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COMPARISON BETWEEN COFFEE AND COMMON LIGNOCELLULOSIC BIOMASS FOR ENERGETIC POTENTIAL PREDICTION

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Abstract

Energy production from renewable and waste materials is an attractive alternative to conventional production chains that involve agricultural products. Residual biomass from cultivars and coffee production chain, despite their widespread availability, aren't enough considered in energy models and economic development. In addition to lignocellulosic biomass, coffee can be considered as a new material usable in such processes. ICO (International Coffee Organization) data showed that the Spent Coffee Grounds (SCG) production worldwide is about 6 million of tons per year. In the work presented, calorific value, ash content, and elemental analysis of lignocellulosic biomass and SCG pellets, were firstly examined. The aim was to compare SCG with conventional lignocellulosic biomass already used in thermal production. Compositional and energetic analysis permit to fix linear models for biomass energetic yield prediction. Models that relate the higher heating value (HHV) to the compositional analysis mostly date to the late 19th century. Estimation of HHV from the elemental composition of fuel is one of the basic steps in performance modelling and calculation for thermal systems. The possibility to perform statistical analysis on data collected in the same laboratory gave the opportunity to reliably compare conventional and unconventional biomass. The linear regression model fitted on the whole dataset had an R Squared of 0.85 showing a good HHV prediction from elemental analysis. Coffee appeared as a feedstock with peculiar characteristics that differentiate it from the others, while herbaceous and arboreal biomass mostly differentiated for ash and moisture content.
SCG showed an HHV higher than any other woody and herbaceous plant, manifesting a great potential from an energetic point of view. According to the concept of circular economy, coffee companies, in their waste, have already a valid resource usable in a heat generator for the roasting process.

Key words: biomass, modelling, spent coffee grounds (SCG), ultimate analysis

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1. Introduction

Large amounts of agricultural and forestry residues, usually treated as waste, can be considered as a significant resource for energy production through biological or thermo-chemical processes (Bianchini et al., 2021; Carnevale et al., 2020; Paris et al., 2019a; Schmitt et al., 2019; Sun et al., 2018). To date, processes and models for the exploitation of ligno-cellosic biomass are mainly based on forest resources (Tomassetti et al., 2019; Torre et al., 2019). Despite the considerable volumes produced, residual biomasses from agricultural crops are rarely considered in energy models and economic development. Alternative energy sources are increasing their importance both to meet the energy

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growing demand and to reduce the environmental impact. Given the high volumes produced every year, soluble coffee residues represent an important unexplored resource in the agro-industrial sector. Coffee has one of the most developed markets in the world and together with tea, it is among the most consumed beverages (Park et al., 2019). Its annual worldwide generation reach the 6 million tons (Mussatto et al., 2011). The organic molecules present in coffee suggest that the recovery of such resource can be economically advantageous, leading to the synthesis of valuable compounds. (Kibret et al., 2021; Kondamudi et al., 2008; Kua et al., 2016; Liu et al., 2017; Murthy and Madhava Naidu, 2012; Mussatto et al., 2018). Studies regarding the potential thermal exploitation of spent coffee grounds (SCG) are increasing and the reason of such interest in coffee waste is explained by its big market volume. ICO (international Coffee Organization) data showed that the apparent consumption of coffee in Italy between 2004 and 2016 oscillates from 5.46 to 6 million of 60 kg green bean bags (Sette, 2017).

The large amount of waste production in the coffee market unavoidably leads to questioning on the possible utilization of such waste inside a circular economy model. Combustion is one of the thermal production processes more rooted and used in common living, especially through the domestic fireplace and stoves. The feasibility of SCG thermal valorization has to be discussed both from the logistic and energetic point of view (Volpi et al., 2019). The possibility to use a new material like coffee in established thermal conversion methods was already investigated in previous works (Colantoni et al., 2021; 2020). Biomass fuels are considered a renewable resource both for their continuous production and because they do not affect the overall balance of CO_2 in the atmosphere.

Knowing the physicochemical properties of biomass is essential for its use in power plants. These raw materials are experimentally characterized by analyzing the elemental composition, energy efficiency, and fusibility of the ashes (Pari et al., 2018). Such analyzes are regulated by standards to ensure the quality and comparability of the measurement results. The calorific value of biomass is a fundamental parameter for the exploitation of this type of fuel in power plants. The higher calorific value (HHV) consists of the amount of heat produced by the complete combustion of a unit quantity (by mass or volume) of fuel under certain conditions, when the reaction pressure is kept constant. The lower calorific value (LHV) is obtained when the energy used for the evaporation of the water formed during combustion is subtracted from the total energy produced. Numerous models have been published to relate the energy produced by the fuel to the elemental composition of the fuel itself. (Friedl et al., 2005). For these reasons, the calorific value of such wastes is regarded as the most significant parameter that defines the fuel quality. The estimation of the calorific value based on the chemical composition of biomass has also been in great demand when reliable analysis results are present.

Macromolecular ingredients such as hemicellulose, cellulose, and lignin account for most of the organic part of the biomass while some others include starch, proteins, triglycerides, lipids, etc. Accordingly, some kinds of biomass, particularly woody ones, are generally defined as lignocellulosic. On the other hand, although these macromolecular components are consisted mostly of carbon, hydrogen, and oxygen, their molecular configurations and structures are highly different (Ozyuguran et al., 2018).

Many correlations for the estimation of HHV from elemental composition are available in literature, the most important have been presented in Channiwala and Parikh (2002), and most of these relations have been derived for coals. Furthermore, the majority of these correlations, when referred to lignocellulosic biomass, use mixed datasets with data provided from different studies, obtained with different instruments and sometimes with different methods. To carry out the analyzes in the same laboratory permits to minimize the data variability coming methods, instruments and operators. For these reasons, the present work is marked with the intention to create a homogeneous dataset to set up the HHV modeling from compositional analysis of different kinds of biomass.

2. Materials and methods

2.1. Biomass description

The biomass coming from different projects and relative works, were collected for more than a year, starting from October 2019. The modeling analysis has been carried out on 41 samples composed of different mixtures of lignocellulosic biomass. The complete biomass description is provided in Table 1.

2.2. Ultimate and proximate analysis

Ultimate and proximate analysis was carried out adopting always the same procedure following European standards for biomass characterization. The biomass humidity was measured through the Memmert UFP800 drying oven at a temperature of 105 ± 2°C for 24 hours, according to ISO 18134-2 (2017). For characterization, the dried sample was grinded first with the Retsch SM 100 cutting mill for a preliminary size reduction and thereafter through the Retsch ZM 200 rotor mill.

Ash content was measured by a Lenton EF11/8B muffle furnace according to ISO 18122 (2015). The higher heating value (HHV) was determined by the Paar 6400 isoperibol calorimeter following the ISO 18125 (2017), while the lower heating value (LHV) was calculated from the higher heating value, according to ISO 18125 (2017).

Table 1. Biomass used for experimental and modeling analysis

Biomass	***Group***	***Appearance***	***References***	***Notes***
Grapevine	Fruit Cultivar Tree	Chipwood	Proto et al. (2021)	*Vitis spp*. Harvested in Calabria, Southern Italy
Olive	Fruit Cultivar Tree	Chipwood	Proto et al. (2021)	*Olea spp*. Harvested in Calabria Southern Italy
Citrus	Fruit Cultivar Tree	Chipwood	Proto et al. (2021)	*Citrus spp*. Harvested in Calabria Southern Italy
Cultivars mix	Fruit Cultivar Tree	Pellet	Vincenti et al. (2020)	Mixed pellet of *Citrus*, *Olea*, and Kiwi (*Actinidia spp*) harvested in Calabria, southern Italy
Wheat straw	Straw Herbal	Chipwood	Paris et al. (2019b)	*Triticum aestuvum L.* produced by the CREA of Monterotondo
Rice straw	Straw Herbal	Chipwood	Paris et al. (2019b)	*Oryza sativa L.* imported from different areas of Pakistan (Punjab, Azad Jammu and Kashmir (AJK), and Sindh)
Hemp	Hemp Herbal	Chipwood	Not published	*Cannabis spp.* Produced by the CREA of Monterotondo
Forest mix	Forest Tree	Pellet	Vincenti et al. (2020)	Mixed pellet of fir (*Abies spp*), beech (*Fagus sylvatica*) and chestnut (*Castanea sativa*)
Coffee	SCG	Pellet	Colantoni et al. (2020; 2021)	*Coffea spp*. Mixed pellet obtained with different sawdust percentages (0, 15, 25, 33, 66)

The elemental composition, carbon content (C), hydrogen content (H), and nitrogen content (N) was measured with the elemental analyzer Costech ECS 4010 CHNS-O according to ISO 16948 (2015).

2.3. Statistical analysis

The statistical analysis was entirely conducted in R ver. 3.6.1. Different statistical tests and analysis resulted useful for the data comprehension. Since the biomass’ description was one of the goals of this study, differences between species were tested through a One-Way ANOVA at the 0.05 significance level, permitting to evaluate the importance of the biomass factor on energetic and compositional parameters. The individuation of such differences is subsequently obtained with the post hoc Tukey-HSD test, able to compare groups means and to define weather the variables assumed significant differences according to the plant species. Shapiro-Wilk and F tests were performed to evaluate both normality and homoscedasticity of biomass characterization variables. Since many variables didn’t show a Gaussian trend, the Friedman test and the Conover test were performed to understand the difference between biomass. The multivariate data analysis was conducted by Principal Component Analysis (PCA) to evaluate the relationships between biomass properties. The cluster analysis was performed by the Ward technique, whose aim is to achieve a hierarchical classification by minimizing the variance of the variables within each group. At each stage, the groups that produce the smallest increase in the total variance within the groups are merged (Ward, 1963).

Since the characterization variables are neither normal nor homoscedastic, the quantile regression (QR) has been used to build linear models able to predict HHV from C, H, and N. This method results more accurate when the basic requirements for applying ordinary least squares (OLS) are not met, particularly in the presence of outlier values. Quantile regression is able to provide a much broader analysis of the relationships between variables than the OLS model. Over the years, QR has been used as an extension of the linear regression model and it allows to do the analogue of what linear regression does for the mean, on quantiles. By exploiting the estimated parameters, it is possible to consider the quantile value of the response variable, depending on a set of regressors. This allows to appreciate the behavior of the response variable not only in average but also in its entire distribution. By varying the quantile of the regression between zero and one (τ) it is possible to obtain the entire conditional distribution. To evaluate the forecast quality, the root means square error (RMSE), mean absolute error (MAE) and mean bias error (MBE), were calculated. The MBE gives information regarding the average forecast error representing the systematic error of a forecast model, MAE gives the forecast errors average magnitude, while with RMSE more weight is attributed to the largest errors (Kato, 2016).

3. Results and discussion

3.1. Proximate and Ultimate Analysis

From the proximate and ultimate analysis (Fig. 1), SCG resulted a biomass with peculiar characteristics, both from a compositional and an energetic point of view. The samples listed in Table 1 were grouped in three branches depending on the physical structure of the biomass: Coffee, Herbal and Tree (Fig. 1). Through the Friedman test applied to compositional variables, real differences are pointed out. It’s clear that SCG has more C and N percentages

(Fig. 1a-b) than herbaceous and arboreal biomass at the expense of H, which shows a very low content for SCG (Fig. 1c). Many other studies, concerning both biomass and hydrocarbons (Demirbas et al., 2018; Ozyuguran et al., 2018), relate the compositional analysis to the HHV. For biomass, in general, it is overt that C is strictly positively related to HHV. In this case, coffee is a very surprising material, inasmuch its HHV is significantly higher than any other biomass taken into account (Fig. 1d). Proximate analysis concerning humidity and ash reveals coffee as a biomass with a higher content in water and normal content of ash.

Regarding the elevated humidity tenor (Fig. 1e), it is due to the nature of SCG which derives from a process where coffee is crossed by water. In this case, processes related to transportation, stock and drying are fundamental (Schmidt Rivera et al., 2020). The other two kinds of biomass, arboreal and herbal, usually behave in a similar way except for C, HHV, and ash. Herbaceous biomass has the worst energetic characteristics with lower HHV and C content, and higher ash production during combustion (Fig. 1f). Such data indicate low potential in thermochemical conversion processes.

3.2. PCA analysis

Some of the trends described above can be more formally elucidated through the application of multivariate statistical techniques. Other studies already tried to classify different lignocellulosic biomass through a multivariate approach (Jenkins et al., 1998). Fig. 2 gives PCA results using the ultimate and proximate analysis for the 41 observations in the dataset. Differences between the four main classes have been highlighted in the figures: straw, coffee, wood pellet, and wood chip. Fig. 2 is a plot of the first principal component PC1 respect to the the second principal component PC2.

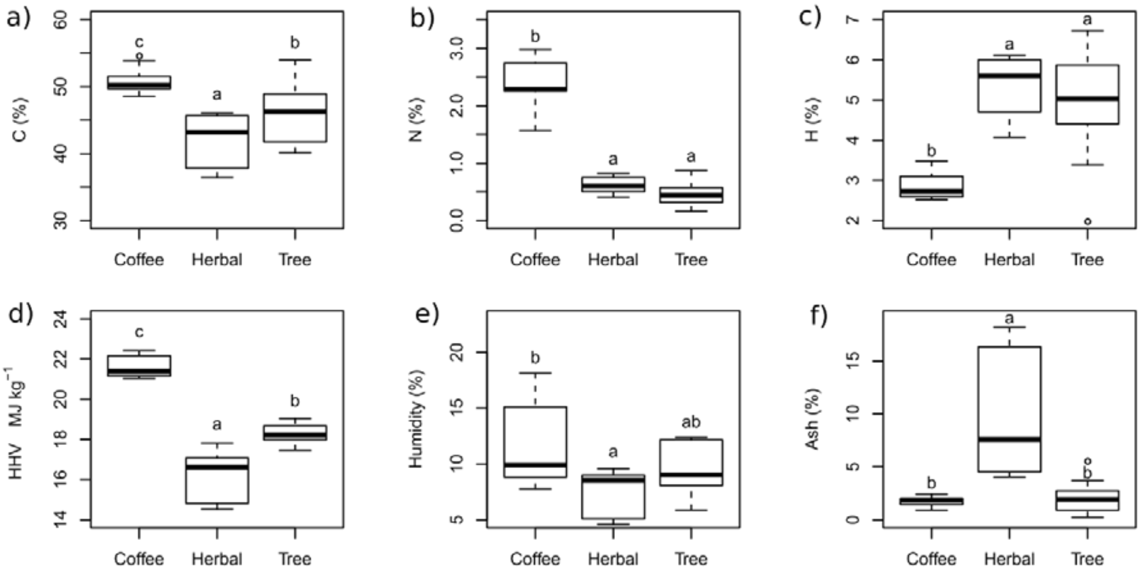

Fig. 1. Boxplots of ultimate and proximate analysis parameters for Coffee, Herbal and Tree biomass. Carbon content (a), Nitrogen content (b), Hydrogen content (c), Higher Heating Value (d), Humidity (e) and Ash content (f). The boxes represent the minimum (Q1 - 1.5*Interquantile Range), 25th percentile (Q1), 50th percentile (Q2), 75th percentile (Q3) and maximum (Q3 + 1.5 Interquantile Range). Groups with different letter are significantly different by using post hoc Tukey-HSD test ($p<0.05$)

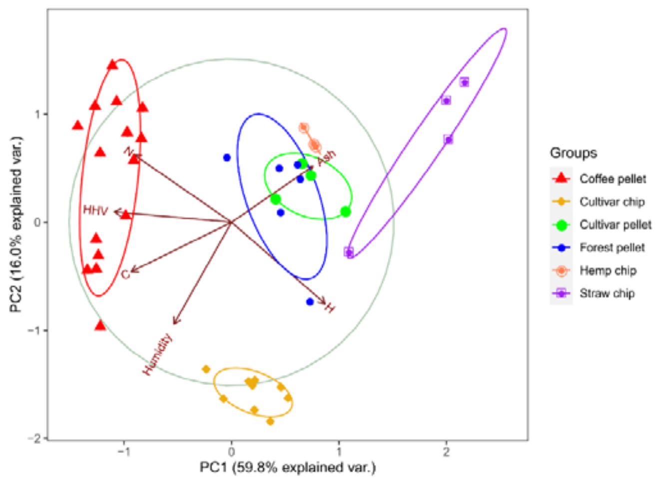

Fig. 2. Principal Component Analysis biplot obtained with the parameters obtained from ultimate analysis and proximate analysis

These two components explain the 75.8% of the total variance in the data. PC1 has a strong negative correlation with HHV, C, and N, while a positive correlation is shown for ash and H. For PC2, the most influent parameter is humidity with whom is negatively correlated. From this grouping it is possible to appreciate how biomass vary depending on many factors. It is evident that woody biomass can vary their moisture content if they undergo a pelletizing process or not. Coffee is clearly an uncommon biomass with HHV and N higher than any other sample considered, as already seen in previous works (Colantoni et al., 2021). Furthermore, the coffee group shows an inner variability explained especially by humidity, this is probably due to the different kinds of blend produced with many sawdust percentages which bring to the moisture content decrease. Close to the woody pellets are placed the hemp samples that, despite the different nature respect arboreal biomass, have comparable composition and energetic yield. Hemp is therefore confirmed as feedstock of interest for many purposes such as textiles, pharmaceutic and energetic (Qamar et al., 2021; Rheay et al., 2021; Vandepitte et al., 2020). Like all herbaceous and straw species, hemp presents higher ash production in combustion, but if compared to the other straw samples, the amount is irrelevant.

Through the hierarchical cluster analysis (Fig. 3) using the Ward's minimum variance method are finally individuated four groups on which have been based the subsequent modeling evaluations. Principally, the arboreal biomass is divided in chipped and pelletized, while the SCG and straw biomass form other two distinct groups. Comparing such results with the trends shown through the ultimate analysis, three different linear models are proposed to better understand the link between composition and heating value in many kinds of biomass.

3.3. Correlations and modeling

From the compositional analysis it has been possible to fix a model for the HHV estimation for the biomass considered. Usually for statistical analysis, ordinary least squares (OLS) are mostly used and the fit quality evaluation is made by the coefficient of determination (COD) R^2. However the RQ models are more robust since they permit a more complete analysis of the conditional distribution of a variable depending on many predictors (Ranganai, 2016).

Despite the R^2 isn't properly used for quantile regression models, which are based on median or other quantiles, its calculation strengthens anyway the models built on the ultimate analysis and resumed in Table 2.When the complete dataset is considered, a strong correlation (R^2=0.85) is indicated for the Eq. (1). This model shows the smallest MBE, indicating a reduced systematic error to under and over forecast, but high MAE and hence higher forecast errors magnitude (Table 2).

Focusing deeply on the different groups identified through the PCA analysis, different models can be proposed for the estimation of HHV from the ultimate analysis. Since SCG has shown a relation between ultimate analysis and HHV closer to the herbaceous plant, the dataset has been divided into two groups: herbaceous and arboreal. Two different regression models are applied to these sub-datasets and the equations are resumed in Table 2.

Fig. 3. Ward hierarchical cluster analysis of the biomass

Table 2. Models and relative accuracy parameters

Group	*Model*	R^2	*RMSE*	*MAE*	*MBE*	*Eq*
Complete	$HHV = 0.14C + 1.22N - 0.16H + 11.81$	0.85	0.1	0.58	0.01	*(1)*
Herbaceous	$HHV = 0.38C + 1.65N + 0.37H - 2.64$	0.96	0.06	0.38	0.02	*(2)*
Arboreal	$HHV = 0.08C - 0.49N - 0.03H + 14.93$	0.51	0.2	0.23	0.07	*(3)*

The higher variability in compositional analysis shown by arboreal species (Fig. 1) is reflected in the model quality too; for this group the smallest coefficient of regression R^2 has been calculated. Furthermore, such variability is detected by the RMSE too, which indicates the presence of large errors in the forecast (Table 2). The quantile regression fitted for herbaceous resulted the most accurate, with the smallest errors (RMSE = 0.06). When the calculated and predicted HHV values are compared, it can be seen that the plotted values are close to the curves of HHV estimated-HHV real, indicating good correlation accuracy (Fig. 4). In particular (Fig. 4), four quantile regression lines, in addition to the medians in bold, have been estimated for four values of τ (0.1, 0.25, 0.75, 0.9) for each model proposed. The same graph shows in blue the quantile regression lines for the herbaceous group, in black the arboreal ones, and in red the complete dataset regression lines. The lines estimated through quantile regression include almost all points on the graph.

Eq. (2) seems to be more accurate compared to Eq. (1) and (3) considering the presence of more outliers produced by the latter. In the upper-right corner of the graph are distinguishable coffee HHV values confirming the high energetic power of this matrix; in the middle part of the graph are present mostly arboreal species with some introgression of other herbaceous species, principally hemp; in the low-left corner the three straw biomasses bring out their lower predisposition to energy exploitation.

Many empirical correlations have been studied to predict the HHV from elemental composition, mostly for coals and other hydrocarbon fuels (e.g., biomass, char, oil) as well. Since it is well established that carbon and hydrogen contribute significantly to the biomass energy potential (Sheng and Azevedo, 2005), these two constituents are taken into account deeply. When hydrocarbons are evaluated it's known that a higher H content brings to higher HHV; saturated hydrocarbons are the simplest of the hydrocarbon species, they are composed entirely of single bonds, saturated with hydrogen and show higher HHV respect the unsaturated species with stronger bonds (Demirbas et al., 2018). For lignocellulosic biomass, the same reasoning can't be valid. In literature is confirmed that a positive correlation exists between C and HHV, while for hydrogen and HHV a clear trend isn't always observed (Jenkins M. et al., 1998).

In Sheng and Azevedo (2005), for example, the positive correlation observed between H and HHV is limited to a slight trend visible from data plotting without any statistical confirmation. In the present study, a positive correlation between C and HHV is observed (Fig. 5c) (Spearman: $\rho = 0.74$), but when H is considered (Figs. 5 d-f) , contrary to what is expressed in other works in literature (Mateus et al., 2021) a negative correlation (Spearman: $\rho = -0.64$) can be observed (Fig. 5f). This behavior is strongly driven by SCG, which presents low H content and high HHV, differentiating itself from the other biomass considered in the models found in literature. Moreover, if we consider all biomass except SCG, the trend between H and HHV is negative tending to 0 (Spearman: $\rho = -0.07$), showing an absence of correlation between these two variables (p-value = 0.72). H content and HHV of arboreal species isn't correlated (Spearman: $\rho = 0.05$) (Fig. 5d), while only herbaceous species, including SCG, showed a negative correlation between the two parameters (Spearman: $\rho = -0.54$) (Fig. 5e).

When C-HHV correlation is examined, it can be noted that SCG better follows the trend shown by the herbaceous plants and the correlation between C and HHV for only SCG and herbaceous species increases till 0.92 (Fig. 5b). If only arboreal species are considered, the correlation decreases due to the higher variability of the compositional parameters. It is also noticeable that the quantile model fitted for only the arboreal species (Fig. 5a) underestimates the higher values of HHV and overestimates the lower ones.

This is probably due to the diversity of the biomass considered; for these biomass different storage methods have been used, furthermore the structural composition of tree biomass is usually considered more heterogenous with samples varying in bark and wood percentage and therefore in lignin and cellulose content (Barmina et al., 2013).

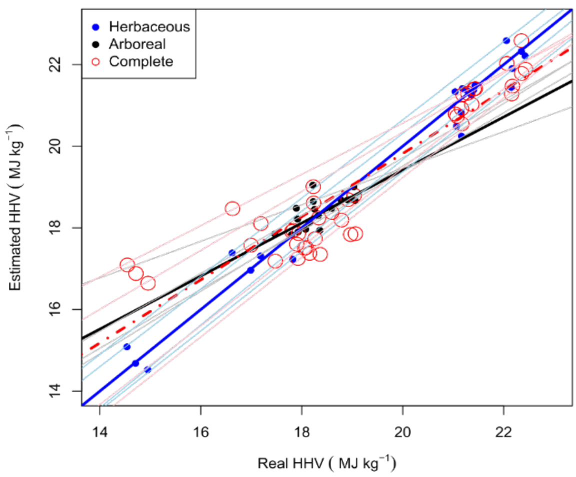

Fig. 4. Comparison between real and estimated HHV values for the three models

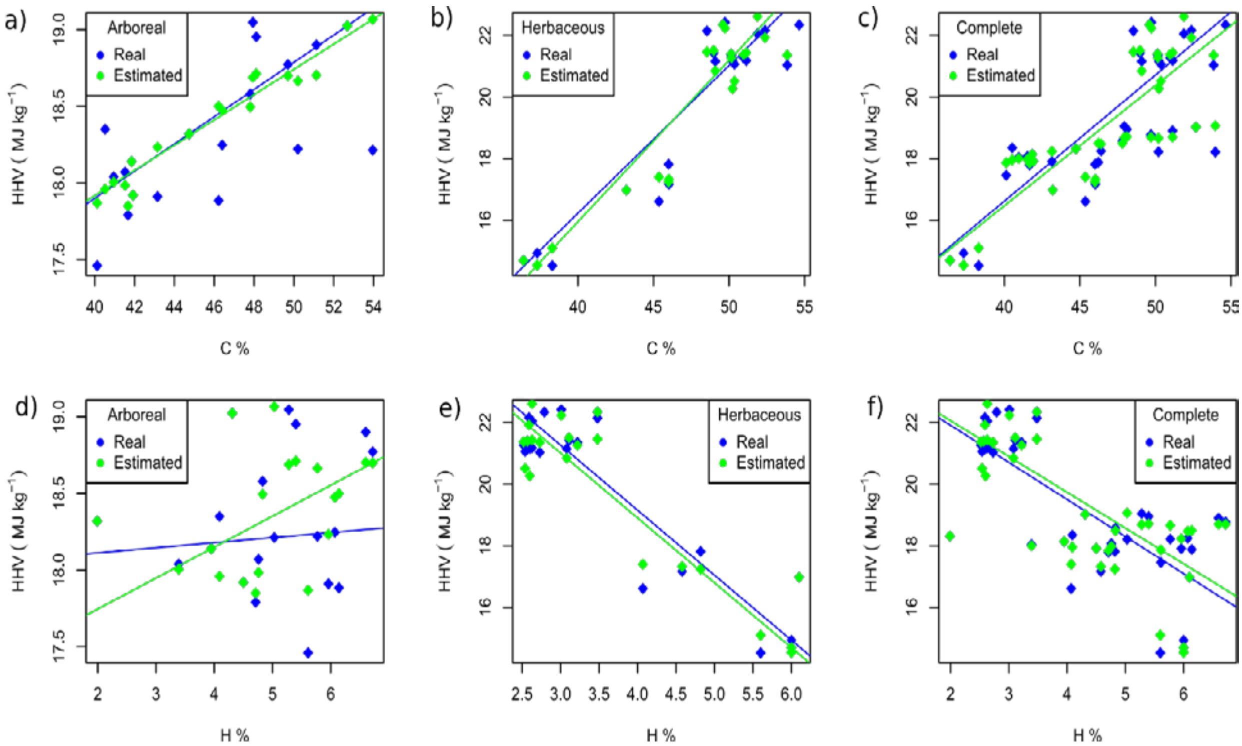

Fig. 5. Correlations between C and HHV for arboreal species (a), herbaceous (b), and for the whole dataset (c). Correlations between H and HHV for arboreal species (d), herbaceous (e), and for the whole dataset (f)

From the observations mentioned above, it follows that the relation between elemental composition and energetic yield isn't so homogeneous when the datasets comprehend many kinds of species with different physiology and physical structure. Studies that deepen and do not neglect such differences, are useful for a better comprehension of the processes involved in biomass energetic valorization, permitting better and wider modeling.

4. Conclusions

Through the PCA and cluster analysis, it has been possible to group the biomass and understand the energetic behavior depending on the ultimate and proximate analysis. In the two main groups highlighted (herbaceous and arboreal), linear quantile models have been applied for the prediction of HHV from compositional analysis (C, H, N). Such models show a good accuracy and confirm themself as a useful tool able to give information on biomass energy potential.

Arboreal species were marked by a higher variability in composition and the model fitted to them resulted less accurate, while Eq. (2) gave the best fit for herbaceous. Despite the typical differences between the studied biomass, Eq. (1) was able to give a good estimate of HHV.

In these models and calculations, SCG always shows the best energetic yield and the predicted values of each model concerning SCG are able to give extremely accurate values for this uncommon biomass. Straw biomass is the worst feedstock from the energetic point of view while arboreal and hemp place themselves between SCG and straw, but especially arboreal ones have already good and easy ongoing practices (harvesting, storage and drying) for their exploiting, thus resulting biomass easier to use in thermochemical processes.

Acknowledgments

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