validation of the methods with respect to the values given by the reference, tests of the paired samples, based on the Student distribution, were performed.

RESULTS AND DISCUSSION

Ash and volatiles with standardized methods

Table 1 shows the statistical description of the percentage of ash and volatiles obtained by the standardized methods EN-ISO 18122: 2015 [5] and EN-ISO 18123:2015 [6] respectively in the different sample types. The values of the asymmetry and kurtosis coefficients were within the range of -2 and +2, which means that they follow a normal distribution. It can be observed that the ash percentage of the sample with 100% wood was the lowest, with a mean of 3.93% and a standard deviation of 0.045% ash.

However, the ash percentage of samples with 100% leaves was the highest, with a mean of 10.85% and a standard deviation of 0.181% ash. It is detected that there is a linear increase in ash percentage when the percentage of leaves increases in the sample. The linear relationship is shown in Figure 1, where the equation obtained has an r^2 of 0.99. It is important to note that the overall average of all samples is 6.64% ash. This value is suggested when combusting pruning residues where the leaves have not been removed, and therefore, their content is unknown a priori.

Table 1. Statistical description of ash and volatile contents in wood and leaves mixtures analyzed with the standardized methods EN-ISO 18122: 2015 [5] and EN 15148: 2009 [4] respectively.

% leaves	*Mean (% ash)*	*Standard deviation (% ash)*	*Coefficient of variation*	*Coefficient of Skewness*	*Coefficient of Kurtosis*	*Minimum (% ash)*	*Maximum (% ash)*
0	3.93	0.045	1.16%	0.66	0.44	3.89	3.98
10	5.23	0.075	1.43%	-0.14	0.67	5.16	5.31
20	5.51	0.113	2.04%	1.21	0.97	5.44	5.64
30	6.49	0.139	2.14%	1.19	0.33	6.40	6.65
40	6.83	0.053	0.77%	1.03	0.96	6.79	6.89
50	7.63	0.047	0.62%	0.98	1.23	7.60	7.69
100	10.85	0.181	1.67%	-1.07	0.26	10.65	10.99
Total	6.64	2.102	31.66%	1.73	0.44	3.89	10.99
% leaves	*Mean (% volatile)*	*Standard deviation (% volatile)*	*Coefficient of variation*	*Coefficient of Skewness*	*Coefficient of Kurtosis*	*Minimum (% volatile)*	*Maximum (% volatile)*
0	81.88	2.14	2.61%	-0.68	0.99	79.54	83.74
10	83.16	0.79	0.95%	-1.08	0.10	82.6	83.72
20	79.71	1.46	1.83%	-0.51	-0.52	78.68	80.75
30	77.77	0.52	0.66%	-1.13	-0.14	77.18	78.14
40	78.86	2.12	2.69%	1.09	0.36	77.36	80.37
50	76.87	1.43	1.86%	0.93	1.08	75.73	78.48
100	74.61	0.12	0.15%	0.09	0.56	74.5	74.73
Total	78.72	3.03	3.85%	1.60	0.83	74.5	83.74

It is also observed that the amount of volatiles decreases slightly with the percentage of leaves in the sample. In Figure 1 it can be seen that the slope is negative but very close to zero. The linear relationship is shown in Figure 1, where the equation obtained has an r^2 of 0.72.

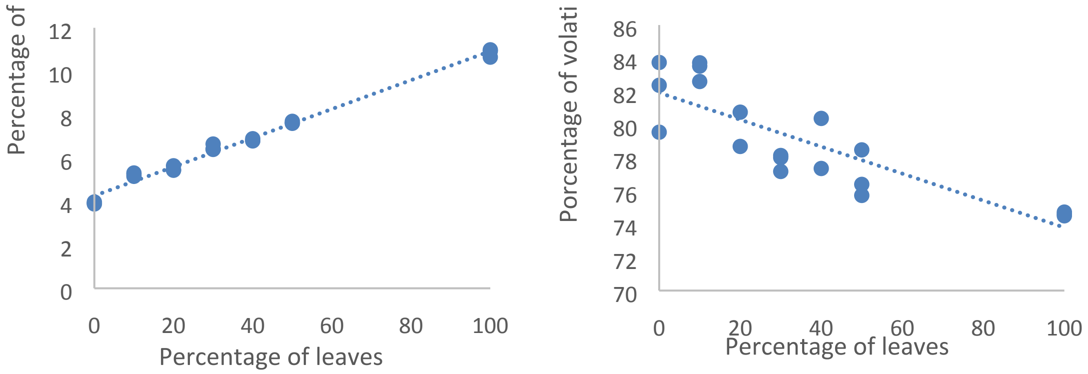

Figure 1. Variation of the percentage of ash and volatiles with the proportion of leaves

The average volatile content in the wood is 81.88% with a standard deviation of 2.14%. The average volatile content in the leaves is 74.61% with a standard deviation of 0.12%. It is detected that the standard deviations of the measurements of volatiles are significantly higher than those obtained in the determination of ash. In addition, when the relation between the percentage of leaves and the percentage of volatiles is studied, the coefficient of determination is lower. This may be due to the method of measurement of volatiles being more imprecise than that the ash method because the decrease in temperature from 900°C to room temperature influences more uncontrollably matter decomposition. It is important to note that the overall mean of all samples is 78.72% volatile. This value is suggested when pruning residues are combusted and the leaf has not been removed, therefore the leaf amount in unknown.

Determination of ash with TGA

Table 2 shows the ANOVA analysis where the influence of the factors was studied on the residual final weight obtained in each of the analysis methods for determination of ash tested with TGA: temperature increase (ramp), flow rate, atmosphere type and leaf percentage. The P-values prove the statistical significance of each of the factors. It can be seen that all factors except the type of atmosphere had significant simple effects. Since their P-values are less than 0.05, these factors have a statistically significant effect on residual weight with a 95.0% confidence level.

Table 2. Analysis of Variance (ANOVA) for residual weight of ash analysis methods with TGA

Factor	Sum of squares	Gl	Mean Square	F	P-value
MAIN EFFECTS					
A:Ramp	810.708	1	810.708	103.35	0.0000
B:Flow	357.626	1	357.626	45.59	0.0000
C:Atmosphere	16.4449	1	16.4449	2.10	0.1521
D:Leaves	4018.66	6	669.776	85.39	0.0000
INTERACTIONS					
AB	0.317138	1	0.317138	0.04	0.8412
AC	0.525523	1	0.525523	0.07	0.7965
AD	170.345	6	28.3908	3.62	0.0035
BC	658.754	1	658.754	83.98	0.0000
BD	110.036	6	18.3393	2.34	0.0408
CD	189.588	6	31.5981	4.03	0.0016
RESIDUES	549.079	70	7.84399		
TOTAL	7427.04	100			

All F-ratios are based on the mean residual error square

It is also observed that the interactions of the factors have significant influence in the results. This fact obliges us to treat all tested methods independently. It is not possible to group the results of the different methods since the results are statistically different.

Mean results obtained are shown in Table 3. It can be observed that residual weight of the sample increases when the percentage of leaves increases in all methods. An analysis of paired samples based on T-Student was performed to verify that there are significant differences between the residual weights derived from the TGA methods and the ash values obtained by the standardized method. According to this analysis, the values obtained with all methods with TGA were statistically different from the standardized method with a 95% confidence level. This means that no method is validated directly. However, it is possible to obtain precise equations that relate these values.

Table 3. Mean and standard deviation ($\overline{x} \pm \sigma$) of the different ash determination methods with TGA

			Percentage of leaves						
Ramp of temperature	Flow ml/min	Atm.	0	*10*	*20*	*30*	*40*	*50*	*100*
25ºC/min + 1min 550ºC	0	Air	1.27±0.08	3.77±0.43	4.11±0.43	10.31±0.43	6.58±0.43	13.49±0.43	22.01±0.43
50ºC/min + 1min 550ºC	0	Air	2.08±0.07	14.32±2.91	9.05±0.43	19.83±0.43	15.50±0.43	21.36±0.43	36.85±0.43
25ºC/min + 1min 550ºC	20	Air	2.88±0.10	16.91±1.28	11.56±0.43	21.41±0.43	26.03±0.43	19.81±0.43	31.19±0.43
50ºC/min + 1min 550ºC	20	Air	2.40±0.07	23.53±0.08	23.68±0.43	25.62±0.43	27.18±0.43	26.69±0.43	32.71±0.43
25ºC/min + 1min 550ºC	0	N	2.39±0.06	6.43±3.29	13.69±0.43	11.75±0.43	19.32±0.43	14.87±0.43	26.58±0.43
50ºC/min + 1min 550ºC	0	N	2.65±0.11	15.63±0.74	16.73±0.43	20.60±0.43	26.20±0.43	20.74±0.43	28.77±0.43
25ºC/min + 1min 550ºC	20	N	2.35±0.12	8.06±1.85	4.92±0.43	13.21±0.43	19.81±0.43	8.74±0.43	26.12±0.43
50ºC/min + 1min 550ºC	20	N	2.61±0.09	14.17±0.32	18.42±0.43	19.03±0.43	25.16±0.43	22.16±0.43	28.68±0.43

Figure 2 shows the decrease of the weight of the sample in relative terms (% of weight) versus temperature and time in the air atmosphere, ash determination test, without any flow. It can be observed that the profile obtained versus temperature with ramps of 25 and 50ºC/min are very similar. However, when it is plotted against time, the graphs are different. This means that the weight decrease is linked to the temperature, regardless of the speed at which it is reached.

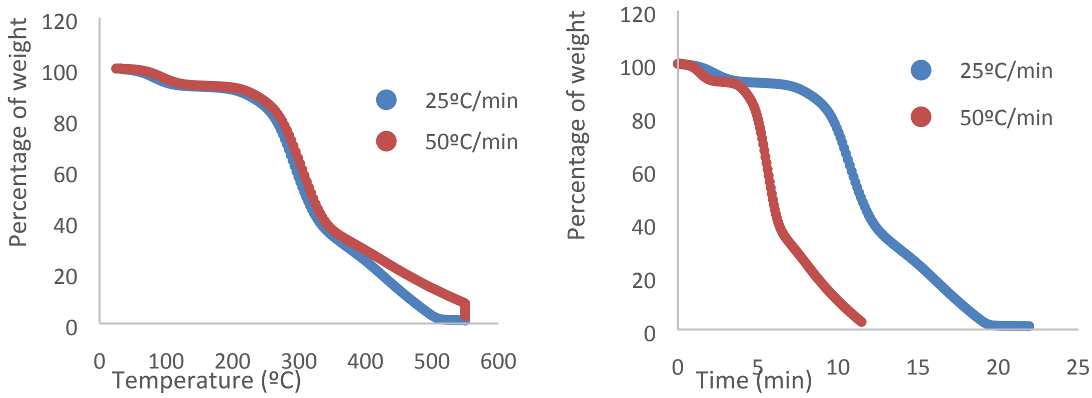

Figure 2. Variation of the weight percentage of the sample versus temperature and time in the ash determination test in air atmosphere and without any flow.

As can be seen, weight loss undergoes 4 stages. First it slowly decreases until 250°C are reached. That is at 10 min when using a 25°C/min ramp, or 5 min when using a 50°C/min ramp. Subsequently there is a rapid drop in weight much more pronounced between 250 and 350ºC. From this temperature the decrease in weight is attenuated slightly until residual weight is reached, 18 min with a ramp of 25ºC/min. It is important to note that when a ramp of 50°C/min is used, all volatiles have not been released when 550°C (11 min test) are reached, but only a part of them. This leads us to conclude that, if it is not desired to exceed the temperature of 550°C, it is necessary to increase the time in which this temperature is maintained; However this increases the test time.

If the object of the method to be developed is to reduce the test time to levels of 10-15 min, none of the direct methods tested with the TGA is directly feasible. However, according to the results, the combination of a direct and an indirect method is proposed. This new method tries to relate by equation the residual weights in experiments with ramps of 25ºC/min and 50ºC/min with the ash content obtained by standardized methods.

The relationship between the percentage of residual weight in each method with TGA and the ash content are shown in Table 4. It can be seen that the methods with the highest coefficient of determination were when a ramp of 25ºC/min without flow was used, with r^2 of 0.95, and when a ramp of 50°C/min with a flow of 20 ml/min was used with r^2 of 0.90. This second method is more convenient because it uses less analysis time.

Table 4. Equations that relate the residual weight from the methods with TGA and standard ash content.

Ramp of temperature	Flow	Atmosphere	Equation*	r^2
25ºC/min + 1min 550ºC	0 ml/min	Air	$y = 0.2631 \cdot x + 4.3253$	0.95
50ºC/min + 1min 550ºC	0 ml/min	Air	$y = 0.1709 \cdot x + 3.7347$	0.79
25ºC/min + 1min 550ºC	20 ml/min	Air	$y = 0.238 \cdot x + 2.0547$	0.67
50ºC/min + 1min 550ºC	20 ml/min	Air	$y = 0{,}558 \cdot x - 7{,}6593$	0.90
25ºC/min + 1min 550ºC	0 ml/min	Nitrogen	$y = 0.2255 \cdot x + 3.5905$	0.72
50ºC/min + 1min 550ºC	0 ml/min	Nitrogen	$y = 0{,}198 \cdot x + 2{,}6807$	0.65
25ºC/min + 1min 550ºC	20 ml/min	Nitrogen	$y = 0.2071 \cdot x + 4.233$	0.68
50ºC/min + 1min 550ºC	20 ml/min	Nitrogen	$y = 0.2078 \cdot x + 2.547$	0.67

*y=percentage of ash; x=%residual weight

Determination of volatiles with TGA

Same as for the methods evaluated for ash determination, all factors studied in the methods for determination of volatiles with TGA influence the final residual weight obtained. The analysis of variance, shown in Table 5, shows that both the rate of increase of temperature (ramp), flow, type of atmosphere and percentage of leaf had P-value less than 0.05, so they have a statistically significant effect with a 95.0% confidence level. This forces to do the analysis of comparison with the standardized value separately with each method. The values of each method evaluated with TGA can not be grouped since they are statistically different.

Table 5. Analysis of Variance (ANOVA) for residual weight from methods of analysis of volatiles with TGA.

Factor	Sum of squares	Gl	Mean Square	F	P-value
MAIN EFFECTS					
A:Ramp	12.0234	1	12.0234	6.65	0.0119
B:Flow	21.9039	1	21.9039	12.12	0.0008
C:Atmosphere	27.3523	1	27.3523	15.13	0.0002
D:Leaves	373.98	6	62.33	34.49	0.0000
INTERACTIONS					
AB	8.26598	1	8.26598	4.57	0.0358
AC	12.6422	1	12.6422	7.00	0.0100
AD	34.2242	6	5.70403	3.16	0.0083
BC	8.6885	1	8.6885	4.81	0.0315
BD	7.76562	6	1.29427	0.72	0.6378
CD	43.1326	6	7.18877	3.98	0.0017
RESIDUES	131.93	73	1.80727		
TOTAL	694.375	103			

The standardized volatile content can be compared to the 100-% residual weight in each TGA experiment. The mean and standard deviation of the values obtained are shown in Table 6. It is shown again that increasing the percentage of leaf content decreases the volatile content. The paired sample tests showed that there are significant differences between the values obtained with TGA and those provided by the standardized method. The values with TGA all differ by excess, which means that thermal decomposition of the mineral fraction may have occurred. However, due to the reproducibility of the experiments, the residual values can be related to the volatile content standardized through the use of regression models.

Table 6. Mean and standard deviation ($\bar{x} \pm \sigma$) of volatiles from the different methods of determination with TGA

			Percentage of leaves						
Ramp of temperature	Flow ml/min	Atm.	0	10	20	30	40	50	100
50ºC/min + 1min 900ºC	0	Air	99.46±0.40	97.29±0.43	96.51±0.02	94.21±2.65	95.44±0.07	95.50±0.01	93.10±0.40
50ºC/min + 1min 900ºC	0	Air	99.79±0.09	97.68±0.11	96.89±0.18	96.11±0.04	90.91±3.69	95.11±0.04	92.69±0.13
50ºC/min + 1min 900ºC	20	Air	97.92±0.36	96.72±0.23	96.84±0.17	95.88±0.10	94.58±1.84	92.90±0.67	93.02±0.06
50ºC/min + 1min 900ºC	20	Air	98.16±0.25	96.70±0.39	95.55±2.39	94.89±1.63	86.20±3.31	89.97±1.17	90.01±3.65
50ºC/min + 1min 900ºC	0	N	98.50±0.08	97.70±0.08	97.25±0.31	96.25±0.22	96.22±0.58	95.00±0.33	92.74±0.56
50ºC/min + 1min 900ºC	0	N	98.73±0.14	97.87±0.33	97.34±0.15	96.68±0.18	95.80±0.10	94.36±1.83	92.91±0.22
50ºC/min + 1min 900ºC	20	N	98.46±0.07	97.33±0.06	96.43±0.85	96.29±0.02	95.33±0.43	94.98±0.87	92.78±0.28
50ºC/min + 1min 900ºC	20	N	98.07±0.12	97.05±0.45	96.51±0.09	95.70±0.22	95.64±0.11	95.25±0.40	92.44±0.01

The regression models that relate the results of each method to the volatile content are shown in Table 7. It can be observed that the method with the highest coefficient of determination was obtained with the ramp of 50ºC/min+1min 900ºC with a nitrogen atmosphere. This reduces the analysis time to 19 min.

Table 7. Equations relating the residual weight of the methods with TGA and standard volatile content.

Ramp of temperature	Flow	Atmosphere	Equation*	r^2
25ºC/min + 1min 900ºC	0 ml/min	Air	$y = 1.4471 \cdot x - 59.933$	0.78
50ºC/min + 1min 900ºC	0 ml/min	Air	$y = 0{,}4199 \cdot x + 39{,}699$	0.58
25ºC/min + 1min 900ºC	20 ml/min	Air	$y = 1{,}0747 \cdot x - 22{,}913$	0.47
50ºC/min + 1min 900ºC	20 ml/min	Air	$y = 0{,}2015 \cdot x + 60{,}534$	0.75
25ºC/min + 1min 900ºC	0 ml/min	Nitrogen	$y = 1{,}5771 \cdot x - 72{,}627$	0.71
50ºC/min + 1min 900ºC	0 ml/min	Nitrogen	$y = 1{,}5409 \cdot x - 69{,}422$	0.84
25ºC/min + 1min 900ºC	20 ml/min	Nitrogen	$y = 1{,}7682 \cdot x - 90{,}408$	0.59
50ºC/min + 1min 900ºC	20 ml/min	Nitrogen	$y = 2{,}324 \cdot x - 143{,}86$	0.61

* y=percentage of volatiles; x=100-%residual weight

Figure 3 describes the weight variation experienced by the sample when ramps of 25 and 50ºC/min, with air atmosphere, and without flow are used. Like in the ash tests, it can be observed that the graphs of weight loss versus temperature reached are very similar regardless of the ramp used. The same conclusion was obtained by Xu et al (2017) [17] working with rape straw with ramps of 20ºC/min, 30ºC/min and 40ºC/min. However they are different when the weight loss is analyzed according to time. The weight loss is faster as the rate of increase in temperature is higher.

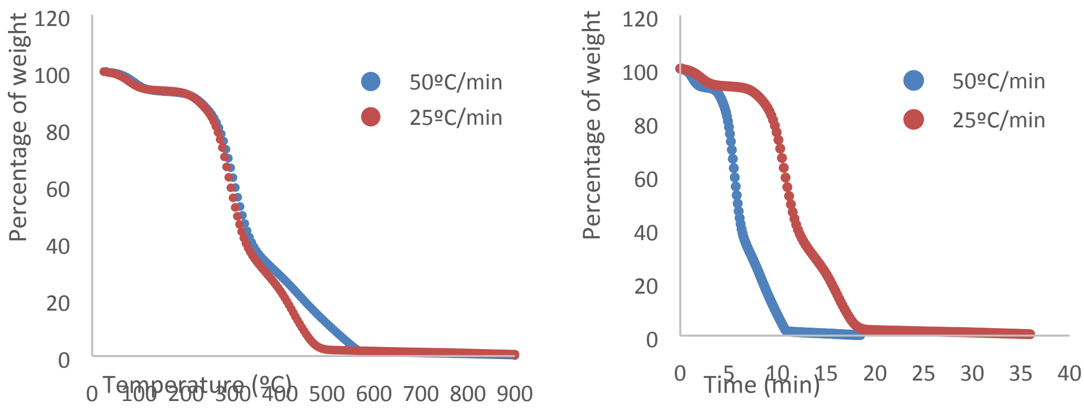

Figure 3. Variation of the weight percentage of the sample versus temperature and time in the test of determination of volatiles in air atmosphere and without flow.

It can be seen that the weight drops down slowly to about 250°C. That is up to 10 min when using a ramp of 25°C/min, or 5 min when using a ramp of 50 °C/min. Subsequently there is a rapid drop in weight much more pronounced between 250 and 350ºC. From this temperature the decrease in weight is attenuated slightly until reaching residual weight at approximately 550°C, from which weight descends very slowly. This is from 22 min when using a ramp of 25°C/min or 11 min when using a ramp of 50°C/min. The profile of weight loss with temperature is a characteristic of the species or material. Morin et al. (2017) [18] described different behaviors for thermogravimetric analysis of the coal obtained by pyrolysis. On the other hand, according to Özsin and Pütün, (2017) [19], the composition of the gas released at each stage is assumed to be different. They worked with a TGA device coupled to a mass spectrometer (MS) and a FTIR.

CONCLUSIONS

In this work we have developed methods for the determination of ash and volatiles with thermogravimetric balance (TGA) for mixtures of wood and leaves of *Euphorbia lancifolia*. The results show that the residual weights after applying ramps of 25ºC/min and 50ºC/min up to 550ºC and 900ºC show significant differences with the values obtained with the standardized methods EN-ISO 18122:2015 [5] and EN-ISO 18123:2015 [6] respectively. However, residual weights obtained with TGA present fixed relations according to regression models.

The equations obtained for the determination of volatiles and ash from methods developed for TGA present an acceptable precision, allowing reduction of the determination times to 11 min.

The procedure of validation demonstrated the low uncertainty of the data obtained by this method and the low propagation of uncertainty when they were applied for the prediction ash and volatile content of the related biomasses, which supports its applicability as an alternative to biomass characterization.

It is shown that the increase of leaf content in the *Euphorbia lancifolia* samples increases the ash content and decreases the volatile content.

The decrease in weight with temperature is independent of the ramp used, presenting a characteristic curve of four stages. It is assumed that the composition of the gas released in each heating step is different. The determination of the gas composition at each stage is proposed for further investigation. To do this, it is necessary to pass the gases through a gas chromatograph and analyze it with a detector that could be a thermal conductivity detector (TCD), or a mass spectrometer (MS).

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Highlights

Determining of ash and volatile from residual weight with fast heating in TGA.

The decrease in weight with temperature is independent of the ramp used

Validated methods with analysis time of 10-20 min.