

Biomass Proximate Analysis using Thermogravimetry

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ABSTRACT

Biomass wastes have several advantages that may convert them in an important energy feedstock. Despite this, some common problems, main related with its heterogeneity, are widely reported in literature. This suggests a comprehensive previous characterization as a tool to determine its suitability as a fuel. Proximate analysis data (moisture, ash, volatile matter and fixed carbon contents) are normally obtained by using international standard methods which are time consuming, tedious and complex. A dynamic technique as Thermogravimetry (TG) measures weight changes during a temperature program, so it can be successfully used as a fast and accurate method, to provide reliable data for biomass proximate analysis.

Key words

Biomass, proximate analysis, thermogravimetry

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1. Introduction

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2 As widely reported, biomass constitutes an important feedstock in the current world
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4 energetic scenario (McKendry, 2002; Muthuraman et al., 2010; Jorquera et al., 2010),
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6 due to several advantages, some of them environmental, such as its neutrality regarding
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8 gaseous CO₂ emissions (Gil et al., 2010; Munir et al., 2009), or its low NO_x and SO₂
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10 emissions (Li et al., 2009; Qian et al., 2011); other social advantages, such as biomass
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12 production provides a source of wealth in rural areas, avoiding depopulation (Bahng et
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14 al., 2009) and some others related to ease of production. In that way, biomass is an
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16 autonomous resource, which partly avoids dependence on fossil fuels, which are
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18 produced in only a limited number of countries. In addition to this, the low price of raw
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20 materials and the development of biomass-consuming energy systems have made them
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22 economically competitive with traditional fossil fuels.
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26 Because of that, biomass appears as an important role-playing fuel in several national
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28 and international policies (Gaska and Wandrasz, 2008; Rosendahl et al., 2007), such as
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30 the European Union White Papers on energy saving, or the PER (Renewable Energy
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32 Plan) in Spain (Lapuerta et al., 2004).
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37 As can be seen, the future of biomass energy conversion appears to be quite optimistic,
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39 but its energetic use also presents some problems, the most important one being related
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41 to its own nature, even though it is a highly heterogeneous fuel, with plenty of different
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43 origins, from a huge variety of industrial wastes to wood transformation industry-
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45 residues or energy crops. Taking this into account, biomass characterization is required,
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47 to reliably predict its behaviour as a fuel. When considering biomass thermal
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49 conversion, proximate analysis is one of the most important characterization methods.
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54 This consists in determining moisture, ash, volatile matter and fixed carbon contents of
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56 the raw biofuel. These values are essential ascertain moisture, volatile matter and fixed
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1 carbon affect both on the combustion behaviour and the plant design. In that way, high
2 moisture values decrease the combustion yield, while high volatile matter/fixed carbon
3 ratios are related with the fuel's reactivity. On the other hand, ash deeply influences the
4 transport, handling and management costs of the process. It is also influential in
5 corrosion and slag formation. Traditionally, these measures are developed following
6 different national and international normative, such as ASTM E-871 for moisture,
7 ASTM E-830, D-1102 or UNE-EN 14775 for ash or ASTM E-872 and ASTM E-1755
8 for volatile matter determination (Demirbas, 2004; Khalil et al., 2008). Fixed carbon is
9 usually determined by difference. All those methods are time-consuming and tedious
10 (Karatepe and Kücükbayrak, 1993), and the success of the operation is highly
11 influenced by the operator's skills. In that way, a fast, simple, reliable and highly
12 accurate method for routine tests, would be desirable. Since all the above mentioned
13 standards basically establish heating a sample under different specific conditions
14 (Mayoral et al., 2001), and a weight difference determination, then a thermobalance
15 and a conveniently adapted thermogravimetric study appears as an effective tool
16 (Warne, 1991), resulting in both time-saving, from several hours to just a few minutes
17 in each experiment (Sadek and Herrell, 1984) and sample quantity reduction, as it
18 requires matter weight in the range of milligrams (Beamish, 1994).

19 As is well known, thermal analysis can be defined as a group of methods consisting in
20 measuring the property of a substance when subjected to a controlled temperature
21 program. It is a highly developed technique with many different uses when applied to
22 biomass. Some authors have used it to study the thermal behaviour of biomass and fuel
23 blends in both oxidative and inactive atmospheres (Ghetti et al., 1996; Varol et al.,
24 2010; Wilson et al., 2010). Others used this technique as a tool to thermally characterize
25 fuels and ashes, by studying its melting behaviour or structural changes (Biswas et al.,
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1 2011; Miranda et al., 2011, Ross et al., 2008) while others used TG as a tool to develop
2 kinetic modelization (Ramajo-Escalera et al., 2006; Wilson et al., 2011). However, but
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4 not so many works have been developed for biomass proximate analysis, whilst, on the
5
6 other hand, thermogravimetry is often used in that way for coals (Ottaway, 1982;
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8 Slaghuis and Raijmakers, 2004).
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11 In this context, the aim of this work is to determinate if TG analysis can be used as an
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13 effective tool to approach ultimate analysis data of biomass fuels and propose a method,
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15 based on modified-coal methods to reliably and accurately obtain these data.
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21 **2. Materials and methods.**

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23 Firstly, thirteen biomass samples were grinded and sieved to 500 µm to guarantee its
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25 homogeneity in a proximate analysis routine by using ASTM standards E 871, E 1755
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27 and E872; for moisture, ash and volatile matter respectively. In addition to this, fixed
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29 carbon content was calculated by difference using the balance:
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$$32 \quad \%FC = 100 - (\%Ash + \%VM)$$

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34 where %FC, %Ash and %VM respectively mean the mass percentages of fixed carbon,
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36 ash and volatile matter of the raw sample.
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39 All these procedures were detailed and referenced in our previous works (García et al.,
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41 2012). After this routine every sample was tested using a Perkin Elmer STA 6000
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43 thermobalance, using 10 and 20 mg of sample, and 40 ml/min of flue gas, for both
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45 nitrogen and air. Samples were selected all around Spain trying to track every possible
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47 biomass origin, commercial fuels, agri-food industry wastes, forest wastes, energy crops
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49 and cereals (Fernández et al., 2012) with the aim of obtaining a general method, suitable
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51 for a wide range of biomass fuels, with different characteristics and compositions.
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1 The bibliographical review search for methods developed for coals showed two basic
2 groups, some simpler ones, which consist in a chosen continuous temperature ramp path
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4 between room temperature and the final set-point (TR1 and SP1, as detailed in table 1).
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6 In this group we may include works proposed by Mayoral et al., 2001(MAY3), Sadek
7 and Herrell, 1984) (SDK1) or (Lapuerta et al., 2004)(LAP). On the other hand, there are
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9 some other proceedings consisting in continuous heating (TR1, 2 or 3 depending on the
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11 number of this steps) combined with intermediate dwellings (DT1, 2 and 3) to reach
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13 different intermediate or final set-point (SP1, 2 or 3). In this group we can include some
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15 other Mayoral proposed methods (MAY1, MAY2 and MAY4), Ottaway–(OTT)–
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17 (Ottaway, 1982), Sadek and Herrel (SDK2), Karatepe and Kücükbayrak, 1993(KAR),
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19 Warne (WAR) (Warne, 1991), and Beamish (BEA) (Beamish, 1994). Table 1
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21 summarizes the conditions required in each of these works, with each temperature ramp
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23 (TR), intermediate and final setpoints (SP) and dwelling times (DT) required when each
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25 set-point is reached. Most of them are conducted in inactive atmosphere (using argon,
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27 helium or nitrogen depending on the author), to measure moisture, volatile matter and
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29 fixed carbon and with a final combustion time in oxidative environment (oxygen or air),
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31 when set-point is reached, to measure ashes. On the other hand, Lapuerta's work is
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33 completely carried out in oxidative atmosphere. Some of these works explain how
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35 relevant data must be obtained from Thermogravimetry. As can be seen in figure 1,
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37 which shows a wood pellets sample that can be considered as a representative TG
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39 diagram, it presents a number of slopes, each kinetics showing different phase changes.
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41 In that way, the first small slope represents moisture release due to drying, occurring at a
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43 temperature under 150°C (Zheng and Kozinski, 2000). In the range between 200 and
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45 900 °C, a huge mass loss is seen. In the context of different phenomena that can be
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47 observed. Thus, between 200 and 600 °C the biggest mass loss occurs due to the release
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of CO₂ and CH₄, these gases coming from hemicelluloses (190-320 °C), cellulose (280-400 °C) and lignin (320-450 °C) decomposition (Strezov, 2004), and a later chemically bonded CO₂ and chemically formed water release (450-600 °C). Finally, from 600 to proximately 900 °C mass loss rate decreases, due to the evolution of carbon-containing species (CO_x, C_xH_y and tars) and char oxidation until constant weight is reached (Haykiri-Açma, 2003).

Five methods originally developed, and described in the literature, for coals and cokes proximate analysis determination, were tested. In this work once observed which of them presents the best results, they were slightly adapted to biomass samples, aiming to reduce the experimental time without impoverishing the obtained results. The tested methods were LAP, MAY1, SDK and KAR. In addition to this a variation of OTT, called OTT* consisting in a second dwelling of five minutes at 550°C, was used.

Obtained results are compared with proximate analysis data determined using international standards, provided in Table 2 (García et al., 2012), experimental errors are calculated and average absolute error values shown in Figure 2.

The error criteria used are the average experimental error (AEE) and the average bias error (ABE) commonly used by several authors in this field (Ahmaruzzaman, 2008; Majumder et al., 2008). In addition to this, the average absolute deviation (AAD) is also used. Those criteria are defined as follows:

$$AEE(\%) = \frac{1}{13} \cdot \left[\sum \left(\frac{100 \cdot |HHV_{calc.} - HHV_{exp.}|}{HHV_{exp.}} \right) \right] \quad [1]$$

$$ABE(\%) = \frac{1}{13} \cdot \left[\sum \left(\frac{100 \cdot (HHV_{calc.} - HHV_{exp.})}{HHV_{exp.}} \right) \right] \quad [2]$$

$$AAD(\%) = \frac{1}{100} \cdot [\sum (HHV_{cal.} - \overline{HHV})] \quad [3]$$

As can be seen in figure 2, the KAR method presents the best results for both moisture and volatile matter determination, and so, because of this will be considered as a base

1 method to develop future variations, trying to improve accuracy in both of this
2 parameters and ash and fixed carbon contents.
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7 **3. Results and discussion**

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9 Once KAR's method **has been chosen** and carried out as the base one, some changes are
10 developed therein, aiming to obtain a more suitable method for biomass proximate
11 analysis data determination. In that way, biomass is reportedly far more reactive than
12 coal, and so, faster heating ramps can be used without losing complete conversion
13 during combustion. In that way, some new methods are tested, proving that the best
14 results were found when beginning with a heating ramp of 50°C/min, from room
15 temperature until obtaining an isothermal 120°C for 3 minutes, then a new 100°C/min
16 heating ramp is programmed until 950°C. **When this point is reached, a cooling process**
17 **with -100°C/min ramp starts until reaching 450°C.** Until this set-point, the process is
18 developed using nitrogen, to guarantee a non oxidative environment, but, when 450°C is
19 reached, flue gas is changed for air. Then, a new 100°C/min heating ramp begins until
20 800°C, which provides better results than previous methods, and is isothermally
21 maintained for 3 minutes, when the program is finished, **totalling 25 minutes** per
22 experiment, enabling two experiments per hour, including cooling and stabilization of
23 the experimental equipment, which entails a great time saving compared with several
24 hours taken for the moisture and ash determination. This method is also more
25 **convenient than ASTM standard, and so, volatile matter determination implies working**
26 **with a furnace at 950°C,** involving physical risk for the operator when introducing and
27 withdrawing samples. **This proposed method, along with TG profiles obtained for the**
28 **selected samples,** are shown in Figure 3, where necessary data is read following the
29 criterion explained in Figure 1. This means measuring, respectively, moisture, volatile
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1 matter, fixed carbon and ash by difference from slope to slope. Volatile matter and fixed
2 carbon values are thus obtained by applying **Beamish's correction which means adding**
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4 **values obtained with the next formulae to the measured value.**
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$$7 \quad VM = VM_{TG} \frac{(Sample\ Weight - M - A)}{VM_{TG} + FC_{TG}} \quad [4]$$

$$8 \quad FC = FC_{TG} \frac{(Sample\ Weight - M - A)}{VM_{TG} + FC_{TG}} \quad [5]$$

9
10 where VM, FC, VM_{TG} and FC_{TG} are, respectively, the obtained volatile matter and fixed
11 carbon and those measured in TG, and M and A, moisture and ash content read on the
12 TG profile. **These corrections are proven to slightly improve the results.**
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14 **Finally, results obtained for each of the samples are detailed in Table 3,** and the average
15 values are compared (named as NEW MET) with the coal-developed methods in Figure
16 2. As can be seen, moisture and volatile matter experimental errors are satisfactory, with
17 AEE under 6 %, resulting in AAD of 0.5 and 4.4 points, respectively. On the other
18 hand, fixed carbon and especially ash results highly improve the values obtained using
19 coal-developed methods, offering values close to 10 and 50 %, respectively. **Taking into**
20 **account that fixed carbon determination is obtained empirically by difference, with the**
21 **entailing precision and accuracy limits, an 11% average error and 2.0 average absolute**
22 **deviation points, can be considered as quite acceptable result.** Regarding ash
23 determination, this involves a problem already referred to by other authors (Mayoral et
24 al., 2001). **As can be seen in Table 3, there exists a big difference in measured EE**
25 depending on the considered sample. In that way, beetroot pellets or wheat grain present
26 accurate results, with an experimental error close to 5%, while the same error in some
27 other samples such as hazelnut shell or both brands of wood pellets approaches 90 %.
28 As can be observed with the absolute deviation, those values are not high at all; in fact
29 the AAD is just over that of the moisture, presenting a 1.6 % value. However, as
30 expected, ash values are really low in biomass, mainly in woody samples. Low absolute
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1 errors imply really high deviations, in relative bases, like AEE, may be due to the
2 formation of highly specific weight oxides when the oxidative environment is reached.
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4 **4. Conclusions**

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7 This work proposes a suitable method to determine the proximate analysis (moisture,
8 ash, volatile matter and fixed carbon contents) of biomass. Obtained results, with
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10 average experimental errors under 6 % for moisture and volatile matter and close to 10
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12 % for fixed carbon greatly improve coal-developed methods, for the same tested
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14 samples. Ash determination entails average absolute deviation of 1.6 points, but the low
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16 expected values imply higher experimental errors. Other important advantages are time
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18 saving and simplicity, as this method requires 25 minutes to obtain all four data sets
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20 while only moisture or ash determination take several hours each, using the standard
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22 normative.
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54 most of the required samples.
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METHOD	INACTIVE ATMOSPHERE						OXIDATIVE ATM.			
	TR1	SP1	DT1	TR2	SP2	DT2	CT	TR3	SP3	DT3
MAY 1	20	105	5	20	900	-	20	-	-	-
MAY 2	20	900	5	-25	450	-	-	20	700	-
MAY 3	80	1020	10	-	-	-	-	-	-	-
MAY 4	20	105	3	80	850	-	-	-	-	-
OTT	250	110	1-5	250	900	1-5	1	-	-	-
SDK 1	100	1000	3	-	-	-	3	-	-	-
SDK 2	100	135	2	100	1000	3	3	-	-	-
KAR	20	110	30	40	950	7	-	-20	750	5
WAR	100	110	2	100	950	3	3	-	-	-
BEA	50	110	5	50	950	7	42	-	-	-
	TR1	SP1	DT1	TR2	SP2	DT2	CT	TR1	SP1	DT1
LAP	-	-	-	-	-	-	18-108	10-60	1100	-

Table 1 – Summary of the studied analysis methods developed for coals and methods assayed for biomass.

Where: TR 1, 2 and 3 are the first, second and third temperature ramps respectively, measured in °C/min. SP is the set-point for each temperature ramp, measured in °C and DT is the dwelling time after each ramp, measured in minutes. CT is the combustion time in oxidative atmosphere when set-point is reached.

Sample	% M	% A	% VM	% FC
Apple tree leaves	9.3	12	71.9	16.1
Beetroot pellets	12.5	9	76	15
Chestnut tree leaves	8.2	4.9	72.41	22.69
Hazelnut shell	8.74	2.2	77	20.8
Miscanthus	7.53	9.6	79	11.4
Nectarine stone	8.2	1.1	76	22.9
Peach stone	8.55	0.5	75.6	23.9
Pine and pine apple leaf pellets	8.25	3.2	74.5	22.3
Pistachio shell	8.75	1.3	82.5	16.2
Soya grain	10.4	4.8	77	18.2
Wheat grain	10.3	2.8	80	17.2
Wood pellets 1	7.96	1.3	82	16.7
Wood pellets 2	7.53	0.66	84	15.34

Table 2 – Data obtained for moisture (M), ash (A), volatile matter (VM) and fixed carbon (FC) content of biomass samples using ASTM normative, measured in mass percentage.

	MOISTURE					ASH				VOLATILE MATTER				FIXED CARBON			
	M	M _v	EE	BE	AD	M _v	EE	BE	AD	M _v	EE	BE	AD	M _v	EE	BE	AD
Apple tree leaves	13.3	8.3	11.0	-11.0	1.0	6.45	46.2	-46.2	5.5	67.3	6.4	-6.4	4.6	16.6	3.1	3.1	0.5
Beetroot pellets	12.1	11.0	11.8	-11.8	1.5	8.43	6.3	-6.3	0.6	62.5	17.8	-17.8	13.5	10.7	28.8	-28.8	4.3
Chestnut tree leaves	13.0	8.1	1.4	-1.4	0.1	2.90	40.9	-40.9	2.0	70.8	2.2	-2.2	1.6	20.2	10.8	-10.8	2.5
Hazelnut shell	14.1	8.5	2.5	-2.5	0.2	0.15	93.4	-93.4	2.1	73.5	4.5	-4.5	3.5	23.3	11.8	11.8	2.5
Miscanthus	11.8	7.9	5.5	5.5	0.4	6.37	33.7	-33.7	3.2	69.6	11.8	-11.8	9.4	13.5	18.6	18.6	2.1
Nectarine stone	18.6	7.9	4.1	-4.1	0.3	0.52	53.1	-53.1	0.6	80.7	6.2	6.2	4.7	21.1	7.7	-7.7	1.8
Peach stone	19.5	7.9	7.4	-7.4	0.6	0.73	46.8	46.8	0.2	81.8	8.1	8.1	6.2	20.4	14.7	-14.7	3.5
Pine and pine apple leaf pellets	13.0	8.8	6.8	6.8	0.6	1.81	43.3	-43.3	1.4	70.5	5.4	-5.4	4.0	21.3	4.6	-4.6	1.0
Pistachio shell	14.7	8.2	6.1	-6.1	0.5	0.53	59.1	-59.1	0.8	79.7	3.4	-3.4	2.8	17.5	7.8	7.8	1.3
Soya grain	19.1	9.4	9.3	-9.3	1.0	2.78	42.0	-42.0	2.0	76.6	0.5	-0.5	0.4	18.1	0.7	-0.7	0.1
Wheat grain	17.0	10.2	0.7	-0.7	0.1	2.95	5.3	5.3	0.1	77.6	3.0	-3.0	2.4	13.0	24.3	-24.3	4.2
Wood pellets 1	14.1	7.8	2.5	-2.5	0.2	0.21	84.0	-84.0	1.1	79.8	2.7	-2.7	2.2	18.4	10.1	10.1	1.7
Wood pellets 2	13.4	8.0	5.7	5.7	0.4	0.08	88.3	-88.3	0.6	81.9	2.5	-2.5	2.1	15.4	0.4	0.4	0.1
Average values			5.8	-3.0	0.5		49.4	-41.4	1.6		5.7	-3.5	4.4		11.0	-3.1	2.0

Table 3 – Values obtained for each of the chosen samples.

Where M is the mass of sample (mg), M_v the measured value (%), EE, BE and AD are respectively experimental error (%), the BIAS error and the absolute deviation for each individual sample. The average values are presented in the last row.

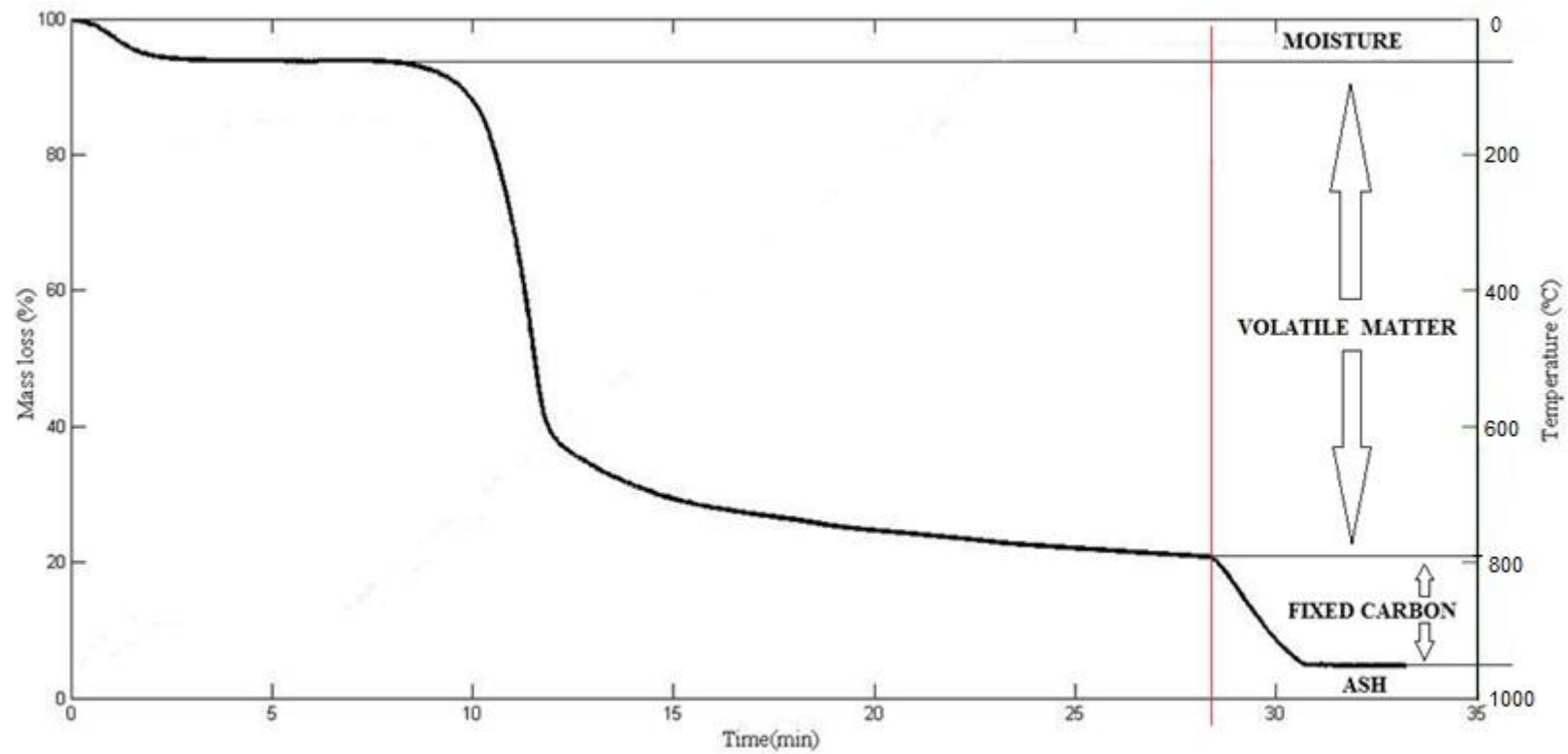


Figure 1 –Proximate analysis data provided by a wood pellets TG diagram.

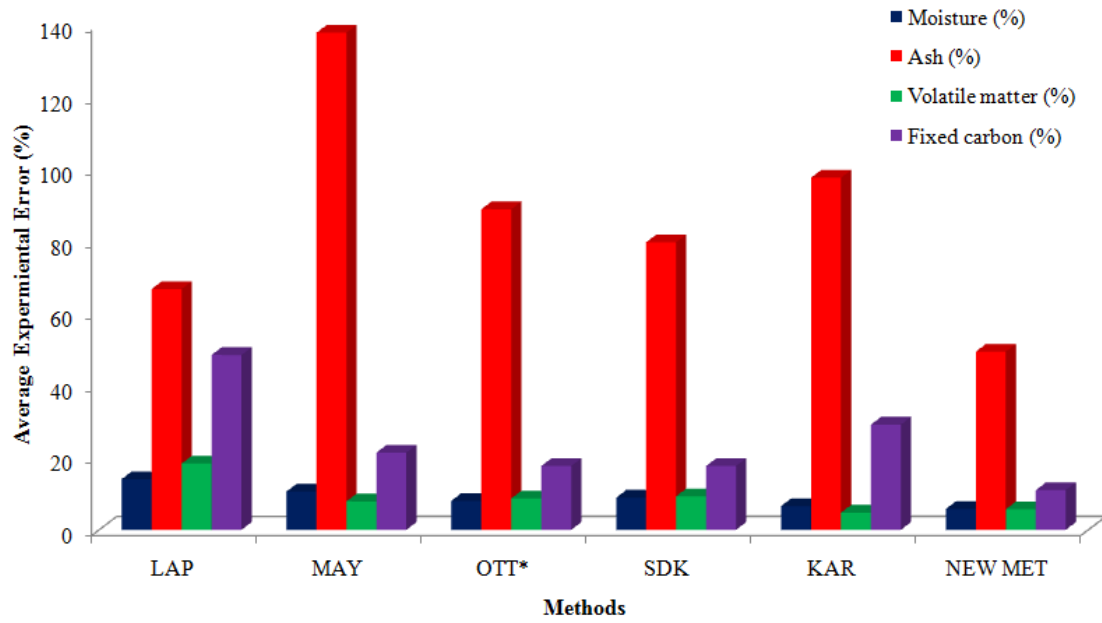


Figure 2 – Average experimental errors **observed** for the tested methods.

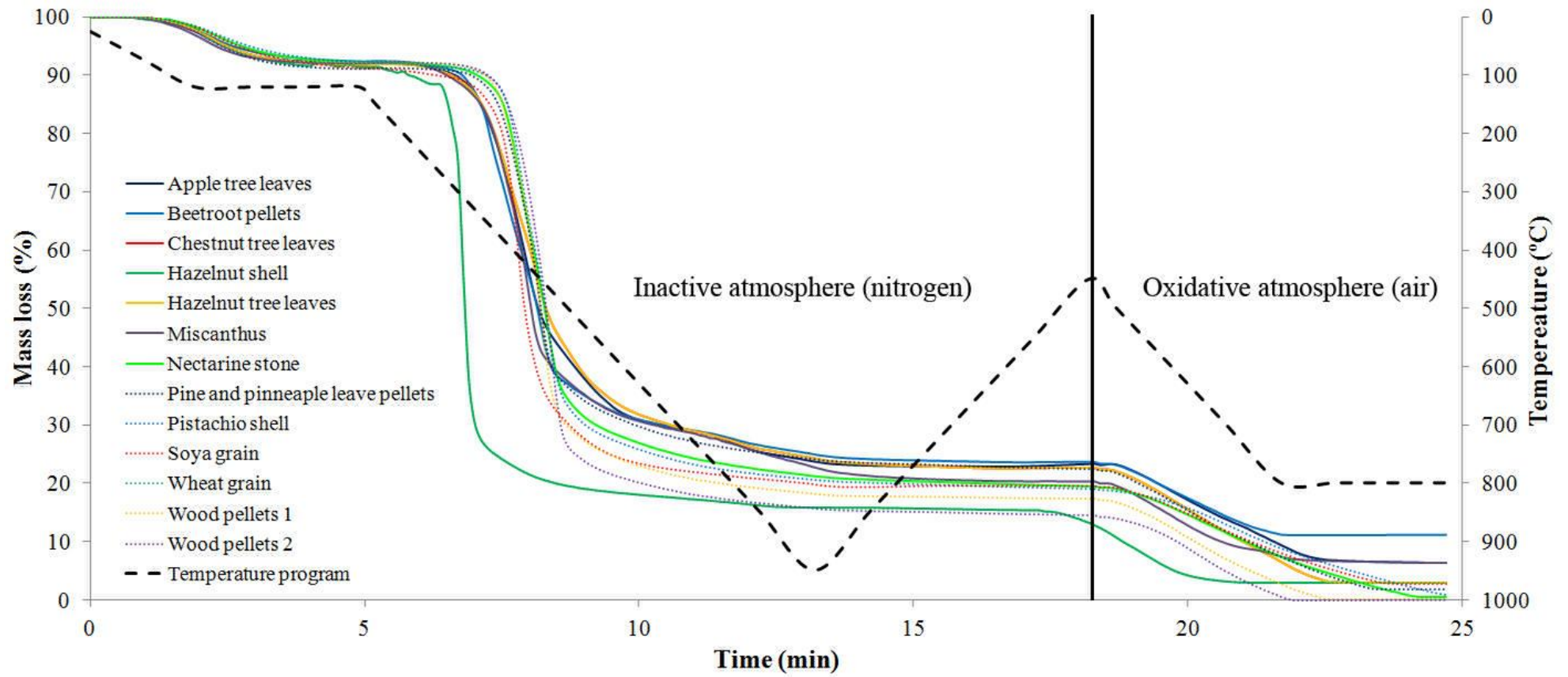


Figure 3 – TG diagrams for the chosen samples and temperature program (discontinuous line).