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Assessment of near infrared spectroscopy for energetic characterization of olive byproducts

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ABSTRACT

The use of biofuels is a key factor in this transition away from fossil fuels. Today, biofuels are only a small share of world total energy supply. The characterization of biomass is a substantial improvement in the valorization of these resources, allowing a rational and controlled use of its energy potential. Therefore, a fast, reliable and cheap analytical technique is mandatory in order to increase the quality control of these products in the bioenergetic industry and enable comprehensive traceability of raw materials and processes in pursuit of a better use of resources. Near-Infrared (NIR) spectroscopy is eligible for the development of quality control systems of products and processes in accordance with the new demands taking into account their high response speed, low cost per sample, absence of sample preparation, versatility for the analysis of many different products and parameters. NIR spectroscopy prediction model for determination of quality parameters such us moisture, gross energetic value, ash content, volatile fraction content, and elemental composition (Carbon, Hydrogen, and Nitrogen) from ground and dried olive residues have been obtained. High accuracy in prediction for a test set has been achieved for all the parameters ($R^2 > 0.7$) except for Hydrogen content. As expected, Standard Error of Prediction (SEP) for ground samples is better than dried samples except for moisture content. This study illustrates the possibility of using the NIR technique in combination with multivariate data analysis to predict economically important properties of olive byproducts for energetic uses.

1. Introduction

The transformation of energy systems from fossil fuels to renewable forms of energy is greatly needed as stated in the Kyoto protocol [1] in order to mitigate climatic change caused by non-neutral CO_2 emissions. In addition, limited oil resources are an argument for renewable energy becoming ever stronger over time. An important step in decreasing the levels of greenhouse gases in our atmosphere is to increase the contribution of renewable energy to our energy supply [2]. Biomass, a key renewable energy source, accounted for 8.4% of the total final energy consumption in Europe in 2011 [3], predominately through heat and power applications. The sustainable utilization of agricultural crops and residues as sources of renewable energy will require optimization of operations within the biomass-to-bioenergy chain [4]. The conversion of biomass to energy is influenced by the type of feedstock, its physical characteristics and chemical composition [5]. Therefore, chemical composition of biomass fuels can influence the choice of conversion technology and process control in the selected energy conversion pathway. Sluiter et al. [6] stated that accurate feedstock compositional analysis will enable evaluation of conversion yields and process economics due to changes in feedstock or process design.

Cellulosic plant materials represent a suitable source for production of valuable products [7]. However, many physicochemical, structural and compositional factors hinder biomass conversion processes [8]. Methods to characterize such modified biofuels for commercial markets and for on-line process control of biofuel conversion in energy plants should be fast, simple and robust.

Depending on the plant species, variety and site, the chemical compositions show large variations. Wood, for example, is made up of ca. 50.7% C, 43.1% O, 5.9% H, 0.2% N and only small amounts of other elements given as weight percent of dry weight [9]. The major factor of interest for biofuel characterization is the energy content.

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The energy content of different covalent bonds contributing to the calorific value are in descending order: C=C > S–H > C–H > C–C > C–N > N–H > C=O > C–O > O–H, which is valid for gases [10]. The variation range in gross calorific value expressed as kilo joules per gram (kJ/g) fresh biomass is highly dependent on the constituents of the material as well as ash and moisture content [11]. Ashes, not only as oxides, can during burning also cause problems such as agglomeration and deposits in the burner or in heat exchanging devices [12]. In addition to this, elemental composition could be also used as a potential indicator of problems during the burning process together with ash content [13].

In the Mediterranean areas of southwest Europe, agricultural and industrial related activities are very important, but they produce large quantities of residues. This is the case of olive tree pruning, olive stone and dry depleted olive-pomace ("orujillo") residues, which have traditionally been used for domestic heating in rural areas and which are an important source of residual biomass [14,15]. Biofuel quality parameters as gross calorific value, ash content and elemental composition, among others, is essential to solid biofuel development [16,17].

Near-infrared (NIR) spectroscopy, in combination with multivariate data analysis, is of interest to characterize biofuels (solids and liquids) because it is a fast and non-destructive method suitable for on-line measurements. Studies have also shown the high potential of NIR spectroscopy to predict not only moisture content [18–20], cellulose, hemicellulose and lignin [21–24], but also calorific value and ash content in biomass samples like stem and branch wood [25], switchgrass [26], corn stover [27] and bioenergetic crops [28].

NIR radiation interacts with overtones of vibrating bonds in polar molecules [29] and penetrates deeper into organic samples than ultra violet, visual or infrared radiation does. The NIR technique is widely used in the chemical, pharmaceutical and food industries for process control and product quality [30,31]. The interpretation of models based on overtone vibrations in NIR is not as straightforward as for the fundamentals found in the infrared spectrum. Therefore multivariate models are, besides being predictive, also useful in the interpretation of overlapping and wide overtone bands. Based on the hypothesis that NIR spectra reflect chemical and physical properties of biomass, the objective was to use NIR data modeled by principal component analysis (PCA) to overview data and by partial least squares (PLS) to obtain multivariate predictive models for moisture, ash, volatile fraction, calorific content and elemental composition in ground and dried olive byproducts such as olive stones, olive tree pruning and "orujillo". In addition to this, external validations of the models along three months have been carried out in order to evaluate the robustness of the method and the following uses in routine analysis.

2. Materials and methods

The olive residues were collected from the Andalusian region, in provinces such as Seville, Malaga, Granada and mainly, from Jaén and Córdoba, where most of Andalusian olive oil residues are generated [14]. A sampling plan was designed to collect olive stone residues from different Andalusian industries, including olive oil factories called "almazaras" and distribution companies, residues of olive tree pruning (woodchip, leaves, branches and mixture of them) from different places and "orujillo" from several energetic companies. A set of 250 olive residue samples were collected from 2010 to 2012 to build the NIR spectroscopy prediction models, and 53 samples were collected in 2013 to validate the model. The collected samples were dried, ground to 0.25 mm and analyzed in Advanced Technological Centre for Renewable Energies (CTAER) laboratory. Results and parameters in NIR spectroscopy model are calculated in dry weight basis.

2.1. Reference analysis

Quality parameters have been determined by official methods established by the European Standard Technology Committee. In Spain, the adaptation of this methodology was established by the Spanish Association for Standardization and Certification (AENOR). Standards and used measurement equipment are shown in Table 1.

2.2. NIR spectroscopy analysis

Two different kinds of samples were analyzed in this study, namely: dried samples, olive residues dried at room temperature for 24 h or oven dried (<40 °C); and ground samples, olive residues dried at room temperature for 24 h or oven dried (<40 °C) and grounded up to 0.25 mm. Ground samples are stabilized at room temperature for 24 h previous analysis. NIR spectroscopy analyses of dried and ground samples were carried out in reflectance mode and using a non-NIR absorbing glass petri dish of 98 mm diameter. NIR spectral data were collected with an FT-NIR spectrometer (MPA, Bruker Optics, Ettlingen, Germany) equipped with a gold integrating sphere and using a rotating module, which allows the scan of the whole sample. The spectral data were collected over the range 12,500–3800 cm^{-1} (resolution 16 cm^{-1}, scanner velocity: 10 kHz, background: 64 scans, sample: 64 scans) at room temperature. In all cases, two repetitions per sample were analyzed and the mean spectrum of both repetitions was used for chemometric data treatment. Instrument control and initial data processing were performed using OPUS software (v. 6.5 Bruker Optics). Spectral repeatability of dried and ground samples was evaluated using the Root Mean Squared (RMS) statistic. This statistic was used to eliminate spectra displaying considerable variations and a poor signal/noise ratio. The RMS statistic is the averaged root mean square of differences between the different repetitions scanned at n wavelengths [32,33]. All samples displaying RMS values higher than the cutoff limit were discarded from the final set before averaging the spectra for each sample.

2.3. Chemometric data analysis

NIR spectrum frequently contains data points carrying overlapping information hence powerful statistical techniques such as multivariate analysis must be employed in order to extract useful information and to minimize noise and redundant information. Multivariate analysis techniques such as principal component analysis (PCA) and partial least squares (PLS) regression can be

Table 1
Biomass quality parameters standards followed and measurement equipment used.

Parameter	Standards	Measurement equipment
Moisture (%)	EN 14774-1	Drying Oven Memmert UFE 700
Ash (%)	EN 14775	Muffle Furnace NABERTHERM LVT 15/11
Volatile matter (%)	EN 15148	Muffle Furnace NABERTHERM LVT 15/11
Gross calorific value (MJ/kg)	EN 14918	Calorimeter Parr 6300
Net calorific value (MJ/kg)	EN 14918	Calorimeter Parr 6300
Total carbon (%)	EN 15104	Analyzer LECO TruSpec CHN 620-100-400
Total hydrogen (%)	EN 15104	Analyzer LECO TruSpec CHN 620-100-400
Total nitrogen (%)	EN 15104	Analyzer LECO TruSpec CHN 620-100-400