1 Study of Biomass Combustion Wastes

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10 Abstract

11 A number of widely referenced environmental and logistic advantages suggest biomass

12 as an interesting feedstock to obtain energy in large quantities. One of the most

13 important problems when using biomass is the amount of solid wastes produced, which

14 causes deposition and corrosion phenomena (slagging and fouling) entailing energy

15 efficiency decrement and maintenance problems.

16 This work focuses on the study of ashes from eighteen different biomass samples,

17 including energy crops, agricultural, industrial and forestry wastes and commercial

18 fuels.

19 Morphology (SEM) and grain size (PSD-LD) studies showed a homogeneous structure

20 with low quantities of health risky fine particles for most samples after 550°C burning.

21 Compositional studies (EDXA, XRF) suggested that some of the studied samples, such

- as almond shell or rice husk, may respectively present high deposition and corrosion
- 23 risks.
- 24
- 25

26 Keywords

Biomass ash, ternary diagrams, XRF, SEM, particle size distribution, TGA

29 **1. Introduction**

Constant growth in mankind's energy requirements over the last century in addition to 30 the high dependence on fossil fuels has outlined important environmental challenges. In 31 32 this scenario, renewable energy sources appear to be a sustainable tool to complement and gradually substitute fossil fuels in energy production. Among them, biomass, 33 regarded as a feedstock for thermal conversion, presents some advantages such as its 34 35 neutrality concerning CO₂ emissions during its life cycle [1] or its low N and S content that entails low NO_x and SO_2 emissions [2]. Besides this, biomass is considered as an 36 autonomous resource which partially avoids foreign energy dependence [3]. Because of 37 38 the advantages when using biomass for energy production, it has experienced a huge development in recent years. Nevertheless, it also presents some disadvantages, being 39 40 one of the most important the generation of solid wastes [4]. Ash presence is highly negative for the combustion process as it involves energy efficiency losses and higher 41 maintenance expenses due to unburnts and depositions (slagging and fouling) that cause 42 43 thermal resistances in heat exchangers, corrosion phenomena and the increase of fumes and aerosol emissions [5, 6]. 44

Ashes generated during the biomass combustion may present a variable composition
with a wide range of mineral and inorganic components included in its structure. These
can proceed from the vegetal biomass itself or from other contaminants added during
pre-treatment or transport phases. Because of this, any quality control criterion suggests
the exhaustive knowledge of ash characteristics, both morphological and compositional.

To that aim, there are several analytical techniques available, commonly used by several 50 51 authors that supply complete information about biomass samples. In that way Scanning Electron Microscopy (SEM) coupled to an Energy Dispersive X-Ray Analyzer 52 53 (EDXA) allows simultaneous morphological and semi-quantitative compositional information of the studied sample. Biagini [7] and Umamaheswaran [8] use these 54 55 techniques to study the structural variations of some biomass fuel after combustion 56 processes. Xiao [9] evaluates the structural evolution of biomass ashes after different ashing temperatures. Nortey Yeboah [10] characterizes coal ashes with high carbon 57 content that will be later co-fired with biomass. Carrasco [11] uses SEM to characterize 58 59 bottom ash from biomass to use in concrete formulation and Abraham [12] studies several ash samples trying to find reuse for them in fertilizer, cement or pollutant 60 61 adsorbent industries. Wang S. [13] employs EDXA to obtain the elemental composition 62 of biomass fly ash. Sample's morphology and grain size information can be obtained by developing 63 64 Particle size distribution (PSD). Bridgeman [14] and Mediavilla [15] sieved and weighted fractions of biomass fuels to study the effect of raw materials size on 65 combustion properties and kinetic parameters, respectively. Becidan [16] determined fly 66 67 ash grain distribution, by previously dividing them in size cuts using an Electrical Low Pressure Impactor. Roy [17] studied particle size distributions of biomass samples by 68 direct measure on SEM images and Wang G. [18] did the same to fly ashes by laser 69 70 diffraction (LD). 71 To obtain chemical composition data other techniques besides EDXA can be used. One of the most common is X-Ray Fluorescence (XRF). Reviews from Vassilev [19, 20] 72 73 provide plenty of information about the elementary composition of several biomass samples. Some other authors also use this technique to study the biomass-ash deposition 74

tendency of different ashes by using predictive coefficients [21, 22] or ternary diagrams 75 76 [23, 24].

Thermo Gravimetrical Analysis (TGA) is used by several authors to thermally 77 78 analyze different biomass samples and determine characteristic points in their burning profiles such as their ignition point, peak temperature, burn out temperature [25, 26] or 79 80 kinetic parameters [27]. Our research group has recently proposed a mechanism to 81 obtain proximate analysis data by using this analytical tool [28]. This work focuses on obtaining ash behaviour data of several different biomass samples 82 and comparing them in order to determine which ones would be most suitable for use in 83 84 further combustion processes. 85 2. Materials and methods 86 87 2.1 Samples In this work, eighteen different biomass samples were tested after air dried and grinded 88 89 to assure homogeneity. They were chosen as represent all the classification groups, e.g. as these suggested by Ávila [29]. Energy crops (sorghum –S- and thistle –THI-), 90 agricultural feedstocks (beetroot pellets -BP-, straw pellets -SP- and rice husk -RH-,), 91 industrial sources (almond shell -AS-, coffee husk -CH-, olive stone -OS-, pine kernel 92 shell –PKS- and vine orujillo –VO-) and forestry wastes (olive tree pruning –OTP-, pine 93 apple leaf –PL-, and vine shoot chips –VSC-). In addition to this some of the most 94 95 common commercial fuels currently available at the Spanish market were studied 96 (briquette -BRI-, charcoal -CC-, pine and pine apple leaf pellets -PPLP-, wood chips -WC- and wood pellets –WP-) 97 General combustion-data for these samples is provided in Table 1. Their ashes obtained 98

at 550°C were also studied. This temperature was chosen as it is considered by several 99

authors [30, 31, 32] to be the optimum one to determine their properties. Proximate and
ultimate analysis data and higher heating values (HHV) are summarized from previous
works by this research group [33].

103

2.2 Experimental equipment

104 SEM images were obtained, in this work, using a MEB JEOL-6100 equipment coupled

to an INCA Energy 200 EDX analyser, to simultaneously obtain 3D images and semi-

106 quantitative elemental analyses. To this aim samples were previously air dried and

107 grinded under 500 μ m and covered with a thin gold layer, as they must be conductant.

Particle size distribution was developed with a laser diffractometer Malvern

109 Intrument's Mastersizer S2000. Samples were originally burned at 550°C and the residue

110 grinded to avoid coalescence, and measure real particle size

111 **XRF** data was obtained using Phillips PW2404 equipment joined to a PW2540

automatic sample loader. Samples ashes were obtained at 550°C and later burnt at

113 900°C in order to obtain the mineral matter. Nine elements data (Si, Al, Fe, Mn, Mg,

114 Ca, Na, K, Ti and P) were obtained, considered as oxides in its highest oxidation level.

115 TGA experiments were developed in a Perkin Elmer STA 6000 thermobalance, using

116 10mg of sample and a slow heating rate (5°C/min) from room temperature up to 900°C

in an oxidant air-atmosphere with an air flow of 40 ml/min.

118 **3.** Theory and calculation

Slagging and fouling are two phenomena, directly related to deposition and corrosion,commonly observed when operating a biomass-powered combustion system. The first

121 of them is produced at high temperature zones, mainly on grills or chamber walls,

122 whilst the second istypical of low temperature zones, like the heat exchanger surfaces.

123 They depend on the fuel's chemical composition, conversion technology used and

124 operating conditions [19].

XRF data is a useful tool to calculate some deposition-predictive indexes, some of
which are included in Table 2, as this phenomenon is usually increased by high
concentrations of low melting point elements, like Na, K, S, Cl (alkali sulphates or
chlorides) and decreased by high melting point ones such as Ca, Mg or S (calcium or
magnesium silicates).

- 130 4. Results and discussion
- 131 **4.1 Morphology and size**

Due to space requirements, only the SEM images that show the most relevant facts are 132 included in this work. In this way a yellow marked fibrous structure can be observed in 133 134 the wood chips sample (figure 1). This is due to the high lignin levels of woody fuels which make them harder and more difficult to grind homogenously. Structural holes 135 136 (blue) that confer this fuel a high specific surface but low density, are also detected. On 137 the other hand, harder samples such as pine kernel shell (Figure 2a) present, before burning, isolated particles of high size and quite regular sphere-shape. Those two effects 138 139 co-exist in the pine and pine apple leaf pellets sample (Figure 2b and 2c) which is a mix 140 between a woody fuel and a harder one. Images observed after 550°C treatment changes due to thermal effect are easily seen. At this point structural chemical bonding has been 141 142 broken so hemicellulose, cellulose and lignin of most biomass samples have turned into 143 gaseous CO₂ and CH₄ having lost up to 70% of their initial weight, giving a finely 144 divided structure. Some particles are outlined (orange) in this structure are unburnts, formed by alkali sulphates with high melting points not vaporized at low temperatures 145 146 that gain relative weight at high temperatures.Low melting point elements may also agglomerate forming particle clusters and high melting temperature compounds. 147 148 Concerning **particle size distribution**, ash particles can be classified in *thin* or *thick* if they, respectively, cross or do not cross a 400 µm mesh sieve [11]. Fly ash is usually 149

considered to have a diameter between 0.2 and 200 μ m and bottom ash as between 200 150 151 and 1000 µm [35]. The concept PM10 (particulate matter 10) meansthe quantity of particles under 10 µm that float in the atmosphere polluting its composition. This group 152 153 includes the PM2.5 (particulate matter 2.5 µm) ones, or *breathable particles*, that can affect human health by penetrating human airways. In this work, PSD results obtained 154 155 by laser diffraction, are divided in five ranges (under 10, 10-100, 100-200, 200-400 and 156 over 400 µm) and their results compared. It is interesting for ashes to have as higher thick or bottom ash fractions as possible (more than 200 µm particles) that are easily 157 removed from the bottom of the chambers, avoiding contamination and health damage 158 159 risks. As can be seen in Figure 3 most of the studied samples have more than 80 % of ash particles thicker than 200 µm, beetroot pellets, pine and pine-apple pine pellets or 160 vine orujillo more than 90 % of them. On the other hand wood pellets and almond shell 161 162 were found to have, respectively, 35 and 45 % of particles under fly ash considered diameter. None of the samples presented PM10 values over 3% and PM2.5 detected 163 164 values were negligible in every case, with only charcoal and pine kernel shell samples reaching 0.1 %. 165

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4.2 Chemical composition

167 Figure 4 presents the results obtained for EDXA analysis after 550 °C ashing temperature as an average of six measure points throughout SEM-observed sample. As 168 can be seen in Table 1, raw fuel structure is, as expected, basically organic with a vast 169 majority of C and O in the sample composition and a C/O ratio between 0.8 and 1 in 170 most cases which is influential in biomass reactivity and indicates higher heating 171 value.Beetroot pellets, sorghum and vine shoot chips present a ratio slightly lower, close 172 173 to 0.7 and rice husk far under this value with a 0.38 ratio, being a highly oxygenated structure that confers low HHV to this fuel. On the other hand charcoal presents a 174

4.68C/O ratio, as it underwent a previous pyrolysis. When these data are compared 175 176 with the ones obtained after 550°C burning (Figure 4), it can be highlighted that at this temperature most of the carbon structure was eliminated and the proportion of high 177 178 melting-temperature elements has increased. C values are commonly between 15-25% while O (which still remains in oxides) carbonates or sulphates has slightly increased 179 180 until 40-60%. Charcoal differs from these results due to the previously explained 181 reasons. Concerning other elements it is remarkable the high silicon peaks observed in charcoal (40%), pine kernel shell or straw pellets (10%). K and Ca, key elements in 182 fouling and slagging generation, are also interesting being the first ones close to 5% in 183 184 most samples, with the exception of straw pellets (10%), charcoal (15%), pine and pine apple leaf pellets (20%) or vine orujillo (30%). Ca values are slightly above K ones, 185 186 with olive stone, wood or beetroot pellets (10%) and charcoal (30%) above the average. 187 Mg presents a nearly constant value of 3-5% for most samples and the low Na values (around 1 are the other remarkable notes. Cl values detected in the rice husk sample are 188 189 extremely high, reaching 30%, this may proceed from fertilizers or a bad homogeneity 190 of measure points, but there are some herbaceous species with high natural values in 191 themselves.

192 **X-Ray fluorescence** measured values are presented in Table 3. These are used to 193 calculate deposition predictive equations and their results compared with ternary diagrams and experimental experience. Every predictive equation proposed in Table 3 194 195 was calculated and meaningful differences were noticed for the same sample. Due to 196 this, only the most referenced equations are proposed and compared in this work, one to predict slag $(R_{b/a})$ and one to predict fouling (F_u) , but both can be used to predict 197 198 general deposition and their results compared. These results are presented in Table 3 following a colour criterion, red, orange and green being high, medium and low 199

200 deposition risk respectively. As can be seen deposition predictions obtained from both 201 equations agree in the samples with high and low values but present some 202 contradictions in the intermediate ones, conceding high or medium deposition risk in 203 some cases depending on the considered equation. When these results are compared with the ones obtained by using ternary diagrams this tendency can be confirmed. 204 205 In this way when a sample presents more than 50% (mass percentage in ashes) of CaO 206 or SiO₂ combined with more than 15% of K₂O, its ashes can easily agglomerate and 207 therefore deposit. This means the samples on the right of the red line drawn on the SiO₂-CaO-K₂O diagram (Figure 5). As can be determined, samples AS, CC, PPLP, PL, 208 209 PKS, VO and WP present high deposition risks, all of them were considered as high or medium risk by using predictive equations. Some contradictions are also noticed, for 210 211 example fuels with the highest deposition predictive values like VSC, THI or CH are 212 not supposed to present high risk according to this diagram. 213 The SiO₂+Al₂O₃+Fe₂O₃+Na₂O+TiO₂-CaO+MgO+MnO-K₂O+P₂O₅+S (Figure 6) 214 diagram is also presented. This classifies samples according to their acidity (high, 215 medium or low) which is influential oncorrosion phenomena and melting point (S, C, K and CK types). S and K types present high deposition risks due to silicates formation 216 217 and potassium presence. C type is expected to have high melting temperature (and 218 therefore, low depositions) due to high Ca levels. CK type is an intermediate between C and K. According to this, results are quite homogeneous if compared with SiO₂-CaO-219 220 K₂O diagram ones, as they both consider PPLP, PL, PKS, SP and VO as high 221 deposition risk samples and AS and WP as medium risk ones. The same contradictions with predictive equations as in the previous case are noticed. 222 223 When compared with experimental experience, it should be stated that most of the

samples except PKS, VO and WP presented no deposition problems when burning on a

224

crucible. These samples are predicted as high deposition risk with both graphic
methods, so they must be considered, for our tested samples, as more reliable.
Regarding acidity, following the explained criterion only RH presents high acidity
values, meaning high corrosion risk in the burning equipment, which agrees with high

- chlorine values measured by EDXA.
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4.3 Thermogravimetric study

ways to study biomass and its wastes. One of the most common uses for the burning
profile of a sample, that relates weight loss and temperature, is to determine
characteristic points: ignition point, when a fuel begins to react, and peak point, when
mass loss speed is the highest in the sample, related with its reactivity. Table 4 shows
the characteristic points obtained for the selected samples. In this work, TGA is also
use to compare different biomass samples char and ash thermal behaviour; this means
when fuel's weight attains a steady speed after peak temperature, and before the

As previously stated, thermogravimetry is a versatile tool that can be used in several

reaction end, from 400 to 850 °C.

As can be seen ignition temperature is in the range 170-200 °C for every sample except

241 THI, that falls 130°C, entailing higher auto-ignition risk if appropriate conditions, like

high powdery atmospheres, are reached, and WC and CC that increase until 212 and
233 °C, respectively.

Peak temperature values, when a sudden volatile matter and a huge mass loss occur, are
usually between 230-330 °C. CC, because of its pyrolytic origin, presents a lower
volatile matter quantity, and a more constant mass loss, this value increasing up to
487°C.

Figures 7 and 8 show the mass loss of the studied sample's from 400 to 850 °C. As can

be seen, every sample (except VO and CC) has lost more than 60% of its original

250 weight at this relatively low temperature. In the focused range, mass loss decreases 251 quite homogeneously until a turning point when combustion reaction ends. This one changes quite a lot depending on the selected fuel, from nearly 500°C of PL, THI or 252 253 RH to 800 °C for AS, CC or VO. It is interesting to have a high reaction-end temperature which permits to obtain fuel yields in a wider operation range. 254 5. Conclusions 255 256 In this work different biomass samples have been characterized by SEM, XRD, PSD, 257 FRX and TG in order to establish which ones are the most desirable for combustion applications. 258 259 SEM images showed that the natural structure of harder biomass fuels (shells or husks) makes them easier to homogenise andhandle, than fibrous ones (wood or straw). The 260 ashes obtained after 550 °C burning present a homogeneous finely-divided structure 261 262 with presence of unburnt. 263 PSD study demonstrated that BP and PPLP generate a vast majority of thick ashes, 264 while the selected brand of WP and AS have more than 35% of fine particles, 265 increasing environmental and health risks with their use. Deposition predictive equations, combined with FRX based ternary diagrams and 266 267 experimental experience suggest that AS, PPLP, PL, PKS or VO present high 268 deposition risks, decreasing the energy yield of the reaction. RH sample has huge corrosion risks due to its acidity which is confirmed by Cl presence measured by 269 270 EDXA. 271 TG study showed that THI presented a low ignition point which has direct influence on auto-ignition and explosive atmospheres generation. AS, CC and VO present wider 272 273 reaction ranges thank to their higher reaction-end temperature.

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289 **References**

- [1] Gil MV, Casal D, Pevida C, Pis JJ, Rubiera F. Thermal behaviour and
- kinetics of coal/biomass blends during co-combustion. Bioresource Technol
 2010; 101: 5601–8.
- 293 [2] Qian FP, Chyang CS, Huang KS, Tso J. Combustion and NO emission of
- high nitrogen content biomass in a pilot-scale vortexing fluidized bed
- combustor. Bioresource Technol 2011; 102: 1892–8.
- [3] Demirbas A. Importance of biomass energy sources for Turkey. Energ
 Policy 2008; 36: 834–2.
- 298 [4] Sebastián F, García D, Rezeau A. Energías renovables-Energía de la
- biomasa (volumen I). Prensas Universitarias de Zaragoza. Zaragoza. 2010.
- 300 [5] Van Loo S, Koppejan J. The handbook of biomass combustion and co-
- 301 firing. Earthscan. London. 2010.

- 302 [6] Fang X, Jia L. Experimental study on ash fusion characteristics of
- 303 biomass. Bioresource Technol 2012; 104: 769-4.
- 304 [7] Biagini E, Narducci P, Tognotti L. Size and structural characterization of
- lignin-cellulosic fuels after the rapid devolatilization. Fuel 2008; 87: 177-6.
- 306 [8] Umamaheswaran K, Batra VS. Physico-chemical characterisation of
- 307 Indian biomass ashes. Fuel 2008; 87: 628–8.
- 308 [9] Xiao R, Chen X, Wang F, Yu G. The physicochemical properties of
- 309 different biomass ashes at different ashing temperature. Renew energ 2011;
- 310 36: 244-9.
- 311 [10] Nortey Yeboah NN, Shearer CR, Burns SE, Kurtis KE. Characterization
- of biomass and high carbon content coal ash for productive reuse applications.

313 Fuel 2014; 116: 438–7

- 314 [11] Carrasco B, Cruz N, Terrados J, Corpas FA, Pérez L. An evaluation of
- bottom ash from plant biomass as a replacement for cement in building
- 316 blocks. Fuel 2014; 118: 272–0
- 317 [12] Abraham R, George J, Thomas J, Yusuff KKM. Physicochemical
- 318 characterization and possible applications of the waste biomass ash from
- oleoresin industries of India. Fuel 2013; 109: 366–2.
- 320 [13] Wang S, Miller A, Llamazos E, Fonseca F, Baxter L. Biomass fly ash in
- 321 concrete: Mixture proportioning and mechanical properties. Fuel 2008; 87:322 365-1.
- 323 [14] Bridgeman TG, Darvell LI, Jones JM, Williams PT, Fahmi R,
- 324 Bridgewater AV et al. Influence of particle size on the analytical and chemical
- properties of two energy crops. Fuel 2007; 86: 60-72.
- 326 [15] Mediavilla I, Fernández MJ, Esteban LS.Optimization of pelletisation
- and combustion in a boiler of 17.5 kW for vine shoots and industrial cork
- residue. Fuel Process Technol 2009; 90: 621-8.
- 329 [16] Becidan M, Todorovic D, Skreiberg O, Khalil RA, Backman R, Goile F
- et al. Ash related behaviour in staged and non-staged combustion of biomass
- fuels and fuel mixtures. Biomass Bioenerg 2012; 41: 86-3.

- [17] Roy MM, Dutta A, Corscadden K. An experimental study of combustion
- and emissions of biomass pellets in a prototype pellet furnace. App Energ
- 334 2013; 108: 298–7.
- 335 [18] Wang G, Silva RB, Azevedo JLT, Martins-Dias S, Costa M. Evaluation
- of the combustion behaviour and ash characteristics of biomass waste derived
- fuels, pine and coal in a drop tube furnace. Fuel 2014; 117: 809–24.
- 338 [19] Vassilev SV, Baxter D, Andersen LK, Vassileva CG. An overview of the
- chemical composition of biomass. Fuel 2010; 89: 913–33.
- 340 [20] Vassilev SV, Baxter D, Andersen LK, Vassileva CG. An overview of the
- 341 composition and application of biomass ash. Part 1.Phase-mineral and
- chemical composition and classification. Fuel 2013; 105: 40–76.
- 343 [21] Fryda L, Sobrino C, Glazer M, Bertrand C, Cieplik M. Study of ash
- deposition during coal combustion under oxyfuel conditions. Fuel 2012; 92:308–7.
- 346 [22] Vamvuka D, Pitharoulis M, Alevizos G, Repouskou E, Pentari D. Ash
- 347 effects during combustion of lignite/biomass blends in fluidized bed. Renew
- 348 Energ 2009; 34: 2662–1.
- 349 [23] Fernández MJ, Carrasco JE. Comparing methods for predicting the
- sintering of biomass ash in combustion. Fuel 2005; 84: 1893–0.
- 351 [24] Vassilev SV, Baxter D, Andersen LK, Vassileva CG, Morgan TJ. An
- 352 overview of the organic and inorganic phase composition of
- 353 biomass.Fuel2012; 94: 1–33.
- 354 [25] Magdziarz A, Wilk M. Thermogravimetric study of biomass, sewage
- sludge and coal combustion. Energ Convers Manage 2013; 75:425–0.
- 356 [26] Sarkar P, Sahu SG, Mukherjee A, Kumar M, Adak AK, Chakraborty N et
- al. Co-combustion studies for potential application of sawdust or its low
- temperature char as co-fuel with coal. App Therm Eng 2014; 63: 616-3.
- 359 [27] VersanKok M, Özgür E. Thermal analysis and kinetics of biomass
- 360 samples. Fuel Process Technol 2013; 106: 739–3

- 361 [28] García R, Pizarro C, Lavín AG, Bueno JL. Biomass proximate analysis
- using thermogravimetry. Bioresource Technol 2013; 139: 1–4.
- 363 [29] Ávila C, Pang CH, Wu T, Lester E. Morphology and reactivity of char
 364 biomass particles. Bioresource Technol 2011; 102: 5237-3.
- 365 [30] Fernández MJ, Carrasco JE. Concentration of elements in woody and
- herbaceous biomass as a function of the dry ashing temperature. Fuel 2006;85: 1273–9.
- 368 [31] Thyrel M, Samuelsson R, Finell M, Lestander TA. Critical ash elements
- in biorefinery feedstock determined by X-ray spectroscopy. App Energ 2013;
 102: 1288–4.
- 371 [32] García-Maraver A, Terron LC, Ramos-Ridao A, Zamorano M. Effects of
- 372 mineral contamination on the ash content of olive tree residual biomass.
- Biosystems Eng 2014; 118: 167-3.
- 374 [33] García R, Pizarro C, Lavín AG, Bueno JL. Characterization of Spanish
- biomass wastes for energy use. Bioresource Technol 2012; 103: 249–8.
- 376 [34] Tortosa-Masiá AA, Buhre BJP, Gupta RP, Wall TF. Characterising ash
- of biomass and waste. Fuel ProcessTechnol2007; 88: 1071-1.
- 378 [35] Grammelis P, Skodras G, Kakaras E. Effects of biomass co-firing with
- coal on ash properties. Part I: Characterisation and PSD. Fuel 2006; 85: 2310-
- 380 5.

Table 1

Tested fuels analytical values.

C	Proximate analysis				TITIX7	Ultimate analysis					
Sample	Μ	Ash	VM	FC	HHV	Ν	C	S	Η	0	C/O
AS	8.68	2.2	82	15.8	18275	0.3	46.35	0.22	5.67	47.46	0.98
BP	12.5	9	76	15	15095	1.19	38.94	0.51	5.23	54.13	0.72
BRI	5.84	0.8	85	14.2	18498	1.24	46.74	0.1	6.39	45.53	1.03
CC	5.29	5.9	26	68.1	29712	0.65	79.34	0.3	2.74	16.97	4.68
СН	9.6	5.8	76.2	18	18236	2.53	45.06	0.48	6.42	45.51	0.99
OS	11	1.4	78.3	20.3	17884	1.781	46.55	0.11	6.33	45.229	1.03
OTP	8.7	13	78	9	17342	1.47	45.36	0.28	5.47	47.42	0.96
PPLP	8.2	3.2	75	21.8	18147	0.4	42.26	0.27	4.81	52.26	0.81
PKS	9.14	1.3	80	18.7	18633	0.27	47.65	0.11	6.33	45.2	1.05
PL	8.33	2.7	77.6	19.7	18893	0.31	47.91	0.6	4.9	46.28	1.04
RH	7.27	13.7	74	12.3	15899	0.21	26.69	0.17	2.88	70.05	0.38
S	6.1	17	62	21	11872	0.73	37.89	0.21	5.94	55.23	0.69
SP	7.3	9.8	79	11.2	16584	0.56	47.89	0.17	5.51	45.87	1.04
TH	11.6	0.2	80.67	19.13	17747	0.48	43.89	0.28	6.46	48.89	0.90
VO	9.5	12.7	79	8.3	17742	1.91	44.15	0.58	5.31	48.05	0.92
VSC	22	9.7	66	24.3	14631	0.61	40.15	0.31	5.02	53.91	0.74
WC	25.6	1.5	68.6	29.9	15162	0.13	42.2	0.27	5.51	51.89	0.81
WP	7.7	1.3	82	16.7	18218	0.6	46.79	0.32	6.13	46.16	1.01

M. ash. VM and *FC* respectively mean moisture Ash, volatile matter and fixed carbon. Measured in mass percentage. *HHV* is the higher heating value measured in J/g. *C. N. H. O* and *S* are the mass percentage of carbon, nitrogen, hydrogen, oxygen and sulphur.

Table 2

Review of deposit	ion-predictive indexes.	
Method	Formulae	Deposition criteria
Base/acid ratio [9, 14, 21, 22]	$R_{b/a} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + TiO_2 + Al_2O_3}$	$< 0.5 \rightarrow low$ 0.5-1 \rightarrow medium
	P_2O_5 may be also added as a Basic oxide [34]	$>1 \rightarrow high$
Silicon/alumina ratio [9, 14, 22] Iron/calcium	$S/_A = \frac{SiO_2}{Al_2O_3}$	$<0.31 \text{ or} > 3 \rightarrow \text{low}$ $0.31-3 \rightarrow \text{high}$ $<0.31 \text{ or} > 3 \rightarrow \text{low}$
ratio [14, 22]	$I/C = \frac{Fe_2O_3}{CaO}$	$0.31-3 \rightarrow high$
Slagging index [14, 22]	$R_S = R_{b/a} \cdot S$	$< 0.6 \rightarrow low$ 0.6-2 \rightarrow medium $> 2 \rightarrow high$
Slag viscosity index [9, 14]	$S_R = \frac{SiO_2}{SiO_2 + Fe_2O_3 + CaO + MgO} \cdot 100$	$>78 \rightarrow low$ 66.1-78 \rightarrow medium <66.1 \rightarrow high
Chlorine content [14]	Weight percentage of Cl. in an "as received" fuel sample	$<0.2 \rightarrow low$ $0.2-0.3 \rightarrow medium$ $0.3-0.5 \rightarrow high$ $>0.5 \rightarrow really high$
Fouling index I [14]	$F_u = R_{b/a} \cdot (K_2 O + N a_2 O)$	$< 0.6 \rightarrow low$ $0.6-40 \rightarrow high$ $>40 \rightarrow extremely high$
Fouling index II [21]	$F = \frac{K_2 O + N a_2 O}{2 \cdot S + C l}$	Higher as higher F
Alkali index [14]	$IA = \frac{1}{HHV} \cdot Ash \cdot (K_2O + Na_2O)$	$>0.17 \rightarrow$ probably fouling $> 0.34 \rightarrow$ sure
I parameter [23]	$I = \frac{CaO + MgO}{K_2O + Na_2O}$	>2 no sinter
Total alkali content [14, 22]	$TA = (K_2O + Na_2O)$	$<0.3 \rightarrow low$ 0.3-0.4 \rightarrow medium $> 0.4 \rightarrow high$
H fouling index [9]	$H = R_{b/a} \cdot Na_2 O \text{ if } \frac{Fe_2O_3}{CaO + MgO} > 1$ $H = Na_2 O \text{ if } \frac{Fe_2O_3}{CaO + MgO} < 1 \text{ and } CaO + MgO > 2$	$<3 \rightarrow$ medium $>3 \rightarrow$ high
Fusion temp index [18]	$F = \frac{SiO_2 + K_2O + P_2O_5}{CaO + MgO}$ le symbol means its weight percentage of obtained fr	Higher tendency as higher F value

Each element/oxide symbol means its weight percentage of obtained from elemental analysis (S), EDXA (Cl) or XRF (oxides). *HHV* is the higher heating value measured in GJ/kg and *ash* the ash mass percentage of the measured sample.

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X-Ray fluorescence data.

	XRF data									Equations		
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	R _{b/a}	$\mathbf{F}_{\mathbf{u}}$
AS	31.0	4.4	1.2	0.1	6.3	25.7	1.4	25.8	0.1	3.9	1.7	46.4
BP	42.3	5.2	1.5	0.1	6.3	35.1	1.2	4.2	0.3	3.8	1.0	5.4
BRI	24.5	9.6	1.8	1.3	7.5	39.2	1.9	10.1	1.7	2.5	1.7	20.2
CC	15.9	3.1	2.2	0.4	7.3	45.0	2.7	15.4	0.2	7.8	3.8	68.1
СН	5.3	1.5	1.9	0.4	14.4	59.4	1.5	11.5	0.1	3.9	12.8	166.8
OS	26.6	6.2	3.1	0.1	11.7	37.0	0.9	11.0	0.4	3.0	1.9	23.0
OTP	50.1	3.9	1.6	0.1	2.6	33.5	0.5	5.5	0.4	1.9	0.8	4.8
PPLP	49.2	5.6	1.1	0.1	4.9	6.5	1.3	27.1	0.1	4.1	0.7	21.2
PL	18.1	4.7	6.3	0.3	14.2	11.5	1.9	35.3	0.1	7.7	3.0	112.3
PKS	51.3	4.1	2.9	0.1	4.8	7.5	1.4	24.6	0.1	3.3	0.7	19.2
RH	88.2	1.3	0.4	0.3	1.1	1.8	0.4	4.9	0.0	1.7	0.1	0.5
S	53.9	7.2	3.3	0.1	1.9	29.5	0.7	2.2	0.5	0.8	0.6	1.7
SP	53.5	1.6	0.6	0.1	2.3	20.6	0.9	17.8	0.1	2.5	0.8	14.3
THI	5.5	1.2	1.5	0.1	10.5	69.3	0.9	5.0	0.1	5.8	12.6	73.8
VO	23.9	4.1	1.3	0.1	9.2	15.9	1.7	32.9	0.1	10.8	2.2	75.5
VSC	6.6	1.0	0.6	0.7	14.7	53.6	0.7	9.5	0.1	12.7	10.3	105.4
WC	28.8	5.1	7.4	0.7	5.2	35.5	1.8	5.7	6.5	3.4	1.4	10.2
WP	21.3	4.8	3.7	0.4	8.8	28.5	1.7	20.9	1.8	8.1	2.3	51.8

Sample	Tignition (°C)	Tpeak (°C)	Treaction-end (°C)
AS	171	296	791
BP	183	232	750
BRI	169	340	611
CC	233	478	775
СН	170	322	550
OS	195	289	609
OTP	180	325	548
PPLP	178	331	697
PL	183	318	506
PKS	194	333	716
RH	188	319	521
S	195	331	525
SP	170	287	619
THI	130	339	531
VO	182	269	804
VSC	195	324	550
WC	212	340	517
WP	200	332	631

Table 4 - Characteristic points of TGA analysis.

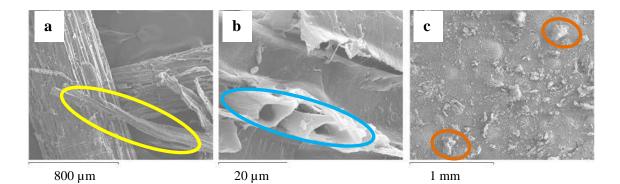


Figure 1. Wood chips SEM captures at room temperature (a x65 magnifications and b x2000) and after 550°C burning (c x50 magnifications).

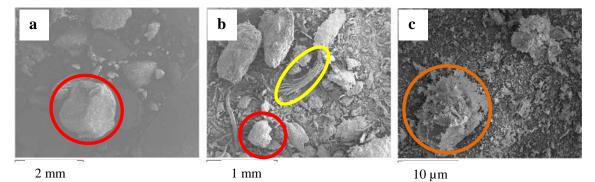


Figure 2. Pine kernel shell (a room temperature x20) and pine and pine-apple leaf pellets' (b room temperature x40 and c after 550°C burning x350) SEM captures

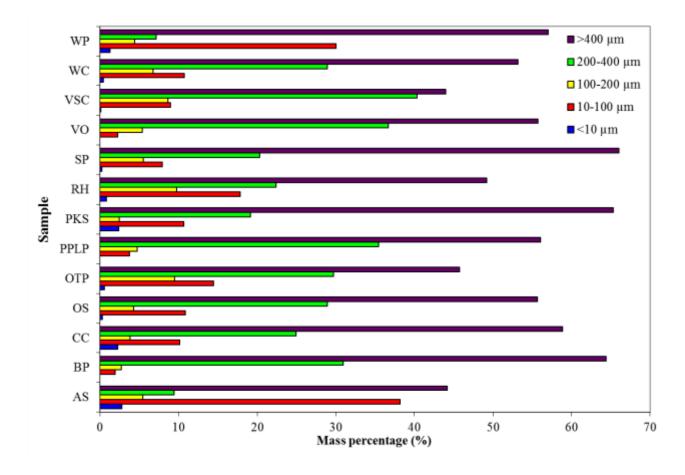


Figure 3. Particle size distribution of the selected biomass samples.

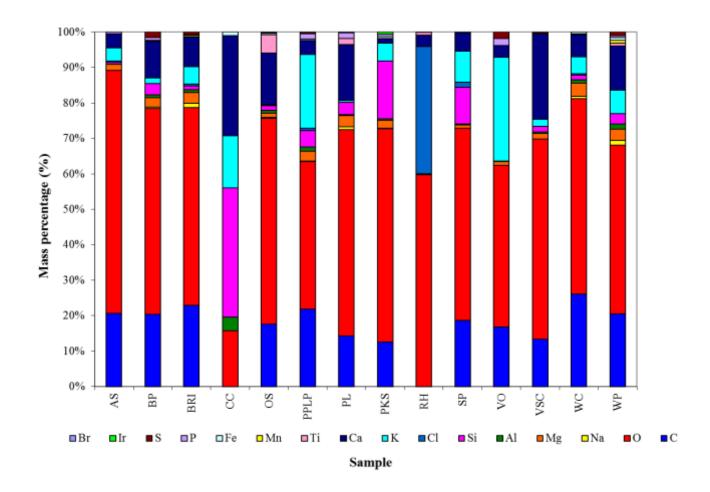


Figure 4. Results obtained from EDXA analysis.

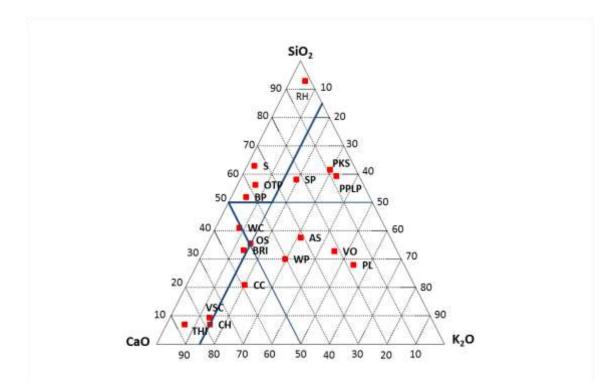


Figure 5. SiO₂-CaO-K₂O ternary diagram.

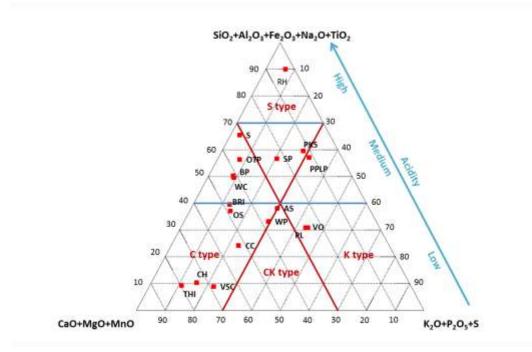


Figure 6. SiO₂+Al₂O₃+Fe₂O₃-+Na2O+TiO₂-CaO+MgO+MnO-K₂O+P₂O₅+S ternary diagram.

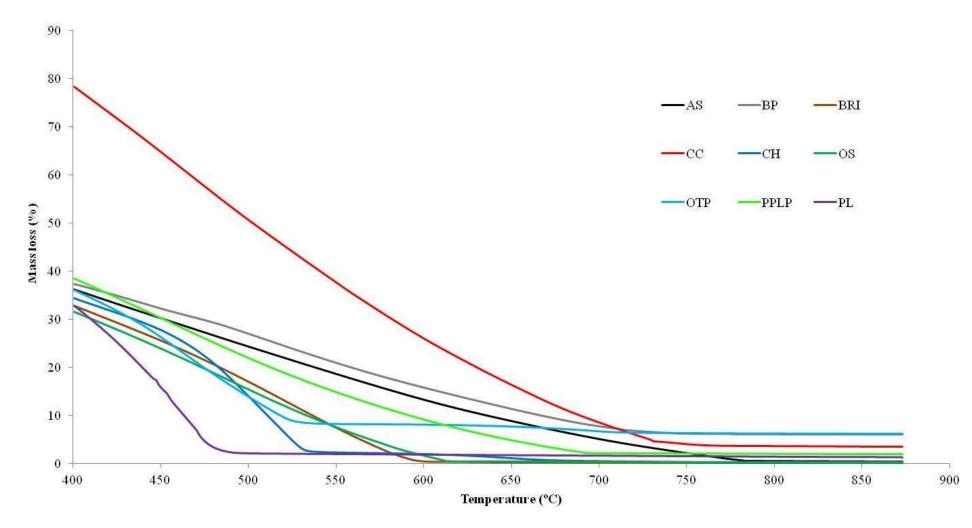


Figure 7. TGA profiles for several biomass samples from 400°C (I).

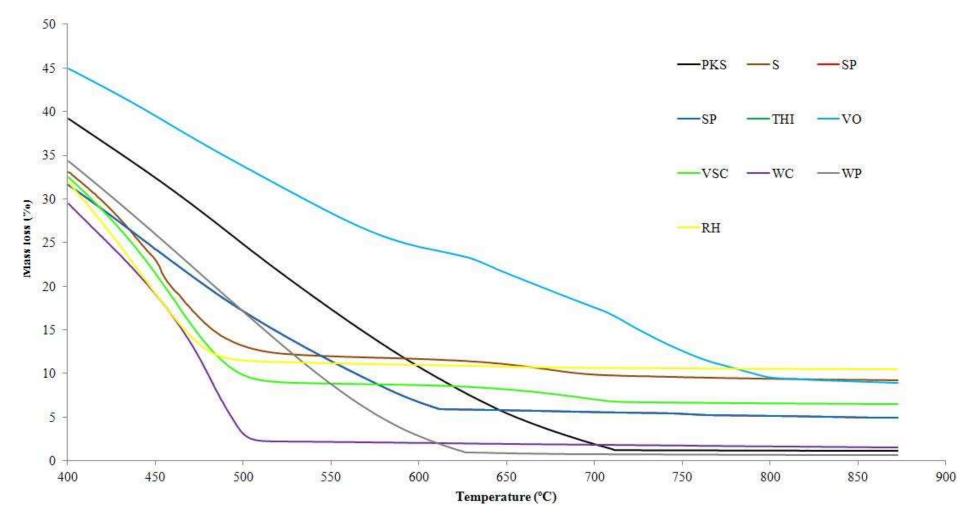


Figure 8. TGA profiles for several biomass samples from 400°C (II).