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Prediction of gross calorific value and ash content of woodchip samples by means of FT-NIR spectroscopy

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ABSTRACT

The use of woodchip, and biofuels in general, is a fundamental step towards the transition from fossil fuel to renewable energy. The growth in the demand for wood fuels and the inherent variability in the properties of woody material lead to the need to verify its quality. EN ISO 17225-4 divides woodchip in different quality classes according to chemical-physical parameters and quality attributes.

In this study, we have coupled near infrared spectroscopy with Partial Least Square regression to model gross calorific value and ash content of woodchip samples. Moreover, variables selection methods were tested in order to improve the models and get better prediction.

Gross calorific value and ash content were predicted with a standard error of 234 J/g and 0.44%, respectively. The results indicate that the models could be used in screening applications and near infrared spectroscopy is a promising tool in the evaluation of biomass quality.

1. Introduction

In recent years, the interest in bioenergy as an alternative to fossil energy is increasing because of the continuously growing energy demand, the decreasing availability of fossil fuels and the need for a reduction of environmental impact. In order to reach these targets European policies is aiming to promote the use of renewable energy sources. Woody biomass is such a source of energy, it is present more or less everywhere, is available in many forms and can be easily stored, especially in comparison with other energy sources [1]. In particular, woodchip is really appreciated because it consists of homogeneous particles with a specific size and it guarantees benefits in terms of increased load density and handling quality [2,3].

In different European countries, and in Italy as well, the number of power plants fueled with woodchip is increasing and accordingly also the demand for wood fuels. As a consequence, the biomass quality could experience a decrease and need to be analysed [4]. Moreover, it is known that there is an inherent variability in the properties of woody material that is influenced by many factors [5,6] and this leads to the need to employ quality standards in order to check the quality of the product.

CEN/TC 335 has established a number of standards to ensure biomass quality. Chemical-physical parameters and quality features (e.g. origin and source) divide the biomass in different quality classes. The identification and characterization of chemical composition of a solid fuel is the most important step during the investigation and application of such fuel. This composition is a unique code that characterizes and determines the properties, quality, application perspectives and environmental problems related to any fuel [7]. EN ISO 17225–4 [8] is the quality standard for graded woodchip for residential, small commercial and public building applications and provides limits for three different woodchip quality classes: A1, A2 and B.

In particular, calorific value is an essential parameter in the specification of biomass quality to set the price of the product. Moreover it is an important characteristic for the planning and control of power plants using biomass fuel [9]. Ash content (Ac) influences combustion efficiency and may cause cleaning and combustion problems, such as slagging in furnaces, fouling of heat exchanger surfaces, corrosion in the combustion device [4,10,11]. Ac is also the most important discriminant parameter among the woodchip quality classes that are related to a maximum Ac of 1.0, 1.5 and 3.0% respectively.

Gross calorific value (GCV) and Ac are normally determined by traditional laboratory analysis, but the process is tedious, expensive and requires specialized experts. As a consequence, it is necessary to develop a technique that is rapid, economic and simple. A good candidate could be Near Infrared (NIR) spectroscopy which is already widely used for quantitative and qualitative purposes in different sectors, i.e. pharmacy, food and agricultural industries.

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A literature research, shows that only a limited number of studies has been performed on the use of NIR spectroscopy in the field of biomass control. Fagan et al. [12] and Gillespie et al. [13] examined the possibility to employ NIR spectroscopy and chemometrics to predict moisture, ash, carbon contents and gross calorific value of *Miscanthus*, willow and herbaceous energy grasses. The possibility to predict calorific value, moisture and ash content was studied also by Lestander and Rhen [14] on Norway spruce (*Picea abies* (L.) Karst.). Moreover, studies have shown the potential of NIR spectroscopy to predict calorific value in dedicated bioenergy crops [15], in *Leucaena leucocephala* pellets [9] and in straw [16]. Saha et al. [17] investigated the possibility to predict calorific values, moisture, ash, carbon, nitrogen, and sulfur content of pine tree biomass using near infrared spectroscopy. Lower heating value and elemental composition were also examined by Pasom et al. using partial least squares regression and considering bamboo samples [18]. The ash content was also investigated in wheat straw by Bruun et al. with good results [19].

All the prediction models developed in the aforementioned studies were based on a specific kind of biomass or wood species. To the authors' knowledge, there are no works based on woodchip samples taken directly from the market, without having information about wood typology. This approach allows the development of more robust and reliable prediction models, which could be employed on a national scale. Furthermore, in the solid biofuels sector, no variable selection methods were applied to NIR models for the improvements of the models performance.

The objective of this study is to develop models based on Fourier Transform Infrared (FT-NIR) Spectroscopy and multivariate analysis (Partial Least Squares) for the prediction of GCV and Ac of woodchip samples. In order to achieve this, a large number of samples from several power plants, representative of the national scene, were prepared and analysed by FT-NIR spectroscopy. The multivariate regression models were further elaborated using chemometric techniques, such as variables selection combined with data pre-processing, in order to get better prediction models.

2. Materials and methods

2.1. Sample collection and preparation

In this study a total of 125 woodchip samples were collected and analysed by the Biomass Lab of Università Politecnica delle Marche mainly during the application of a long-term monitoring of biomass quality employed in several installations. The woodchip samples comes from several power plants (district heating and combined heat and power plants) and different parts of Italy so that they could be considered representative of the national scene for number and type of suppliers, origin and biomass typology.

It should be taken into account that the samples were chosen considering the requirements of UNI EN ISO 17225-4:2014 for the woodchip quality classes. As a consequence only samples with Ac at around 4% and GCV of at least 16,300 J/g were taken into account.

According to UNI EN 14780:2011 standard, the material was first stabilized at 45 °C for 24 h then ground down to 1 mm of particle size by means of a cutting mill (mod. SM 2000, RETSCH).

2.2. Compositional analysis

The analytical methodologies adopted for the determination of GCV and Ac refer to the standards UNI EN 14918:2010 and ISO 18122:2015, respectively.

The ash content of air dried ground material (Ac_{ad}) and its moisture content were determined using a thermo-gravimetric analyzer (mod. 701 Leco). The Ac_{ad} was determined as the ratio between the residue remaining after the sample was heated in air at 550 ± 10 °C to initial biomass. The average Ac_{ad} was calculated based on two measurements per sample. The ash content on a dry basis (Ac_{db}) was obtained for each sample by multiplying Ac_{ad} by its dry matter content in percentage.

A subset of samples (n = 86) was selected for GCV analysis. Gross calorific value of air dried ground material (GCV_{ad}) was determined in a dynamic mode at 25 °C using a bomb calorimeter (mod.C2000 basic, IKA). The calorimeter was calibrated using a benzoic acid standard (IKA Benzoic Acid C723). The analyses were performed in duplicate for each sample. As for Ac, gross calorific value on a dry basis (GCV_{db}) was obtained for each sample by multiplying GCV_{ad} by the dry matter content in percentage.

2.3. Near-infrared spectroscopy

The near infrared spectra were collected using a FT-NIR spectrophotometer (mod. Antaris II, Thermo Fisher Scientific Inc., USA) equipped with a halogen lamp as a source and an InGaAs detector. The samples were acquired in diffuse reflectance mode using an integrating sphere and were kept in rotation during the acquisition by means of a sample cup spinner to increase the representativeness of the material.

Each spectrum has been computed as an average of 32 successive scans acquired at a wavelength range from 10,000 to 4000 cm^{-1} and with the spectral resolution of 8 cm^{-1}. All measurements have been performed at room temperature (18–20 °C) and each sample is recorded in duplicate. A blank spectrum was acquired every hour to exclude the signals not associated to the sample, but to the instrument or environment.

2.4. Data processing and Partial Least Square Regression

NIR spectroscopy requires chemometrics to extract as much relevant information as possible from the analytical data [20]. Partial Least Square Regression (PLS) is a common method applied in spectroscopy for quantitative analysis. It finds the relationship between a y-value - the parameter to be quantified - and the spectral data matrix, maximizing the covariation between them. PLS finds a new smaller set of variables, called latent variables (LVs), that are linear combinations of the spectral data and relevant for the determination of the parameters of interest [21].

In this study, PLS models were calculated to predict Ac and GCV of woodchip samples both air dried and on the dry basis. Prior to PLS regression, in order to minimize the effect of baseline shifts and noise, the spectra were pre-processed [22]. Different pre-treatments including Standard Normal Variate (SNV), first and second derivative spectra (Savitzky-Golay [23] with 13 or 21 smoothing points and 2nd order polynomial) were applied. As no replicate outliers were found, each sample was averaged across the replicates. Residual vs. leverage, observed vs. predicted response and PLS score plots were utilized in order to identify possible sample outliers.

PLS regression models were validated using Venetian blind-cross validation (5 segments). In this type of validation, n validation models are created from the original data set in order to assess the performance of the prediction model. For each validation model, the test set is obtained taking out samples at every n position in the original data set, while the remaining samples represent the training set which is used to build up the model. Therefore, a group of samples is left out from the calibration data set and the model is calibrated on the remaining data point. Then the values for the test set are predicted and the prediction residuals are calculated. The procedure is repeated until each subset has been left out once. As a result, all prediction residuals are combined to calculate validation residual variance and the root mean square error of