1 Spanish biofuels heating value estimation based on structural analysis

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10 Abstract

11 The importance of waste biomass as an energy source is likely to increase during the coming years as a result of European energy policy objectives, and 12 because of the wide range of possibilities that it offers: it is a cheap fuel, 13 widespread, and available in large quantities. In addition to crops and forestry 14 15 operations, the Spanish fruit, olive and wine industries generate large amounts 16 of currently undervalued solid wastes such as stones, branches, pulps or pomaces. The use of these by-products offers environmental benefits like 17 removing waste and preventing fires at the same time as providing an energy 18 19 yield. A proper energy valorization will require a complete physicochemical characterization. In this article, a structural and thermal characterization is 20 21 developed from twenty samples from the olive and wine industries, as well as from forest and agro wastes. In addition, predictive equations are proposed to 22 determine higher heating value (HHV) from chemical composition. For this 23

purpose, the chemical extraction method (also called the 'classic' method) was
used, and results were obtained in accordance with the data shown in the
bibliography. Two predictive equations were developed: one based on lignin
and hemicellulose content, and the other based on lignin quantity. Both present
an absolute average error (AAE) of 0.87% and 1.13%, respectively.
Keywords: Biomass, high heating value, structural analysis, chemical
composition

31

32 **1. Introduction**

During recent years, waste biomass has gained in importance as an energy
feedstock due to requirements for developing various renewable energy
sources to reach European goals for the years 2020 (the "three 20s" target) and
2050.

Among complementary energy resources, biomass offers great possibilities, 37 38 including those involving direct (combustion) procedures and indirect (extractive 39 or transformative) procedures of reuse, recovery and revaluation (Barbanti et 40 al., 2014). Since biomass as waste is cheap and available nearly everywhere 41 (Masnadi et al., 2014), and is also responsible for lower emissions of 42 environmentally detrimental gases like sulphur dioxide (SO₂) and nitrogen oxides (NO_x), the combustion of biomass also plays a positive role in reducing 43 44 global acid rain formation (Zhang et al., 2010). In addition, biomass contributes 45 approximately 14% of worldwide energy consumption (Demirbas and Demirbas, 2007), meaning 63% of all renewable energy sources (García-Maraver et al., 46

2012). The work of (Krzyżaniak et al., 2014 and 2015 *in press*; Salaheldeen et
al., 2014), are worthy of mention as recent contributions. Woody crops
management, like orchards, olive groves or vineyards, generate huge amounts
of waste (Godin et al., 2013).

To achieve an efficient reuse of residual vegetable biomass, the availability of the raw matter (quality, quantity, location of origin) must be reconciled with the characteristics of the chosen or available technical alternatives (fundamentals of procedures, optimal design capacity and location of the consumers of commercial energy). The technical and economic success of most of the options is thus strongly associated with geography, climate and customer requirements.

58 In Spain, the biggest potential biomass source belongs to Andalucía and Castilla-La Mancha, which together provide nearly 50% of all woody crop 59 wastes (Rosúa and Pasadas, 2012). It should be noted that, due to high 60 production, olive and wine industrial wastes are plentiful in Spain, but not 61 sufficiently valued. These two industries produce a large quantity of several 62 types of biomasses with different properties. Spain's Surfaces and Crop Yields 63 64 Inquiry (ESYRCE) shows an overall vineyard-crop cultivation area of 963,644 hectares, while the olive growing area amounts to 2,593,523 hectares, meaning 65 5.7% and a 15.1%, respectively, of overall cultivated surface area in Spain. 66

The main organic wastes obtained from the olive industry are olive pomace, extracted olive pomace (coming from oil mills), olive vegetable water (also called "alpechín"), a mixture of olive vegetable water and pulp (known as

"alperujo") and, in lower quantities, olive stones. Figures 1a and 1b show a
diagram of olive oil production using the three existing procedures and an
extractive plant flow chart.

The main organic wastes from the wine industry are pomace (pressed grape
waste), lees (fermentation and maturing precipitates), wine wash water
(vinasse), and the grape stalks that are separated in the destemmer. Figure 2
shows a white wine production chart, indicating wastes obtained in each phase
of production. Red wine production is slightly different, but the same types of
wastes are obtained.

Figures 1a, 1b and 2 illustrate olive and wine production wastes organized according to colour. Thus, the green boxes are solid wastes, which are the subject of interest in this work, while the liquids, which are not studied here, appear in yellow. Finally, end or tail products for each process are marked in blue, and sub-products and other wastes are marked in grey.

In addition to the woody crops, there are other biomass sources like the
harvesting of shrubland areas or of whole trees not necessarily coming from
agro-crops. The thinning out of wooded areas and the proper treatment of
shrubs is a useful tool for preventing disease while sustainably exploiting
Spain's woody regions. Olive groves, vineyards and orchards require regular
pruning, which generates a huge amount of biomass available for energy use
(Spinelli and Picchi, 2010).

On the other hand, extensive neglected scrubland zones are an undesirable
fuel source and the main spreader of forest fires in Spain, and they represent a

significant environmental impact because of adding to the greenhouse effect.
The valorization of these wastes could be an incentive for environmental cleanup, considering that forestry biomass reaches 18,715,359 tonnes per year,
while the whole biomass potential in Spain alone reaches 88,677,193 tonnes
per year, as shown in Table 1.

In fact, not all of these waste materials are usually properly managed. For example, prunings are commonly burned in the same place where they are gathered (Velázquez-Martí et al., 2011). The energy use of these wastes not only contributes to sustainable energy production, but also improves the management of waste materials *in situ*.

Taking into account the lack of accurate biomass standardization, particularly in terms of physicochemical, process and environmental indicators, the evaluation and selection of raw materials for obtaining better process efficiencies presents many difficulties. Therefore, a proper characterization is required for the adequate use the wastes previously described.

The properties of commercial fuel are usually well known. Nevertheless, some waste-biomasses, like the ones studied in this article, are not fully standardized and do not follow any specific, existing normative (that for pellets, for example), so it becomes necessary to study their characterization in depth. This research group has previously developed studies on the proximate and ultimate analysis of biomass fuels (García et al., 2014a, 2014b). A chemical composition study of those materials is thus required in order to fully complete this work.

The main structural components of biomass are cellulose, hemicellulose and lignin. Cellulose appears in the largest quantities in lignocellulosic biomass, which is a linear polymer formed by ß-glucose units joined together by ß-1,4glucosidic bonds. In addition, as a whole, it possesses a fibrous structure in which hydrogen-bridge bonds between hydroxyl groups of alternate glucose chains are formed, making it tough and insoluble to water (Smook, 2002).

Hemicelluloses, as cellulose, are polymers made of pentoses, hexoses and
uronic acid units. They are smaller than cellulose and, also being amorphous
polysaccharides, each unit generally contains more than one kind of sugar
(Carrier et al., 2011).

Lignin is a 3D polymer formed by three units of phenylpropane (conipheryl, sinapyl and coumaryl alcohols). Lignin possesses a huge variety of functional groups and 10 different bond types (Tejado et al., 2007).

128 Figure 3 shows the 3D order of the main biomass chemical components as well

as the proportion in which they usually appear. The images were obtained using

a Scanning Electron Microscope (SEM), at a magnification of 110x, 250x and

131 130x for lignin, cellulose and hemicellulose, respectively.

132 In Figure 3, depicts how cellulose appears as long fibres surrounded by a net of

hemicellulose, joined by hydrogen-bridge bonds. Lignin is placed as a matrix

between the strings formed by the merging of cellulose and hemicellulose.

135 These fractions are joined by hydrogen-bridges and covalent bonds (benzyl

esters, benzyl ethers and phenyl glycosides (Smook, 2002)).

Chemical composition is closely related to the potential applications of a
material and therefore to its energy use because higher heating value (HHV)
greatly depends on these compounds. This relationship can be observed by the
existence of varying HHV-predictive equations based on chemical composition.

141 The common methods for determining Lower Heating Values (LHV, defined as 142 excluding heating losses through sub-products of combustion) and Higher 143 Heating Values (HHV), may be classified into three inter-connected basic 144 groups: theory, direct experimentation and empirical correlations. In fact, 145 thermodynamic models based on rigorous state theories have the drastic 146 inconvenience of needing detailed and precise analysis of all of the thousands 147 of molecules present in such a natural product in order to reliably integrate (if previously available) a significant number of reactive internal energies or 148 enthalpies. Experimentation must be carried out using original and sophisticated 149 150 laboratory techniques or by precise, consolidated and commercially welldeveloped ones, e.g., by calorimetric bomb. Empirical estimations attempt to 151 shortcut time-consuming experimental calculations, thus reaching the typical 152 153 engineering compromise between requirements and accuracy. This question has been thoroughly discussed in some of our previous contributions (García et 154 155 al., 2014a, 2014b).

The purpose of these last methods, particularly useful in a practical context, is to avoid slow and cumbersome procedures correlating HHV and LHV with less onerous available data (i.e., structural analysis is preferable to elemental analysis) while maintaining reliability within acceptable limits.

This work proposes several equations, based on experimentally obtained data,
which enlarge the inventory of equations previously proposed by other authors,
and which is summarized in Table 2.

163 As can be seen in Table 2, equations obtained after bibliographical review can

be categorized for specific biomass groups (like TIL or WHI, exclusively for

woody fuels) or with broad, general applicability. They can also be defined from

just one biomass fraction (like ACA or DEM01, 03 and 04) or from more than

one, such as J&G, which uses all structural biomass components in their

proposed correlation. In addition, fractions used to calculate HHV values may

169 be expressed on a different basis by different authors.

170 The new equations proposed here for estimating HHV are based on the

171 chemical structural analysis of biomass samples.

172

173 **2. Samples and methods**

174 2.1. Samples

175 Chemical composition and HHV were determined for twenty biomass samples

belonging to agro-forestry wastes and industrial wastes. For the purpose of

illustration, Figure 4 shows some of the analyzed samples.

As a pre-treatment to sort and isolate the analyzed fractions, all studied

samples were grinded and milled until particle size was in the range of 250-

180 500 μm (TAPPI, 2007).

181 2.2. Experimental procedure

Biomass chemical composition can be obtained through a chemical extraction process that is summarized in Figure 5. Data for different fractions are expressed on the basis of free dry, ash and extractives. Every experimental run, except the singular extractive determinations, was performed three times to assure reproducibility according to a pre-established accuracy.

187 2.2.1. Sample preparation

188 Before quantifying different biomass fractions, it was necessary to homogenize sample size distribution. Once this was achieved, samples were subjected to a 189 two-stage extraction process to eliminate a group of substances known as 190 "extractives" that may interfere with a rigorous characterization. The first of 191 these stages consisted of an acetone treatment in a Soxhlet extractor lasting 7-192 8 hours to get rid of resins, waxes, sterols, fats and fatty acids. The second 193 phase was carried out with boiling water for 1 hour: tannins, gums, sugars and 194 195 coloured matter were removed. Once both phases were completed, the refined 196 biomass was air-dried to reduce its moisture content to below 15 %.

197 2.2.2. Holocellulose fraction determination

198 This quantity was obtained from an extractive-free biomass using an acetic acid

and sodium chloride treatment, according to the ASTM D-1104 standard (Test

for Holocellulose in Wood) (ASTM International, 1978).

201 2.2.3. Cellulose fraction determination

202 Cellulose quantity was determined from the holocellulose fraction obtained

203 previously. This procedure consisted of a sodium hydroxide treatment according

to the TAPPI T 212 standard (TAPPI, 2002). Hemicellulose content can be

- 205 derived from the difference between holocellulose and cellulose quantities.
- 206 2.2.4. Lignin fraction determination
- 207 Lignin quantification was determined according to the NREL/TP-510-42618

standard (A. Sluiter et al., 2008), which consists of a two-stage acid hydrolysis,

with the first step using concentrated sulphur acid and the second stage with

- the same diluted agent at high pressure.
- 211 2.2.5. Ash fraction determination
- An ash quantification test, following the NREL/TP-510-42622 (A. Sluiter et al.,

213 2005) standard, was carried out. This procedure consists of a thermal treatment

of each fraction at 600° C for every previously calculated fraction.

- 215 2.2.6. HHV determination
- The quantification of this energy content indicator was carried out using an IKA
- 217 Werke C5000 calorimetric bomb, and following the ASTM E711 (ASTM
- International, 1987) standard. HHV data used in this article are shown in
- 219 Table 3.
- 220
- 221
- 222

223 3. Results and discussion

3.1. Structural Analysis

Analysis data obtained by chemical extraction for each studied sample are 225 shown in Table 4. Contents of structural components are normalised to 100%. 226 227 Analysed samples demonstrate a wide range of extractive matter ratios, from 0.35% for chestnut tree chips, to 67% for extracted olive pomace. The variability 228 229 in structural component quantity is not as wide. As expected, values between 230 21% and 39% were found for lignin, but grape stalk was exceptional with a value of over 50%. The range for cellulose was 27% to 60%, while for 231 hemicellulose the indices obtained were between 10.68% for olive stone and 232 233 42.79% for corncob. The exception, once again, was grape stalk, which exhibited just 2%. These results were been compared with others available in 234 the literature such as those of (Vassilev et al., 2012; Mendes et al., 2013; Prozil 235 et al., 2012; Matos et al., 2010), and there is a notably strong agreement among 236 237 them.

3.2. HHV estimations

The first step consisted of determining which of the parameters is the most influential on an HHV estimate. Matlab's command *corrcoef* was used for this purpose. R and P matrixes were obtained, with R being a squared matrix of correlation coefficients, with as many rows and columns as compared variables. The P matrix contains the P-values, and is the result of checking the noncorrelation hypothesis. The results for the tested variables are shown in Table 5.

246 According to the statistical protocol, the closer to 0 a P-value comes, the higher the probability of dependence there is between the correlated variables, so the 247 248 corresponding R-values can be considered significant. An examination of Table 5 shows that correlations obtained for cellulose demonstrate P-values much 249 higher than 0.05, so the relationship between HHV and this parameter is 250 meaningless. Therefore, no cellulose-based correlations have been proposed. 251 Nevertheless, the P-values obtained for lignin and hemicellulose were low, so 252 253 these fractions should be considered as important in determining HHV.

After choosing the most important parameters, the Matlab command *regress* is used to obtain linear equations based on the selected parameters or linear combinations thereof. The correlations thus obtained were statistically checked using three criteria: *absolute average error* (AAE), *average bias error* (ABE), relative errors commonly used by several authors (Callejón-Ferre et al., 2014; Sheng and Azevedo, 2005) and *average absolute deviation* (AAD). They are defined as follows:

261
$$AAE (\%) = \frac{1}{n} \left[\sum 100 \frac{|HHV_{calc} - HHV_{exp}|}{|HHV_{exp}|} \right]$$
(1)

263
$$AAD = \frac{1}{n} \left[\sum \left| HHV_{calc} - HHV_{exp} \right| \right]$$
(3)

264

Proposed equations and their error values are shown in Table 6. Based on
structural analysis data, these equations show a lower value for AAE (1.13%)

compared to the AAE values of correlations based on proximate or elemental
analysis data (5% to 7%) proposed by the authors (García et al., 2014a,
2014b).

In Figure 6, the relationship between the predicted values (X-axis) and those
obtained experimentally (Y-axis) using data from the bibliography (Telmo and
Lousada, 2011; Demirbaş, 2001) are shown in order to validate the equations
proposed in this article.

As can be seen in Figure 6, all of the data are within a range of 13% of errorwith respect to the experimental values.

276

277 4. Conclusions

278 Chemical analysis confirmed that the main component of lignocellulosic

biomass is cellulose (27% to 60%), followed by lignin (21% to 39%) and

280	hemicellulose ((10% to 43%).
200			'

Results obtained and shown in this article are in good agreement with thoseobtained by other authors.

Higher Heating Value is related to the content of biomass structural compounds,

mainly lignin. Existing equations for predicting HHV are focused on specific

biomass groups, while the ones proposed in this work have a general character.

286 The equations presented in this work depend on structural biomass

components, predicting HHV values with an average absolute error (AAE) of

less than 1.13%.

289

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432	Figure captions
433	Fig. 1a. Olive oil production flowchart: olive oil mill (hydromechanical method)
434	Fig. 1b. Olive oil production flowchart: olive pomace extractor (mass transfer
435	method)
436	Fig. 2. White wine production flowchart
437	Fig. 3. 3D biomass structure
438	Fig. 4. Pictures of the samples analysed
439	Fig. 5. Experimental procedure chart

440 **Fig. 6.** Predicted vs. experimental HHV from data in the bibliography



Fig. 1a. Olive oil production flowchart: olive oil mill (hydromechanical method).



Fig. 1b. Olive oil production flowchart: olive pomace extractor (mass transfer

method).





Fig. 2. White wine production flowchart.



Fig. 3. 3D biomass structure



Almond shell



Dried oil-mill stone



Cherry-tree chips



Eucalyptus bark



Chestnut tree chips



Extracted olive pomace



Corncob



Extracted olive pomace pellets



pellets

Fig. 4. Pictures of the samples analysed.

oil-extractor



Fig. 5. Experimental procedure chart.





Fig. 6. Predicted vs. experimental HHV from data in the bibliography.

- **Table 1.** Available potential biomass (t/year) and average production cost (\in /t)
- 458 in Spain (IDAE, 2007)

Origin		Biomass (t/year)	Biomass (tep/year)	Average costs (€/t)
Existing forest	Wood harvesting remains	2 984 243	636 273	25.59
areas	Whole tree harvesting	15 731 116	3 414 158	43.16
Agricultural residues	Herbaceous Woody	14 434 566 16 118 220	6 392 631	20.97
Herbaceous biom implementation in	ass susceptible to agricultural land	14 737 868	3 593 148	53.39
Woody biomass s implementation in	usceptible to agricultural land	6 598 861	1 468 173	36.26
Woody biomass susceptible to implementation in forest land		15 072 320	1 782 467	42.14
Total potential b	iomass in Spain	88 677 193	17 286 851	

AUTHOR	CORRELATION (HHV, MJ/kg dry basis)	COMMENTS
S&D (Shafizadeh et al., 1976)	HHV=0.17389[Ce]+0.26629[L]+0.32187[E]	Lignocellulosic biomass.
TIL (Tillman, 2012)	HHV=0.17389[Ce]+0.26629(100-[Ce*])	Woody biomass.
WHI (White, 1987)	HHV=17.9017+0.07444[L*]+0.0661[E*] ^a	Not extracted wood. Neither R ² ajust, not SE available
	HHV = 17.6132 + 0.0853[L*] ^a	Extractive free wood. Neither R ² ajust, not SE available
	HHV = 17.4458 + 0.0907[L*] ^a	Extractive free softwood. Neither R ² aiust, not SE available
	HHV = 18.0831 + 0.0637[L*] ^a	Extractive free hardwood. Neither R ² ajust, not SE available
	$HHV = 17.7481 + 0.0800[L^*](100-[E])/100 + 0.0886[E]^a$	Not extracted wood. Neither R^{2}_{ajust} , not SE available
J&G (Jiménez and González,	HHV=(1-[Ash]/([Ce] + [L] + [E]))(0.17389[Ce] +	Vegetal biomass. Neither R ² ajust, not SE available
DEM_{01} (Demirbas 2001)	HHV**=0.0889[I **] + 16.8218	Vegetal biomass. SE not available
2 =	HHV**=0.0893[I **] + 16.9742	Wood and bark. SE not available
	HHV**=0.0877[L**] + 16.4951	Not woody vegetal biomass. SE not available
DEM ₀₂ (Demirbas, 2002)	ΔHHV = 0.00639[E]2 + 0.223[E] + 0.691	Vegetal biomass. SE not available.
DEM ₀₃ (DEMİRBAŞ, 2003)	HHV**=0.0864[L**] + 16.6922	Bark and shell. SE not available
DEM ₀₄ (Demirbas, 2004)	ΔHHV = 0.383[E]-0.0387	Vegetal biomass. Neither R ² ajust, not SE available
ACA (Acar and Ayanoglu, 2012)	HHV = 0.0979[L] + 16.292	Vegetal biomass. SE not available

Table 2. Structural composition-based models (Calleión-Ferre et al., 2014). 461

Ce: cellulose + hemicellulose; L: lignin; E: extractive both measured in dry basis percentage * Indicates composition (%) in dry and extractive free basis. ** Indicates composition (%) in dry ash free and extractive free basis.

Not SE: not standard error available.

^a These correlations can be converted to MJ/kg as: 1 Btu/lb = $2,3261 \times 10^{-3}$ MJ/kg.

Table 3. HHV data used in this article (García et al., 2014a) and (García et al.,

463 2014b).

Sample	HHV (kJ/kg)
Almond shell	18.275
Cherry-tree chips	17.595
Chestnut tree chips	17.485
Corncob	17.344
Dried oil mill stone	18.092
Eucalyptus bark	17.752
Extracted olive pomace	18.186
Extracted olive pomace pellets	18.182
Grape pomace	17.019
Grape seed flour	16.467
Grape stalk	18.809
Hazelnut +alder chips	17.555
Horse chestnut burr	17.165
Mimosa branches	16.237
Oil-mill stone (ar)	16.484
Olive stone	17.884
Olive tree pruning pellets	18.720
Olive-pomace oil-extractor	18.687
Poplar branches	18.411
Wheat straw	17.692

Table 4. Chemical composition of biomass samples obtained by chemical

466 extraction.

Sample	E ^a	HoloC ^b	Cp	HemiC ^b	I.L. ^b	S.L. ^b
Almond shell	8.02	69.12	55.07	14.05	28.37	2.51
Cherry-tree chips	1.88	75.64	46.51	29.13	22.13	2.23
Chestnut tree chips	0.35	72.61	43.39	29.22	24.74	2.65
Corncob	8.72	72.50	29.71	42.79	24.49	3.02
Dried oil mill stone	2.30	72.61	50.31	22.30	25.79	1.61
Eucalyptus bark	11.30	65.73	37.31	28.42	32.37	1.90
Extracted olive pomace	67.79	57.27	27.60	29.67	38.89	3.84
Extracted olive pomace pellets	55.96	62.58	31.05	31.53	34.25	3.17
Grape pomace	26.06	46.76	28.83	17.93	51.74	1.50
Grape seed flour	9.82	53.55	37.75	15.80	45.54	0.91
Grape stalk	39.34	46.37	43.97	2.40	51.80	1.83
Hazelnut +alder chips	12.30	65.84	34.77	31.08	31.92	2.23
Horse chestnut burr	43.66	62.85	44.82	18.03	36.05	1.11
Mimosa branches	16.81	68.68	40.18	28.51	29.76	1.56
Oil-mill stone (ar)	7.99	71.96	44.72	27.24	26.51	1.53
Olive stone	2.98	69.61	58.93	10.68	28.64	1.75
Olive tree pruning pellets	13.51	71.47	59.05	12.42	27.55	0.98
Olive-pomace oil- extractor	36.84	68.24	38.20	30.04	29.31	2.45
Poplar branches	8.02	72.97	46.16	26.81	25.63	1.40
Wheat straw	25.70	75.73	38.56	37.17	21.71	2.56

	R	matrix	
HHV	Lignin	Hemicellulose	Cellulose
1.0000	0.8291	-0.6686	0.0740
	Pi	matrix	
HHV	Lignin	Hemicellulose	Cellulose
1.0000	0.0009	0.0175	0.8191

Table 5. P and R coefficients matrix (chemical extraction and TG).

Table 6. Equations based on chemical composition.

	Equation	AAE (%)	ABE (%)	AAD
4	HHV=17.0704+0.0449·L-0.0202·H	0.87	0.02	0.15
5	HHV=16.1964+0.0555·L	1.13	0.02	0.20

L: lignin; H: hemicellulose (measured in mass percentage in dry ash and extractives free basis); HHV: higher heating value (MJ/kg in dry basis).