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Energy characteristics assessment of olive pomace by means of FT-NIR spectroscopy

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ABSTRACT

Biomass is an important renewable energy source, in particular if obtained by residues it becomes even more sustainable. In Italy, residual biomass coming from olive oil industry, i.e. olive pomace, is produced in a significant amount and is concentrated in olive oil extraction sites, making interesting a possible valorisation of these residues. The different extraction processes employed influence the pomace quality and, consequently, it is fundamental to find a rapid technique to assess its physical and chemical characteristics for a correct valorisation. The aim of the work was to develop a NIR-based methodology to obtain in a fast and cheap way information about olive pomace. Several samples (n = 104) were collected in Marche region and analysed according to standards methods. NIR spectra were acquired using both fiberoptic probe and integrating sphere and subsequently were elaborated with multivariate techniques, i.e. principal component analysis (PCA) and partial least square regression (PLS). Results show that information on extraction process and composition of the pomace can be obtained. Prediction models with performance suitable for quality control applications were obtained for moisture and ash contents, whereas gross calorific value model was suitable only for screening application.

1. Introduction

The recent environmental policies are focused on increasing process efficiency and on the partial substitution of energy and materials produced from fossil fuels with renewable sources in order to tackle climate change [1,2]. Biomass is an important renewable source for bioenergy and biomaterials and can give a significant contribution in reducing the greenhouse gas emissions. Residual biomass is considered the most sustainable option because not affected by the impact of a dedicated production but its utilization is linked to the characteristics, often not well known and variable, hindering the practical exploitation [3]. The production of bioenergy or biomaterials is influenced by physical and chemical characteristics and the knowledge of these characteristics is thus fundamental for a correct valorisation of these residual materials. For energy application, the most important parameters are linked to the energy content of the material and to possible problems occurring during combustion. Among others, gross calorific value, ash content and moisture content are mainly considered. These parameters can be significantly variable in residual biomass [4–6].

In south western Europe and specifically in Italy residual biomass produced from agricultural and agro-industry activities is present in high quantities. Olive oil industry in particular, is producing a significant amount of residual biomass as olive pomace, concentrated in olive oil extraction sites that makes interesting a possible valorisation. Unfortunately, the olive oil extraction is based on different extraction systems [7–10] producing different typologies of olive pomace, introducing difficulties for a correct valorisation of this residual material.

In fact, the oil separation after crushing and milling of olives can be performed with different technical solution, i.e. pressing (or traditional extraction), three-phases and two-phases centrifugation. These separation processes produce pomaces with different qualities (and quantities), in particular related to moisture content, in consequence of different amounts of water employed and separation efficiencies [8].

In the last 15 years (2002–2016) the annual production of olive oil in Italy was 530 kton on average, which is equivalent to 2650 kton of initial olives using an extraction yield of 20% [11].

Considering an olive pomace yield of 50% as an average of the three commercial olive oil extraction systems, i.e. traditional 35%,

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three-phase 55% and two-phase 80%, the olive pomace produced was around 1300 kton, with peak values of 1900 kton of pomace for olive oil production of 795 kton in 2004 [12,13].

The knowledge of the characteristic of olive pomace and most of all the possibility to perform a rapid analysis of such characteristics could be instrumental to find the best valorisation and for the development of a related market.

A possible technology suitable to develop a tool for a rapid analysis is the near-infrared spectroscopy (NIR) combined with multivariate analysis. This analytical technique is fast and non-destructive also useful for online applications. Different studies have been performed on the application of this technique in many sectors and on different matrices [14–16] to find models for predicting several parameters. In fact, the infrared technique is already employed in the olive oil production chain, with focus especially on the feedstock material [17] or on the more valuable final product, the oil [18–21].

Literature research shows that some studies have been already performed on the use of NIR spectroscopy for the prediction of olive pomace parameters. Muik et al. [22] and Barros et al. [23] have studied the possibility to apply near infrared spectroscopy for the prediction of olive and water content. Sanchez et al. [24] tried to develop prediction models for the determination of olive pomace quality parameters, such as moisture, gross calorific value, ash content, volatile fraction content, and elemental composition (carbon, hydrogen, and nitrogen) with good results. The samples were collected from the Andalusian region and are only representative of that area. The great novelty of this work is the application of infrared technique on Italian olive pomace samples and the consequent development of models suitable for the national scene. Moreover, to our knowledge no studies have been carried out trying to assess the type of biomass (S: olive pomace; SD: de-stoned olive pomace) and extraction methods (P: press; C: continuous system) of olive pomace.

The aim of the study was to perform a standard characterization of olive pomace produced in a region of central Italy, representative on the Italian situation, to give an overview of the variability of the characteristic on this material as well as an innovative characterization carried out by NIR analysis together with Principal Component Analysis and Partial Least Squares. Different prediction models were developed and validated by external validation for gross calorific value, ash content and moisture content in order to produce a useful tool for rapid assessment of the quality of this residual biomass. The results can support in particular an energy valorisation of this residual material.

2. Materials and methods

2.1. Sample collection and preparation

In this study a total of 104 olive pomace samples were collected in 11 different oil mills of the Marche region with different characteristics of storage methods, type of biomass (S: olive pomace; SD: de-stoned olive pomace) and extraction methods (P: press; C: continuous system). To preserve their original characteristics all the samples were hermetically sealed in plastic bags after sampling at the mills. Before the analysis, part of each sample was thermally stabilized at 45 °C for 24 h and then ground under 1 mm of particle size by means of a cutting mill (mod. SM 2000, RETSCH).

2.2. Pomace characterization

Moisture content (M), ash content (A) and gross calorific value (GCV) were determined according to the current European standards on solid biofuel (Table 1).

Table 1
Chemical parameters analysed and related reference methods.

Parameter	Unit	Normative references
Moisture content (M)	$\%_{ar}$	EN ISO 18134-2:2015
Ash content (A)	$\%_{db}$	EN ISO 18122:2015
Gross calorific value (GCV)	kJ $kg^{-1}{}_{db}$	EN 14918:2010

ar: as received, db: dry bases.

The moisture content of the material as received (M) was determined drying the sample at temperature of 105 ± 2 °C in air atmosphere using forced ventilation oven (mod. M120-VF, MPM Instruments) until constant mass is achieved. The loss in mass of the sample was used to calculate the percentage of M, which was obtained averaging two measurement series per sample. The analysis was performed according to EN ISO 18134-2:2015.

The ash content of the ground material was determined using a thermo-gravimetric analyzer (mod. 701, LECO). The sample was incinerated to a controlled temperature of 550 ± 10 °C using a muffle furnace and the mass of the residue left was used to calculate the percentage of ash content air dried. The ash content on a dry basis (A) was obtained for each sample by calculation from the ash content air dried and its moisture content. The average A was calculated by two measurement series per sample. The analysis was performed according to EN ISO 18122:2015.

The gross calorific value air dried was determined on ground material by means of an isoperibolic bomb calorimeter (mod. C2000 basic, IKA). The calorimeter was calibrated with benzoic acid standard (IKA Benzoic Acid C723). The gross calorific value air dried and its moisture content were used to obtain the gross calorific value on a dry basis (GCV). The analyses were performed in duplicate for each sample. The analysis was performed according to EN 14918:2010.

2.3. Near-infrared analysis

Antaris II FT-NIR spectrophotometer (Thermo Fisher Scientific Inc, USA) was used for collecting the near infrared spectra. The instrument is equipped with a halogen lamp as a source and an InGaAs detector. The samples were acquired in diffuse reflectance mode using a NIR fiberoptic probe and an integrating sphere.

The fiberoptic probe was used to analyse the material directly in its plastic bag. For each sample three replicates were collected on three evenly spaced positions: under the bag, behind the bag and over the bag. Before each replicate a background spectrum was acquired without sample by placing a free-portion of each plastic bag in between of fiber and spectralon, in order to eliminate signal coming from the container, also from instrument or environment.

The integrative sphere was used to acquire the diffuse reflectance spectra of the samples stabilized and ground (<1 mm). During the acquisition the samples were kept in rotation by means of a sample cup spinner to increase the representativeness of the material. Each sample was analysed in duplicate and, to exclude the signals not associated to the sample but to the instrument or environment, a blank spectrum was acquired every hour.

Each spectrum has been computed as an average of 32 successive scans acquired at a wavelength range from 4000 to 10,000 cm^{-1} and with the spectral resolution of 8 cm^{-1}. All measurements have been performed at room temperature (18–20 °C).

2.4. Data processing and multivariate analysis

Before multivariate data analysis, the spectral database was pre-processed using scatter-correction methods (i.e. Standard Normal Variate) and first and second derivatives (smoothed with