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Physico-chemical properties and thermal degradation characteristics of agropellets from olive mill by-products/sawdust blends

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ABSTRACT

This study aims to produce agropellets composed by olive waste, an olive mills by-product, blended with pine sawdust for 6 different mass fraction compositions. Thermal and physicochemical properties of these pellets such as moisture, ash content, bulk density and heating values were determined. In addition, thermogravimetric analyses were performed under inert and oxidative atmosphere in order to assess the thermal degradation behaviour of the produced agropellets. Results show that during the pelletization process, the high value of moisture in olive waste decreases. Values of ash content for each considered sample remain in the accepted agropellets French standards. Thermogravimetric analysis shows that the thermal degradation of the different pellets follows the usual behaviour of lignocellulosic materials. Furthermore, a quite continuous zone corresponding to the not readily char combustible part is detected during TGA under oxidative condition. However, a higher reactivity for PS/OW pellets is observed compared to those reported in literature. Such results prove that olive waste agropellets may be an alternative fuel for producing energy in domestic boilers.

1. Introduction

Reducing the electrical energy cost, especially, with the rising costs of fossil fuels' prices (gas, petroleum) constitutes a challenge for researchers all over the world. Moreover, concerns related to climate change and its environmental impact remain outstanding. Besides, the security of energy supply has motivated research in renewable energy sources worldwide [1,2]. Hence, biomasses in general and agro-industrial residues in particular seem to be realistic alternative fuels, providing benefits such as reducing CO_2 emissions from fossil fuels combustion [3] and reducing NO_x formation via the decrease of nitrogen content in corresponding biofuels [4].

Studying the state of the art in Tunisia and EU countries allows identifying the available biomass resources in different regions. It is well known that the production of olive oil has risen in recent decades, as a result of objective considerations, and especially the increase of olive oil price due to its nutritional values. For Tunisia, palm tree residues (produced in the desert oases) and especially, olive pomace, provided by olive oil manufacture (in the South-East in general, and in the Sahel region in particular), are the most available biomass resources (about 400.000 tons of olive pomace per year). In the EU countries, particularly in France, large amount of forest residues (oaks, pines, holm oaks and cork oaks) [5] and agriculture residues [6] (olive waste, apple waste, pectin of citrus shell, sunflower husk, spent ground coffee …) represent the bulk of available biomass resources.

Technologies based on the use of residual products from agro-industry and agriculture/forest residues for energy purpose have already been developed [6,7]. However, they have some drawbacks such as a lower bulk density and/or the generation of potential emissions affecting negatively either the furnace or the composition of the exhaust gases. Furthermore, the olive oil industry produces a by-product similar to a paste called olive cake or olive pomace. Such material represents a serious waste problem difficult to manipulate (e.g. slow drying) [8]. Note that, in olive oil sector, one recognizes three different technologies: traditional pressing technologies, a two-phase decanting system, and a three-phase decanting system. The estimated olive waste quantities in EU are about 6.8 million tons/year [9]. The olive waste is mainly composed of pulp residues and pits (seeds) of the fruit, which holds important quantities of organic matter, among which remains a non-negligible amount (about 4%) of residual olive oil. The latter compound gives the raw olive waste a higher potential for energy production [10–13].

The blending processes for different biomass materials as well as pelletization constitute a subtle way for a best valorisation may represent effective strategies for improving their physical–chemical characteristics [14]. First, they provide energy densification, the control of reactive surface available to combustion (and then the air/fuel ratio). Second, they enable the control of ash, nitrogen, sulphur and chlorine ratios up to given contents tolerable by some standards such as the French agropellets and the European EN 14961–6 standards. Several

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blends of biomass materials have been previously investigated and tested. Serrano et al. [15] studied blends composed of pine and barley straw. Effects of the pelletization process on the physicochemical properties of agropellets, and especially the effect of the small amount of pine addition in the blends, have been studied. These authors have found that the optimum moisture for producing barley straw pellets must begin in the range of 19–23% and end in the range of 6–8% after pelletization. Moreover, 95% durability value is reached under this moisture interval. Furthermore, this durability is enhanced, reaching 98% when small amounts of pine were added to the barley straw. Besides, the water or pine addition improved the agglomeration, which influences the mechanical durability and the pellet length of ground particles. Serrano et al. [15] also noted a small decrease of the heating value due to pelletization. However, they concluded that, when adjusting the moisture content to 12%, mechanical durability was better; and due to high lignin content in pine, the calorific value increases. Unfortunately, even though the ash content in pine is small (less than 1%) it maintains a high ratio in the blended pellets (10%).

Mediavilla et al. [16] analyzed blends from vine shoots and industrial cork residue. They found that the energy demand for pelletization was notably decreased when adding cork residue. Also, they observed that industrial cork residue effects consist of decreasing the ash content, increasing the heating value, and decreasing their physical properties. As for the combustion tests, it is worth noting that the blended pellets (cork residue/vine shoots) reduce significantly the trend of the ash to accumulate and to sinter in the pellet burner. Moreover, carbon monoxide emission was reduced. However, the most important result obtained, associated with both pelletization and combustion efficiency, is the optimal mass fraction compositions between vine shoots and cork residue (70 wt.%–30 wt.%) [16].

Dorge et al. [17] investigated the pyrolysis and combustion of Miscanthus pellets TGA tests, for different rates of heating, under inert (N_2) and oxidative atmosphere. The studies were carried out with gas and particle matter emissions analysis. Under inert atmosphere, these authors established a kinetic model with detailed rate parameters, which are not affected by heating rates. Also, the particles sizing study showed that gaseous emissions include PM10 at fractions of 10^{12} particles/g of sample. Agglomeration of these particles are governed either by nucleation centred at 0.04 μm and a temperature range between 190 and 253 °C, or by coagulation centred at 0.5 μm for a temperature range between 253 and 310 °C.

Wei Yan et al. [18] carried out a study on the pyrolysis of row loblolly pine and hydrothermally carbonized (HTC) loblolly pine. During their thermal degradation investigation, heating rates of 5, 10 and 20 $°C\cdot min^{-1}$ were imposed, while the temperature range was between 105 and 800 °C. They found that more significant decomposition occurred with pyrolysis of raw biomass compared with HTC. Thus, raw biomass disposes of a much higher volatile content and lower fixed carbon content. This study shows that pyrolysis of (HTC), within the temperature range of 360 °C–425 °C, progresses less rapidly than that of raw biomass. Also, results of kinetic analysis (based upon the assumption that thermal degradation obeys first-order kinetics) show analogous values of activation energy for both biomasses.

The main chemical components of olive waste are cellulose, lignin, proteins, oil, polyphenols and water. The water proportion varies from one year to another according to the rain averaging, which is very random in Tunisia and for all countries located in the southern Mediterranean countries. Moreover, the moisture ratio depends closely on the oil extraction process. Indeed, it is lower for olive waste obtained by pressing than the one obtained by decanting (two or three phases) [19]. The moisture growth in the latter processes is due to the raw olive washing before kneading and also to water addition during the separation phases. For decanting processes the average of water supply is 4 l/l of extracted oil.

In a recent paper [20], authors noticed that olive by-products' characteristics vary from a region to another in a same country (Croatia). Consequently, agropellets prepared from olive waste mixed with pine sawdust may have different qualities from a country to another. This issue is due to climatic considerations, to soil characteristics and to the olive tree species. Hence, the main objective in this work, mainly important for the Tunisia energy policy, is to investigate the quality of agropellets that can be used as an alternative fuel. The choice of pine sawdust to be mixed with olive waste is based on its high potential energy and on its low ash content [7]. Based on previous works [6,7,14–18] consisting of blending biomasses in different proportions, an attempt to prepare agropellets from olive waste and pine sawdust in 6 different mass compositions is performed. To assess the quality of pellets their chemical and physical characterizations as well as thermogravimetric analysis (TG) under inert and oxidative atmosphere were performed.

2. Materials and methods

2.1. Samples preparation

Olive waste used in this study is obtained from the Zouila oil press company situated in Mahdia (Sahel region of Tunisia), specialized in the double extraction of olive oil from olive pomace, and in the soap industry. However, the pine sawdust was provided from a French wood manufacturer situated in the east of France. After being well mixed, the blend moisture was adjusted when necessary to about 12% by weight. Then, the blend was transformed into pellets using a KAHL 14/175 pelletizer. After pelletization, pellets where stored for 24 h under room conditions in order to stabilize their moisture and temperature. The obtained products are cylindrical pellets of 6 mm diameter and 15–25 mm length approximately. Six samples were prepared with different fractions of olive waste from 10 (wt.%) to 60 (wt.%). The pelletizer operates in the optimal regime when it reaches a frequency of 50 Hz and a temperature of 75 °C. Pellets are characterized by their brightness and their rebounding aptitude when thrown against a solid surface without breaking. Initial moistures were about 49% for olive waste, and about 9.7% for pine sawdust. Thus, the following samples were prepared:

90PS10OW: composed of 90% pine sawdust and 10% olive waste.
80PS20OW: composed of 80% pine sawdust and 20% olive waste.
70PS30OW: composed of 70% pine sawdust and 30% olive waste.
60PS40%OW: composed of 60% pine sawdust and 40% olive waste.
50PS50OW: composed of 50% pine sawdust and 50% olive waste
40PS60OW: composed of 40% pine sawdust and 60% olive waste.

In addition, to the above samples, two reference samples 100PS composed of pure pine sawdust, and 100OW composed of pure olive waste were prepared. These latter samples will help understand the thermal behaviour of the studied pellets.

2.2. Samples characterization

The moisture content of the different samples was obtained by introducing a fixed mass in a stove at 105 °C during a period time of 24 h. Moisture content was obtained by weighing using Balance precisa XT 220A. Calculations are carried out by averaging three values of moisture for each pellets type. Moisture degrees are expressed in percentage by wet basis.

In order to obtain the ash content, a fixed sample mass was placed in the muffle furnace (Nabertherm P330). Then, the temperature is increased up to 900 °C at a heating rate of 5 °C/min and maintained at 900 °C for 1.5 h. The ash content (wt.%) was obtained by weighing the residual mass at the end of the experimental test.

The high heating value (HHV) of each sample type was directly determined using a calorimetric bomb (IKA C200). The low heating values (LHV) were calculated using the following formula:

$$LHV = HHV - L_V \times \left(9 \times \frac{\%H}{100} \times \left(1 - \frac{\%Hu}{100}\right) + \frac{\%Hu}{100}\right). \quad (1)$$