Study of main combustion characteristics for biomass fuels used in boilers

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Abstract

The declining reserves and fluctuating prices of fossil fuels led to intensive search an alternative to replace or complement petroleum derivates as main fuel resource. In this context biomass appears as an attractive feedstock, because of that a comprehensive characterization is needed, focusing morphological study, using scanning electrone microscope (SEM) and particle size distribution, composition with X-ray dispersive energy (EDX), thermal analyses, using thermogravimetry and combustion gases analysis, to select the best behaviour as a fuel from six biomass samples (almond shell, rice husk, straw, vegetable coal, wine pomace and a randomly chosen commercial brand of wood pellets) trying to comb al the range of commercial fuels most commonly available in the Spanish solid biofuels market.

Keywords

Biomass, Thermogravimetry (TG), Scanning electrone microscope (SEM), Particle size
 distribution (PSD), Energy-dispersive X-ray spectroscopy (EDX), gaseous emissions
 analysis

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1. Introduction

38	The decrease of fossil fuel reserves and constant variability of their prices led to
39	intensive search an alternative to replace or complement petroleum derivates as main
40	fuel resource. In this context biomass, which can be defined as "all kinds of materials
41	directly or indirectly produced, not too long ago, from photosynthesis reactions from
42	vegetable matter and its derivates: wood-fuel, wood derived fuels, fuel crops,
43	agricultural and agro-industrial by-products and annual by-products" [1] appears as an
44	attractive feedstock, because some main reasons:
45	• It can be considered neutral regarding the emissions of the greenhouse gas CO ₂
46	[2], because it fixes during photosynthesis the same amount of CO_2 as the one
47	released during combustion, with the reaction [3]:
48	$C_{42}H_{60}O_{28} + 43O_2 \rightarrow 42CO_2 + 30H_2O$
49	• Biomass and biological wastes are an autonomous fuel resource, which partly avoid
50	dependence on foreign energy supplies, improving a country's trade balance and
51	economical sustainability.
52	• Socially, the development of biomass and energetic crops as fuel permits the
53	creation of employment, avoiding the depopulation of rural areas.
54	Comparing with traditional fossil fuels, biomass presents some advantages too:
55	• It has low sulfur and nitrogen contents, generating much lower emissions of NO _x
56	and SO_2 than fossil fuels. Otherwise the carbon composition of biomass is much
57	lower than coal's, which confers it a lower higher heating value.
58	• Volatile content of lignocellulosic fuels (80-90 %) is at least twice that of coal. The
59	ash content is very low, comprising 1 % in most wood samples.
60	• The fuel application of wood wastes supposes a cheap energy source. One liter of
61	diesel used for heating, corresponds (on average) to 2 kg of biomass, while its prices
62	are respectively $1 \notin$ and between 0.15 and 0.25 \notin , in Spain.
63	Nowadays, biomass is one of the major energy sources providing proximately 14%
64	of the world's energy needs, representing in industrialized countries, from 9 to 14 % of
65	the total energy supplies, but growing until 35-40 % in developing countries, amounting
66	in many of them to a 90 %, a large part of it, non-commercial [4].
67	The use of wood as an energy source depends on the awareness of its fuel value,
68	because of this a comprehensive biomass characterization is needed.
69	The aim on this work is to get a reliable comparison among six of the more
70	common biomass fuels present in the Spanish market to choose which one would be the
71	most suitable for thermal energetic conversion, relying on the morphological properties
72	(SEM, PSD) and composition (EDX) of both raw fuel andwastes. In addition to this
73	thermal properties (TG-DSC) and gaseous emissions of fuels were studied too. Of
74	course to get a deeper knowledge of biomass samples more paremeters are needed,
75	such as its properties as a fuel, this means proximate, ultimate and calorimetric analysis
76	or physical and mechanical properties, but these have been taken up in other works of
	this group [5].

77 Biomass fuels can be divided in different groups depending on its origin,

commercial fuels (CF), industry wastes (IW), forest wastes (FW), energy crops (EC)

and cereals (CER) [5], so the choice of the raw samples was done trying to comb a

range of commercial fuels as wide as possible by using almond shell (CF, IW), rice

81 husk (CER), straw (EC), wine pomace (IW) and wood pellets (CF, FW).

82 In addition to this vegetable coal (IW) was studied too because of the special

properties that make it different from most of biomass fuels, and quite more similar tocoal.

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2. Materials and methods

Four types of experimental procedures were carried out in order to the above mentionedcharacterization:

88 2.1 <u>SEM (scanning electron microscope):</u>

89 Scanning electron microscope is a technique widely used to know the physic nature of solid surfaces. The provided images give a detailed surface's view and a general sight 90 of the sample, being the most common tool used to observe micro-structural 91 transformations that occur during thermal degradation of the biomass [6]. Used 92 93 equipment is a conventional scanning electronic microscope, model MEB JEOL-6100, 94 joined to a dispersive energy microanalysis unit (EDX) used to determine the elemental composition of the sample in a semi-quantitative way. 95 Many researchers have applied this technique to biomass in different ways. For 96 example Szemmelveisz et al. [7] analyzed the ash composition trying to determinate 97 98 which of the compounds are more important to slagging processes. Haykiri-Acma et al. [8] used SEM microanalysis to reveal the structural differences between untreated 99 biomass and some of its isolated compounds, such as lignins, celluloses and hemi-100 celluloses. Others, such as Blesa et al. [9], used SEM studies, along with other techniques 101 102 like FT-IR to physically and morphologically characterize carbonizated wastes of biomass leading to explain mechanical differences of some materials. Finally Bridgeman 103 et al. [10] and Umamaheswaran et al. [11] used this technique to determine the particle 104 size distribution of different fuel samples. SEM images are a useful tool to determinate 105 106 important parameters regarding reactivity and residence time in chambers, such as size (so physical and chemical properties depend on it), shape and porosity, as developed by 107 108 Biagini et al. [12]

This work has adopted an eclectic procedure. In that way, SEM analysis has been already used to determine the physical variations of both raw biomass materials and wastes after cobustion at two different temperatures chose basing on proximate analysis items: 550°C burning temperature is used for ash determination [13] and 950 °C is used to ensure volatile matter is releasing [5].

Adding to this EDX analysis allows to know the elemental composition of
untreated samples and wastes after burning program at the previously chosen
temperatures in order to compare the composition evolution in both situations. To carry
out these experiments properly the sample must be electro-conductive, so it is covered

with a thin gold layer, which can mask or add some components. The other option
would be graphite covering, which should be much worse in the case of organic
compounds. Likewise it must be noticed that the obtained results may be used in a
qualitative way in order to evaluate if some of the ashes contain any hazardous or
useful compound which may suggest any specific reuse or special treatment to get rid of

123 fit minimizing environmental damage.

124 2.2 <u>PSD (particle size distribution):</u>

125 This technique was used by several authors in different ways. One of the most common procedures, consists on separing the sample by sieving in defined size 126 127 fractions and weighting each of them, expressing the result in weight percentage. This 128 was used by Mediavilla et al. [14] or Bergström et al. [15] to study the effect of raw 129 material size in the combustion properties of fuel. Molav et al. [16] put the same tool 130 into practice for coal combustion and Bridgeman et al. [10] applied the same for energy 131 crops and the size influence in kinetic parameters, which are directly affected by it. In that way Tinaut et al. [17] studied the effect on this parameter over the whole 132 gasification process in a fixed bed gasifier and Yang et al. [18] developed the particle 133 size influence in a packed bed working order showing that generally higher particle 134 135 sizes implied lower conversions, and with lower solid temperatures into the bed and 136 lower concentration of some gases, such as methane, this means lower combustion richness. 137

In other works Moisio et al. [19] and Sorvi et al. [20] used particle size distribution
technique to study the particles emitted during combustion process collecting them by
means of a gravimetric impactator which fractions them automatically in different sizes
ranges.

This technique may be applied after, processing SEM [21], TEM or optical
microscope images using proper software. Kamalak Kannan et al. [22] measured
emissions of particulate matter during combustion.

Some authors such as Wang et al. [23], Rajamma et al. [24] and Bahador et al. [25]used laser diffraction to examine fly ashes in concrete.

In this work samples were grinded in a farming blade mill, and later stifted with a
100 fine screen sieved to achive homogeneity and small size for the sample to enable
complete combustion during the burning process, as large particle sizes result in a lower
burning rate [18]. After this the ready sample was burnt at 550 °C and 950 °C, before
and after the release of volatile matter, in a furnace during 5 hours, and get to room
temperature in a desiccator, so they are ready to measure their PSD by laser diffraction
in a Malvern Instruments Mastersizer-S equipment.

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2.3 TG-DSC (thermogravimetry-differential scanning calorimetry):

155 TG measures the mass variation of a sample when is subjected to a temperature

156 program in a controlled atmosphere. This procedure is commonly used to gain a

157 comprehensive knowledge of combustion properties of carbonaceous materials. Some models can be used to properly interpret TG and its derivatives profiles [26, 27], to

obtain information about ash composition and fusion temperatures, phase changes orkinetics of studied samples.

The representation of the mass loss (absolute or in percentage), versus the 160 temperature evolution is known as burning profile, which presents a slope variation 161 (accumulative form) or a number of peaks (derivative form). A general biomass DTG 162 163 profile consists on 3 peaks, as stated in most works [28-33] occurring at slightly 164 different temperatures, depending on the composition of the studied sample. The first of these peaks corresponds to drying by moisture evaporation, and is situated generally at 165 a temperature proximate to 105 °C, but some works as Miranda's one [31] increase it to 166 the 200 °C. The second big phase change corresponds to biomass volatilization and 167 168 volatile matter release due to hemicelluloses, cellulose and lignin decomposition, this is usually situated in a range between 190 and 450 °C (190 to 320 °C for hemicelluloses, 169 280 to 400 °C for cellulose and 320 to 450 °C for lignin), an can also be split in two 170 smaller peaks if hemicellulose concentration is high. The last peak, beginning more a 171 172 less at 550 to 600 and following until 900°C when constant weight is reached,

173 corresponds to char oxidation or combustion of carbonaceous residue without flame.
174 The most important characteristics of the burning profile are the ignition

temperature, consisting on the point when a sudden rise is undergone and the peak
temperature when mass loss speed is the highest. This value is commonly used as a
measure of the sample's reactivity.

178TG experiments are widely used by different authors to study the thermal behaviour179of biomass, wastes and blends of biomass and coal in combustion, pyrolysis [34] and180gasification [35] in different atmospheres, oxidative or inactive, depending on if O_2 or181N_2 is supplied [36].

Some of the developed studies can be the thermal characterization of different fuel samples [37], the study of melting behaviour of both fuels and ashes [38], or comparing structural changes after undergoing treatment [39]. TG can already be joined to a TG-MS [40] or a FT-IR [41] analysis equipment to study solid or gaseous emissions during combustion process. Nowadays is quite common to apply this technique to kinetics research and modelization [29, 33, 42] or to determine, too in a simple way the proximate analysis data of fuel samples [43].

189 In this work a Perkin-Elmer STA 6000 simultaneous thermal analyzer was used, 190 following a program which consisted on reaching 50 °C from run temperature, then 1 191 minute of purge with N_2 is applied. Once this happens, the gas is changed to air and the 192 temperature increases until 900 °C using a ramp of 10 °C/min.

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2.4 Combustion gases analysis:

Low SO₂ and NO_x emissions are one of the most important environmental advantages of biomass combustion, so they are acid rain precursors and cause important corrosion damages in the combustion equipment and were intensely studied and reported in several author's works, most of them focusing on fluidized bed combustors and NO_x

- emissions, like N_2O [44], or NO, relating those emissions with measured CO, O_2 and
- SO_2 [45] or comparing emissions of this gas between coal and biomass and coal blends
- 201 [46]. Kuprianov et al. [47] controlled CO and NO_x emissions, using the first one as a
- 202 measure of the combustion efficiency. Finally Kaynak completed those works by
- measuring CO, SO₂, C_xH_y and NO_x emissions for peach and apricot stones burning,
- alone [48] and blended with coal [49], studying the influence of the air excess supply.
 In the present work the emitted gaseous O₂, CO, CO₂, NO_x and SO₂ were
- 205 In the present work the entited gaseous 02, eco, eco2, ttox and bo2 were
 206 continuously measured using a Testo 350 XL-Testo 454 gas analyzer. This worked
 207 connected to a Carbolite MTF 12/38/850 tubular furnace with a tubular quartz reactor.
 208 A sample of approximately 1 g is put inside a combustion boat and supplied with 3 l/
 209 min of oxidizing using air with a Bronkhorst mass flow controller, trying to guarantee
 210 excess of air, complete combustion and a controlled combustion atmosphere for every
 211 studied sample, making the results comparable among them.

The sample is then subjected to a temperature program, trying to simulate the behaviour in a chamber, as follows; firstly temperature goes from run temperature to 150 °C in a 5 °C/minute ramp. Then it dwells for 90 minutes, to secure sample drying. As this segment ends, temperature rises to 500 °C in a new 5 °C/min ramp. As soon as it gets 500 °C, it is kept steady for another 90 minutes . When it finishes, the program ends. Both income oxidizing air and gas emission temperatures are continuously controlled using a Testo 177-T4 data logger.

219 **3. Results and discussion**

220 3.1 <u>SEM:</u>

In this section the morphological evolution of the samples is shown. The first in each group of pictures is the one corresponding to the raw material, called "as received". It has not undergone any treatment aside for atmospheric-air drying, to eliminate external moisture which could affect to its morphology. The other two images in each figure are the ones observed after 550 and 950°C combustion respectively. These images are presented at different magnifications, as indicated in the scale under each , trying to show different details.

228 During thermal conversion large amounts of volatile matter flows from the solid 229 material in a short time, that varies the particles surface, shrinking and splitting it. As can be seen in the figures 1 to 6, the evolution in every studied sample is quite similar. 230 231 Therefore there is a big morphological difference among the three phases. Initially, at raw, just grinded samples the fibrous structure, with long fibers, according to its 232 233 vegetable origin can be determined. This can be easily noticed especially in the rice 234 husk, straw and wood pellets samples. On the other hand, harder structures, such as almond shell particles present nearly spherical shape and vegetable coal, as coming 235 from a previous pyrolisis present a much thinner distribution after grind. All these 236 details are surrounded in red colour in the images. 237

After 550°C combustion every sample presents a quite homogenous structure, a kind of amalgam of tiny particles, probably because of agglomeration phenomena due to melting of alkali compounds described at Biagini's work [12]. In this case, again
vegetable coal samples present a different behaviour, with a much more defined
structure, rich in silicon, potassium, sodium and aluminium oxides.

Lastly, after 950°C combustion volatile matter release completely splits the
particles, which originates holed-like forms and structures full of channels, like in
almond shell, rice husk, vegetable coal and wood pellets which may have taken the role
of chimneys during gases release. Straw presents a defined fibrous structure again.
These structures are marked blue in the corresponding figures.

EDX analysis results are shown in figures 7, 8 and 9, where results are presented in mass percentage of the sample, as semi-quantitative analysis. They were obtained by the analysis of five different points of the sample, so the average obtained value is presented.

As can be seen in figure 7, all raw materials are basically organic structures with 252 253 huge amounts of carbon and oxygen in its structure. All of them, except, as expected 254 vegetable coal, present carbon values between 45 and 60 percent. Vegetable coal 255 reaches very high levels, compared with other biomasses, over 90 %, because it suffered 256 a previous pyrolisis and most volatiles were released. Talking about oxygen, most samples have values approaching 45 %, except again, vegetable coal, with a low value 257 258 under 10 %. The combination of those two values confers biomass a quite large higher 259 heating value, but quite lower than vegetable coal's one.

Some other elements were found too. In that way both rice husk and straw present appreciable quantities of silicon and traces of calcium. Traces of aluminium were found too in rice husk and chlorine and potassium were found in straw samples. Especially concerning are chlorine traces that appear in straw, probably wastes of fertilizers used during growing of the crop, that may cause corrosion problems in the chamber and environmental non friendly emissions during combustion.

An important possibility given by this analysis consists on the identification of slag generating alkalis in ashes, considering them as oxides, hydroxides and carbonates of alkaline and alkaline earth metals, such as sodium, potassium, magnesium and calcium, in the way, combustion wastes with higher quantities of them should be considered as potential slag precursors.

271 When studying samples after 550 °C combustion, presented in figure 8, can be 272 noticed that the composition has completely changed. Every sample present oxygen values over 50 % and much lower of carbon, nearly 20 %, in fact vegetable coal has 273 274 nearly no presence of carbon. Silicon remains as an important element in those ashes 275 composition. Finally important quantities of slag precursors, like calcium and potassium appear in every sample at this temperature, especially high in the case of wine pomace, 276 these results may be enough to discard this potential fuel against any of the others. 277 Magnesium and sodium appear too, in lower quantity, main in wood pellets. 278

Finally, figure 9 shows the results obtained after 950 °C burning in volatile matter releasing conditions [5]. A can be determined afterexposure this high temperature, the composition has again changed, remaining the hardest carbon, oxygen and silicon structure, while most of the slag precursors, are still there, but in really low quantities, near 3% of the whole mass for potassium and calcium and under those levels for sodium
and potassium, which only remain in straw sample. Wine pomace presents quite
particular results, with really low values of carbon and high values of slag precursors,
main potassium and calcium, if compared with the other samples.

In addition, the presence of some elements such as phosphorus or potassium and calcium, aluminum and silicon and their oxides in valuable quantities in some of the obtained wastes, suggest a future deeper study trying to obtain further re-uses of these ashes in compost or concrete industries. XRF experiments maybe an adequate tool to this end.

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293 3.2 <u>PSD:</u>

294 Results of these experiments are shown in figures 10 and 11. Figure 10 presents the particle size distribution experiments for raw samples previously ground and sieved 295 using a 1 mm diameter grid. As can be seen they can be divided in two clear tendencies, 296 297 the first group would be formed by rice husk, vegetable coal and wood pellets, where 298 two slopes can be differenced, a first one, the highest for each of them is found at more 299 a less 100 μ m size, representing more a less the 6% of the volume of grains which crossed the measure cell. After this, there is a second less pronounced slope, between 300 301 350 and 550 µm, depending on the sample with values near 5 % of volume percentage, 302 presenting as a whole a quite homogeneous curve. On the other hand, the other three samples (almond shell, straw and wine pomace) draw a completely different curve, with 303 304 only one marked slope at the range 350-400 µm representing between 8 and 11 % of the volume percentage. This means those three samples are heavier to grind and 305 306 homogeneize, because of their vegetable fibrous structure (like straw or wine pomace) or its hardness like almond shell. 307

Figure 11 shows data obtained for the PSD of the wastes obtained after combustion
at 550 and 950 °C, using a continuous and dotted line respectively. As can be seen all
samples, except wine pomace, present really different distributions after undergoing
thermal conversion at both temperatures.

312 Firstly, studying the continuous lines which present 550^aC combustion, can be noticed that almond shell, rice husk, straw and wood pellets samples present a first soon 313 314 slope of fine particles, with a size lower than 100 µm, approaching 4 % of volume 315 percentage. This presumes that some of these particles will not be trapped by cyclones. so they will be released to the atmosphere, with the environmental and health hazards 316 this may poses. Every studied sample's ashes after 550°C burning present a maximum 317 between 10 and 15 volume % at a size over 500 µm, and volumes for 900 µm over 7%. 318 319 When studying wastes after 950°C combustion much more homogeneous profiles

are found, except almond shell (with a 5 % volume under 50 µm) any other sample
presents a slope of fine particle, in fact they present maximum sizes between 300 and
500 µm representing a percentage of volume between 7 and 10 %. There are neither too
many fines, nor too many gross particles, representing sizes near 900 µm volumes lower
than 3 %. This difference in structure may be caused by the releasing of gas

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bubbles that reduced the spherical structure of the ashes obtained at 950 °C in smaller
pieces while melting made a heavier distribution at 550 °C.

Lastly wine pomace presents a particular dispersion , quite similar, in both cases, to the one it has as a raw material, presenting a quite sharp curve with a maximum value near 500 µm representing proximately a 13 % of the volume.

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332 3.3 <u>TG-DSC:</u>

TG experiments were carried out to determine important information such as phase changes temperatures and weight loses during combustion process for the six studied biomass samples. DTG consists on the derivative of the TG curve, giving basically the same information, but in a much more visual way. They both are presented in figure 12, where each peak at the burning profile curve means a change in the TG curve, or a phase change.

If TG and DTG profiles are studied, can be seen that a first really smooth peak appears in every sample at the region between 90 and 110°C, this is the first of the three peaks commented at point 2.3. As samples were kept in the laboratory, in a quite dry space and avoiding weather inclemency and humidity, they have low moisture levels, so the mass loss is quite small. In fact none of the samples lost more than a 10 % of its original mass, which is the reason of this smooth peak. Wetter samples will have much more aggressive peaks at this temperature.

The next studied step is situated in the region between 200 and 450 °C. As can be 346 347 determined every studied sample, except vegetable coal, sustained in this range its biggest mass loss, from a 50% sustained by wine pomace to a quantity proximate to 70 348 349 % sustained by wood pellets and straw. Almond shell and rice husk lost in this stage a 350 65 % of their weight, more a less. As this peak shows the reactivity of a sample, it must be said that wood pellets and straw are the most reactive ones. Straw is the sample 351 352 which presents a more aggressive peak, this is the most vertical TG profile, or the 353 highest mass loss in a shortest time, meaning a short combustion time. The same 354 characteristic, in a lower mode is shown by wine pomace. Other samples, like almond 355 shell, vegetable coal and wood pellets present a much smoother profile, that means a longer (in temperature range) combustion, which is interesting for a fuel. In that region, 356 357 straw and wine pomace clearly present two peaks, the first one at, more a less 270 °C 358 and the next one in the region of 350-370°C, that shows the previously commented 359 difference between hemicellulose and cellulose de-composition and the latter lignin 360 volatilization. That clear difference means that these samples present a higher quantity 361 of the former.

Lastly the region between 550 and 900°C is observed. A can be easily determined
that every sample underwent here a second structural change, which consists on the char
(or carbonaceous residue) combustion, without flame. The first peak that can be found
in that region is that of the rice husk, undergoing a rapid char oxidation at more or less
575°C, and reaching its constant weight at this temperature. The next fuels that are
rapidly consumed are wood pellets and straw next to 600°C. Almond shell and wine
pomace are the fuels with a longer "combustion life", reaching their constant weight
near 800°C. They both have

a quite particular burning profile, so they nearly lose a 20 % of its weight in this region,while with the other samples it does not go beyond 5%.

Finally vegetable coal's behaviour is completely different from all the other studied fuels, as coming from a previous pyrolisis, the hemicellulose, cellulose and lignin structures are broken, so any peak is found at the expected temperatures, by the way a combustion profile with a constant mass loss speed from 250 to 750 °C is presented, when it undergoes it highest mass loss, thanks to char reaction.

Every studied sample has their ignition point near 230 °C, except straw which is a bit lower, nearly 210 °C. The peak temperatures are in a narrow range, too, with values between 282 and 332 °C, when the combustion reaction is strongest, consuming lignocellulosic matter and developing a great weight loss, to transform that matter in gases such as CO₂ and water, and solid wastes, like ash.

Finally TG analysis can also give important information about presence of ash after combustion, as can be determined this varies in a wide range from values proximate to 0 %, like almond shell and wood pellets, other like straw and vegetable coal with acceptable values reaching 5 % and finally rice husk and wine pomace near 10 %, maybe a too high value.

386 3.4 Combustion gases analysis:

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These experiments were carried on to determine which of the studied fuel has bigger non-environmental friendly gaseous emissions during a parameter-controlled combustion process. As a 3D image may be less representative and more difficult to determinate the most interesting combustion points, four figures, from 13 to 16 are presented to show the obtained results, and how they relate with one another.

392 In that way, figure 13 shows the temperature program and the oxygen consumption, thus showing wich of the samples need a higher combustion air quantity to ignite and 393 what temperature does it occur. As can be seen the wood pellets sample is the one with 394 395 a highest O₂ consumption, with a clear peak happening at a temperature slightly over 200 °C. Wine pomace and rice husk presents two peaks of oxygen waste at temperatures 396 proximate to 300 and 400 °C respectively, probably due to cellulose and lignin separate 397 releasing, as previously discussed in 3.3. The oxygen consumption of the second is 398 399 slightly slower than the first. Straw presents only one peak corresponding to a 400 temperature of, more a less 370 °C. Finally almond shell and vegetable coal have a quite 401 similar property showing a continuous oxygen consumption in a range from 350 to 450 402 °C in the case of almond shell and from 270 to 470 in the case of vegetable coal. It may be mentioned that almond shell have a lower oxygen consumption, as expected, due to 403 404 particular characteristics of vegetable coal.

Figure 14 relates the O_2 consumption with the release CO. As can be seen each O_2 peak, at a previously known temperature, has a complementary CO peak. This figure, complemented by figure 15, determinates which of the fuels has a lower combustion rate at the studied conditions. As can be seen vegetable coal and wood pellets have the worst values, the first one with a continuous plateau proximate to 2000 ppm and the second with a peak over 6000 ppm. Those values are too high, proving that in the studied conditions, their combustion characteristics are bad, and they need a really big

air supply, with the risk of not getting complete combustion in non auspicious

413 conditions. Every other studied sample gave much better values in this study, with
414 emissions, all of them under 600 ppm. Straw sample presents a peak value of CO

emissions under100 ppm in the related conditions.

Figure 15 presents the relationship between CO and CO₂ measured emissions, 416 417 complementing and endorsing the conclusions obtained from figurewhat was observed in fig 14. The bigger the relationship of CO/CO_2 , the worse is the combustion rate. In 418 the picture, the dotted and the continuous line represent, respectively the CO_2 and CO_2 419 measured emissions. As previously stated this relation for vegetable coal and for wood 420 421 pellets samples are too high, over 30 %, whilst for every other sample is under 10 %. This data again, recommends discarding the use of this brand of wood pellets and 422 423 vegetable coal in chambers.

Finally figure 16 presents the NO_x ans SO₂ emissions measured for all these
samples. As can be seen wood pellets present a really high peak for NO_x emissions, near
100 ppm, while the next hazardous samples were straw, rice husk and wine pomace
with values proximate to 20 ppm. The other samples present peaks under 10 ppm.
About SO₂, the only measure that may be considered is vegetable coal's one, which is
under 10 ppm, all the others present nearly no emission of this gas. Anyway all those
values are much lower than legislation permitted limits.

431 **4.** Conclusions –

In this work the results of five different experiments (SEM and PSD morphological,
EDX elemental analysis, TG and DTG profiles and emitted gases analysis) for six
biomass samples and their wastes were analyzed, trying to obtain which of those six
samples is the most suitable for thermal conversion in chambers.

436 SEM analysis showed notable morphological and compositional differences among
437 raw materials and ashes before and after complete release of volatiles .

EDX showed that straw presents chlorine traces as raw material. A high concentration of slag precursors alkalis were found in nearly every sample, especially hazardous were this levels in vegetable coal ashes. The levels alkalis are much bigger in 550°C combusted ashes than in 950 °C ones, therefore high combustion temperatures are recommended.

PSD analysis showed sharp dispersions for raw samples of almond shell, straw and wine pomace, suggesting that these samples may be difficult to homogenize. In addition to this ash samples generally present much more fine particles after 550°C than 950°C combustion, which mean an environmental risk if these particle's size is not adequate for the cyclone's efficiency when separating them from the released gases. As dispersion is much more homogeneous after 950°C combustion, this again suggests the use of high combustion temperatures.

The study of TG and DTG profiles indicates that rice husk and straw samples
present an aggressive soon mass loss, this means a too fast and unsteady combustion,
which makes them unsuitable for use for thermal conversion. Some samples such as rice
husk or wine pomace left near a 10% mass as ashes, while others like almond shell or
wood pallets present nearly 0 % waste.

- 454 In conclusion, analysis of emitted gases showed that some samples, like almond
- shell, need a quite lower air supply to get nearly complete continuous combustion,
- 456 while the sample with higher supply need is wood pellets, which together with
- 457 vegetable coal is the ones with worst combustion rate in the studied conditions. Finally
- 458 wood pellets was the sample with highest NO_x emissions and vegetable coal the one 459 with highest SO_2 ones.
- 460 After analyzing these aspects, must be said that the sample more suitable to used as 461 combustion fuel in chambers is almond shell.

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Fig. 1. Evolution of almond shell, being a) as received, b) after 550 °C burning and c) after 950°C.



Fig. 2. Evolution of rice husk, being a) as received, b) after 550 °C burning and c) after 950°C.



Fig. 3. Evolution of straw, being a) as received, b) after 550 °C burning and c) after 950°C.



Fig. 4. Evolution of vegetable coal, being a) as received, b) after 550 °C burning and c) after 950°C.



Fig. 5. Evolution of wine pomace, being a) as received, b) after 550 °C burning and c) after 950°C.



Fig. 6. Evolution of wood pellets, being a) as received, b) after 550 °C burning and c) after 950°C.





Fig. 8. EDX obtained elemental composition after 550°C combustion.



Fig. 9. EDX obtained elemental composition after 950°C combustion.



Fig. 10. Particle size distribution of raw samples.



Fig. 11. Particle size distribution of the obtained wastes.



Fig. 12. TG and DTG data obtained for the studied samples.



Fig. 13. O_2 consumption for in the experimental conditions for the studied samples.



Fig.14. CO emissions at the experimental conditions for the studied samples, related to O_2 consumption.



Fig. 15. CO and CO₂ compared emissions at the experimental conditions for the studied samples.



Fig. 16. NO_x and SO_2 emissions at the experimental conditions for the studied samples.