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New techniques developed to quantify the impurities of olive stone as solid biofuel

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ABSTRACT

Solid biofuels lead towards the replacement of fossil fuels. The olive industry offers potential for biomass production because of the waste generated in olive groves and olive oil industries. Fines and pulp are two substantial components of the olive stone with negative characteristics for combustion processes. Therefore, the main objective of this study is to develop an analytical method to separate olive pulp contained in an olive stone sample and to quantify it at laboratory scale. Thus, fines and pulp have been characterized. Knowing their physicochemical properties, a new separation methodology has been tested to quantify these fractions. Then, a feasibility study of Near-infrared (NIR) spectroscopy in combination with multivariate data analysis has been implemented to check if olive pulp content fraction could be controlled by using this fast technique. On the one hand, the new methodology based on differences in density of the impurities has achieved excellent results. On the other hand, the feasibility study of NIR spectroscopy applied to this analysis has been performed with good results. R^2 of 0.867 for olive stone fraction and 0.908 for olive pulp fraction respectively show the possibility of using this technique as routine analysis.

1. Introduction

Bioenergy is the word used for energy associated to biomass, and biofuel is the bioenergy carrier, transporting solar energy stored as chemical [1]. Currently, biomass represents about 14% of the world's final energy consumption [2] and about 4% of the European Union total primary energy [3]. Biofuels for heat and power generation are steadily expanding in Europe, mainly in Austria, Germany, the United Kingdom, Denmark, Finland and Sweden, where residential/domestic heating and bioelectricity are mostly produced from wood residues in heating devices and cogeneration plants respectively. In Mediterranean areas of European Southwest, agricultural and industrial activities are very important and a great amount of waste biomass is produced. A biomass market, with particular characteristics that differ from the rest of Europe, is starting specifically in Spain. Likewise, in this country, there is a large production of native solid biofuels, such as those from the olive industry in Andalusia (south of Spain), which are very different from that derived from forestry activities [4].

Within this context, olive industry presents a high potential for solid biofuel production because of the residues generated from olive groves and those by olive oil industries [5]. Olive groves represent over 1,400,000 ha of the cultivated land in Andalusia and the olive oil production is over 800,000 tons per year [6]. Moreover, olive stone (also called olive pit and olive kernel) is one of the most important residues of this sector, being generated above 450,000 tons per year [7]. The vast majority of the produced olive stones are used as solid biofuel to thermal power generation for heating sector due to its high heating value, low moisture, uniform size and high density [8].

The olive oil is a product of particular importance within the Mediterranean and Spanish agricultural food system, and more specifically in Andalusia, owing to be the world's main production area [9]. Olive oil processing, in general, consists of three operational steps: olive crushing, milling and oil separation; where oil is extracted/separated from the remaining wastes. Currently, there

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are three commercial olive oil extraction systems available on the market (traditional, three-phase and two-phase centrifuge), differing in two main aspects; in the physical force used to recover oil (press or centrifuge) and; in the amount of water (if) added to the paste during oil extraction. This, however, has an important impact on the quantity and quality of products and residues obtained, producing, in addition to oil, one or two streams of wastes [10]. The vast majority of the olive mills in Andalusia use an extraction system of two-phase centrifuge [11]. Quality and quantity of olive stone obtained in this process depends of type of extraction. The pit content varies from 30% in pressing plants to 12% in the two-phase continuous systems with a moisture content over 20% [12]. Normally, the moisture is then reduced to values of between 6 and 12% using natural or artificial drying methods [13]. Nowadays, drying methods are usually carried out by distribution companies to improve olive stone properties as biofuel before consumption. Olive stone is dried and cleaned (pulp and olive stones fines are removed from the biofuel) to obtain the greatest energy efficiency in combustion processes [14].

The olive stone residues aim at being consolidated in biofuel markets and being commercialized through storage and distribution companies thus guaranteeing biomass characteristics and quality parameters [15]. The olive stone physicochemical properties must therefore be studied in order to achieve an optimum efficiency in the combustion within different heating appliances. Focusing on the current situation of the biomass thermal process sector, specifically the domestic heating field, most of the biomass heating appliances used in Andalusia are devised based on Central Europe countries knowledge. As result, design, construction and operation of these devices are based on combustion of European biomass (mainly pine wood pellet), whose properties are different from some Mediterranean solid biofuels, for instance olive stone, leading to lower energy efficiency in heating appliances.

The olive stone residues usually include olive pulp, which is olive skin crushed into fragments and holding an average of 25% of water and a quantity of oil making it susceptible to rapid decomposition [16]. This oil presents a higher heating value but it causes troubles in combustion processes within domestic heating appliances, due to its chemical composition and low weight, resulting in uncontrolled combustions and emissions. In addition, residues and slags are generated by the pulp combustion, which has a high content in ash, nitrogen and sulfur [14]. Other problems with the olive stone residues is the size distribution of the particles. Fines particles are very important because they produce emissions and an uncontrolled combustion [17]. Research has demonstrated that the concentration of impurities and crucial ash-forming elements, increase, in most cases proportionally with decreasing fuel particle size [18]. Consequently, most of these smaller elements should be effectively removed from the fuel particles [1].

In the biomass market, an important amount of olive stone not cleaned or dried properly are being commercialized and used, with the consequent adverse impact on combustion processes [14].

According to the new Spanish standard UNE 164003:2014 about the olive stone as solid biofuel [19], elaborated by the Spanish Association for Standardization and Certification (AENOR) with data obtained of BIOMASUD project [20] and scientific literature [8,14]; fines content are quantified with the official standard of size distribution EN 15149-1:2011 [21] for solid biofuels but there is not official method for solid biofuels to separate and quantify olive pulp contained in an olive stone sample and it must be carried out with EN ISO 658:2002, which is an official method for oilseeds. In this sense, laboratory analytical methods are often expensive and time-consuming; therefore, Near-infrared (NIR) spectroscopy is of interest to characterize biofuels (solids and liquids) because it is a fast and a nondestructive method suitable for online measurements. Studies have also shown the high potential of NIR spectroscopy to predict other solid biofuels parameters such as cellulose, hemicellulose and lignin [22–24], or parameters such as moisture, ash content, calorific value, chlorine and sulfur in olive stone residues [25,26].

The main objective of this study is to develop an analytical method to separate olive pulp contained in an olive stone sample and to quantify it at laboratory scale. For this reason, the fines and pulp of olive stone have been characterized, and based on their physicochemical properties, it has been defined a separation methodology to quantify these fractions. Afterwards, a feasibility study of NIR technology, in combination with multivariate data analysis has been implemented to check if the olive pulp content could be controlled by using this technique.

2. Materials and methods

2.1. Raw material

A sampling plan was designed to collect olive stone residues of different varieties of olives (*Picual*, *Hojiblanca* and *Picuda*), from different Andalusian industries including olive oil factories and distribution companies. Eighty-two untreated olive stone samples have been analyzed with different amounts of pulp and fines particles.

To check the methodology developed, olive pulp has been collected from olive stone distribution companies, after sieving and blowing industrial processes. Moreover, olive stone fines (<1 mm) have been obtained with an industrial sieving machine of one olive stone distribution company.

2.2. Determination of quality parameters and equipment

The olive stone fines and pulp parameters have been determined by official methods established by the European Standard Technology Committee [27]. In Spain, the adaptation of this methodology was established by AENOR. The standards and the measurement equipment used are shown in Table 1.

The content of oxygen has been calculated from the difference between 100 and the sum of carbon, hydrogen, nitrogen, sulfur, chlorine and ash content [28]. The low heating value (LHV) has been calculated based on ultimate analysis and HHV experimental values [29].

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

Parameter	Standard	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
Total sulfur (%)	EN 15289	Analyzer LECO TruSpec S 630-100-700
Total chlorine (mg/kg)	EN 15289	Titrator Mettler Toledo G20
Bulk density (kg/m^3)	EN 15103	Standardized container
Major elements (mg/kg)	EN 15290	ICP OES VARIAN 715-ES
Oil content (%)	UNE 55030	Soxhlet extraction