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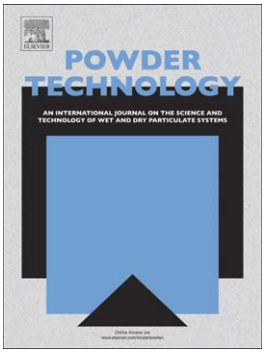

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Dry fractionation of olive pomace as a sustainable process to produce fillers for biocomposites

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Abstract

Olive pomace (OP) is the agro-industrial residue of olive oil extraction composed of residual pulp and stone. This work aims at exploring the possibility of using dry fractionation (combination of grinding and sorting processes) to produce pulp-rich and stone-rich fractions with the highest purity and yield. The physical-chemical characteristics (composition, thermal stability, color, surface free energy) of the obtained powders were discussed in relation to the applied processes. It was shown that dry fractionation could be successfully used to convert OP into valuable fractions using processes avoiding the consumption of water and the generation of effluents or co-products. Results revealed that the separation of the pulp from the stone using friction solicitations in a ball mill operating in mild conditions (2 min at a frequency of 15 Hz) was as efficient as wet fractionation in terms of powder characteristics, achieving a total yield of 99.4% against only 82.1% in the case of wet fractionation and without using water while a water:biomass ratio of 5:1 was required for wet fractionation. Produced powders exhibited contrasted biochemical composition (either rich in lignin or cellulose) and surface free energy, and were thermally stable up to at least 210°C. It was concluded that they could be interestingly used as raw resources for the production of fillers that will be further incorporated in polymer matrices to produce a range of biocomposites.

Keywords: Olive pomace, dry fractionation, grinding, sorting, characterization.

1. Introduction

In recent years, an increasing public concern has been noticed over the harmful effects of fossil-based plastic materials on the environment. The development of alternative materials that are both biodegradable and produced from natural resources is thus gaining considerable attention owing to environmental, economical, societal and technical advantages as compared to conventional synthetic polymers. Lignocellulosic fillers based biocomposites constitute a promising answer since they allow to joint current requirements regarding the need to reduce our dependence to fossil resources, environmental pollution, while offering a way of sustainable eco-conversion of lignocellulosic solid wastes and by-products. A large range of lignocellulosic residues obtained from agro-food industries have already been explored and effectively used as fillers in biocomposites due to their interesting properties, biodegradability, high availability and low price [1]. Among this available lignocellulosic biomass, one valuable lignocellulosic biomass is olive pomace [2, 3]. Recently, some studies highlighted the potential of olive pomace (OP) as reinforcing agents in polymer matrix [4, 5].

Over 95% of the world's olive trees (*Oleaeuropeae*) are found in the Mediterranean basin, due to environmental factors that make the soil and the climate ideal for their cultivation, flowering and production of their fruit. Among the emerging producing countries, Algeria is considered as a new extra-virgin olive oil exporter. *Chemlal* is the most common olive cultivar grown in this country, with 40% of the orchards. Recently, this variety has become associated with high olive oil production, due to its large distribution and its high olive oil yield, *i.e.*18 L/100 kg of olives [6]. One hectare of olive tree originates on average about 2500 kg of olives. Generally, 100 kg of olives produce 20 liters of oil, 35 kg of olive pomace and 100 liters of wastewater [7]. So, about 875 kg of OP are generated by hectare.

It is estimated that the production of OP reaches 2,881,500 tons/year worldwide [8]. OP is not easily degradable under natural conditions and its disposal causes serious environmental problems, particularly in the Mediterranean countries, where abundant quantities are produced during a short period of the year. It is responsible of inhibition of microorganisms' activities, reduction in the seed germination, and alteration of soil porosity and humus concentration. Thus, in order to reduce its harmful environmental impact, several works have been recently dedicated to its valorization in various fields, such as animal feed, composting, energy and biofuels, cosmetics, food industry, and pharmaceutical areas. Only few studies are describing the use of olive pomace (quasi exclusively olive stone) as raw materials for the production of reinforcing fillers [3, 4, 5]. The intrinsic characteristics of fillers obtained from agro-residues, including their composition and surface properties, are considered as key criteria for their use in composite materials and should be thus well controlled [9]. Furthermore, many studies demonstrated that the development of biocomposites at industrial scale requires a better control of the filler/matrix interface, which can be tricky in the case of fillers derived from heterogenous and complex agro-residues.

The olive fruit can be structurally separated into three compartments, *i.e.* (1) the skin, called epicarp, which contains chlorophylls, carotenoids and anthocyanins that account for the color, (2) the pulp or flesh, called mesocarp, which is the reserve supply of all the constituents (oil, ashes, proteins, cellulose and lignin), and (3) the stone, called woody endocarp, which contains the seed and is mainly composed of crude cellulose[10]. OP is a mixture of residual skin, pulp and fragments of the crushed stone. The distribution of the various constituents and the physical-chemical characteristics of the OP are complex and fluctuate according to the fruit variety, cultivation practices, geographical origin, stage of

maturity, storage time and process of oil extraction [7]. The structural heterogeneity and complexity of OP constitute one of the obstacles to subsequent eco-conversion especially in biocomposites application. Existing pre-treatments used to separate the pulp from the olive stone are based on chemical multistep processes consuming large amounts of water and chemicals and generating effluents that have to be treated. They include cleaning and washing with hot water [2, 3, 11, 12,13], with hot water and solvent (acetone-hexane) to remove the pulp [14], or hot treatment by solvent (acetone and/or hexane) followed by separation with ventilation of the stone from the pulp [4, 5].To raise this bottleneck and allow a better exploitation of OP, it would be more relevant to apply a non-polluting fractionation process in order to produce contrasted powders whose properties will be adapted to composite applications.

In this context, dry fractionation appears as a promising alternative for the production of pulp-rich and stone-rich fractions without any consumption of water nor chemicals and therefore generate very few wastes [15, 16]. Dry fractionation processes combining grinding and sorting technologies (air classification, electrostatic separation or sieving) have attracted a great deal of attention due to their use in various fields including electronic waste valorization, food industry, pharmaceuticals, ceramics and materials science [17, 18]. Dry fractionation has been widely applied to several lignocellulosic biomasses with promising results, namely wheat straw [15, 19], rice straw [17], bagasse [16] and rapeseed press cake [20]. To our knowledge, these processes have never been applied to the treatment of OP.

In this context, the present study aimed at exploring the use of dry fractionation to produce pulp-rich and stone-rich fractions with the highest purity and yield from crude OP, that

could be further used as raw ressources for the production of fillers for biocomposites. Different milling modes (compression, shearing and impact, friction) were considered and combined by selecting appropriate equipments (knife milling, impact milling, ball milling). The ground powders were then separated in interesting fractions by sorting steps (sieving or electrostatic fractionation). Some intrinsic properties (color, biochemical composition, surface free energy and thermal stability) of the resulting fractions were characterized and discussed in relation to the applied dry fractionation route. These properties were characterized in such a way (i) to assess the efficiency of the sorting route and (ii) to estimate the potentiality of using obtained fractions as raw resources for the production of fillers, with a focus of the estimated affinity with polymer matrices. A wet separation process was tested for comparison. Finally, in view to draw an optimized biorefinery scheme for the conversion of OP, different added-value routes of valorization were proposed for each resulting powders, besides to their potential application as fillers in biocomposites.

2. Materials and methods

2.1. Materials

Olive pomace was obtained from the oil extraction of the *Chemlal* variety using a traditional press system. It was kindly supplied by local olive producers in the region of Azazga (Tizi-Ouzou) in north-central Algeria, in February 2016. This residue was composed of partially crushed stones, pulp and skin. Olive pomace was dried in ambient air for three days and then, stored at 4°C and shielded from the light until its use. Only one batch of olive pomace was considered in the present study.

Sulfuric acid, arabinose, xylose and glucose (SIGMA-ALDRICH), formamide, diiodomethane (Acros Organics, Geel, Belgium), ethylene glycol (Aldrich chemical Co. Inc., Milwaukee, USA) and glycerol (Merck, Darmstadt, Germany) were used for characterization of olive pomace fractions.

2.2. Fractionation of olive pomace

Fractionation of crude olive pomace was carried out to produce pulp-rich and stone-rich fractions following different routes (Figure 1). All the obtained fractions came from the same initial olive pomace batch.

Figure 1.

2.2.1. Wet fractionation

200 g of crude OP were mixed with 1 L of distilled water and left during 24 hours at room temperature. Then, this suspension was placed under agitation at 400 rpm and 30°C for 24 hours. The mixture was first sieved through a 1 mm sieve in order to separate the humid stone-rich fraction from the humid pulp-rich fraction. The residual liquid fraction was centrifuged at 10.000 rpm during10 min in order to separate the pulp-rich fraction from the liquid effluent. The two obtained fractions were dried in an oven at 50 °C during 24 hours and were designated as wS (stone-rich fraction) and wP (pulp-rich fraction) (Figure 1).

2.2.2. Dry fractionation

The crude OP was first ground using a knife milling (SM 300, Retch, Germany) with a grid size of 4 mm, and then passed through a second grinding with a grid size of 2 mm to obtain the fraction F0. Then, two types of sorting were tested in order to separate the pulp from

the stone, *i.e.* sorting according to the particle size by sieving (route A1), sorting according to the particle surface charge by electrostatic separation (route A2). Given the crumbly character of the pulp tissue that can be easily mechanically detached from the stone, another sorting route has been investigated, *i.e.* friction (route B) using mild conditions of ball milling without preliminary grinding of crude OP (Figure 1).

Sorting by sieving (route A1). 200 g of F0 sample were passed into a ROTEX mechanical sieve through a 0.8 mm mesh for 10 minutes. Two fractions were obtained. The first one contained the particles with a diameter greater than or equal to 0.8 mm and corresponded to the stone-rich fraction (dS1) while the fraction constituted of particles with a size smaller than 0.8 mm represented the pulp-rich fraction (dP1).

Electrostatic sorting (route A2). 200 g of F0 were further ground using impact milling (Hosokawa-alpine, type UPZ, Augsburg, Germany) with a grid size of 0.3 mm. Resulting fine particles displayed a median diameter, measured by laser granulometry (d_{50}), of about 100 µm. A pilot-scale TFS (TEP System, Tribo Flow Separations, Lexington, USA) was used for the electrostatic fractionation (EsF), using fine particles as starting material. This technology is based on the separation of particles according to their surface properties (chemical composition and charges), in which lignocellulosic particles are trained in a charging line where they are charged by tribo-electricity. The charged particles are subsequently moved to a separator chamber containing a high electrical field (10 kV), generated by two high voltage electrodes. The positively charged particles are attracted by the negative electrode (F+) and the negatively charged particles are attracted by the positive electrode (F-) [15, 17]. Positively charged fractions are generally richer in proteins and water-soluble carbohydrates in comparison to the initial F0 material. By contrast,

negatively charged fractions are rather richer in lignin and structural carbohydrates (and thus cellulose) in comparison to F+ [20]. The powders obtained with this process are designated by (dS2) and (dP2) for the stone-rich fraction and the pulp-rich fraction, respectively (Figure 1).

Sorting by friction and sieving (route B). 200 g of crude olive pomace were submitted to vibrations using a ball mill (MM 400, Retch, Germany), under a frequency of 15 Hz for 2 min in the presence of three steel balls with a diameter of 15 mm. The obtained powder was then sieved into a ROTEX mechanical sieve 1 mm mesh for 10 minutes, in order to separate the pulp from the stone (Figure 1). Coarse particles with a diameter greater than or equal to 1 mm were retained on the sieve and corresponded to the stone-rich fraction (dS3), the fine particles were recovered from the bottom of the sieve and represented the pulp-rich fraction (dP3).

2.3. Characterization of olive pomace fractions

All fractions, except those obtained by electrostatic fractionation (EsF), were ground with a ball mill (MM400) at a frequency of 25 Hz for 2 min in order to get homogenous samples before being analyzed. This was not necessary in the case of dS2 and dP2 fractions because they were already fine enough for further analyses.

2.3.1. Color

The color attributes of each fraction were measured with a colorimeter (Minolta), using the *L**, *a**, *b** color system. The *L** value characterizes the luminance while *a**and *b** values are indicators of sample color (a* from green to red and b* from blue to yellow). The

measurements were made in duplicate. The total color difference (ΔE) between the fraction and the starting biomass was calculated following Equation 1 [21].

$$\Delta E = [(L^* - L^*_{F0})^2 + (a^* - a^*_{F0})^2 + (b^* - b^*_{F0})^2]^{0.5} \quad \text{Equation (1)}$$

with L^*, a^* and b^* the color components of the obtained powder. L^*_{F0}, a^*_{F0} and b^*_{F0} are the color components of the starting biomass.

2.3.2. Biochemical composition

The composition of olive pomace fractions was measured after concentrated acid hydrolysis according to Barakat et al. [15]. The lignin content in samples was determined by the Klason method. HPLC analysis enabled to quantify monosaccharides (glucose, xylose, and arabinose). The sugars analysis was done with a combined HPLC water system, using a BioRad HPX-87H column at 40°C and 0.3 mL.min^{-1}. All analyzes were carried out in triplicate for each OP fraction. The concentration of cellulose was determined by the glucose levelwhereas xylose and arabinose were used to calculate the hemicellulose concentration in the lignocellulosic complex of each fraction. Biochemical analyses were done in triplicate. Humidity and ashes contents were determined by thermogravimetric analysis (TGA) under air (see paragraph 2.3.3) by considering the weight residue at 130°C and 900°C, respectively. Protein contents of the different fractions weredetermined with (N x 6.25) according to Jones [22], after estimation of the nitrogen content in each sample by elementary analysis. TGA and elementary analysis were done in duplicate.

2.3.3. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out in order to study the thermal stability of the different fractions. Samples (about 10 mg) were heated from room temperature up to

900°C, at a heating rate of 10°C.min^{-1} under air and nitrogen flow (50 mL.min^{-1}). The degradation temperature (T_{peak}) was measured from the maximum value of weight loss derivative. Measurements were done in duplicate.

2.3.4. Contact angle measurements

Contact angle measurements were carried out on tablets obtained by compression of powders in a mold (diameter of 13 mm) using a hydraulic press (Perkin-Elmer) and a pressure of 10 tons. Resulting tablets were dried during 30 min under vacuum and in presence of silica gel before measurement. Contact angle measurements were performed using a Digidrop (GBX, France) instrument. The volume of the drop was 3 µL in all cases using a micro-syringe. The measurement of the contact angle was carried out at the moment of the stabilization of drop above the surface of the pellet. Five reference liquids were used in order to estimate the surface free energy of compressed powders (polar and dispersive components), *i.e.* distilled water, formamide, diiodomethane, ethylene glycol and glycerol. Surface energy values were calculated by using the Owens-Wendt formula [23]. The work of adhesion between the two solid constituents of the biocomposite, *i.e.* the polymer matrix (m) and the filler (f), was predicted using the following harmonic-mean equation:

$$W_{mf} = 2x\left(\sqrt{\gamma_m^d \gamma_f^d} + \sqrt{\gamma_m^p \gamma_f^p}\right) \qquad \text{Equation (2)}$$

3. Results and discussion

The two fractions (pulp-rich and stone-rich fractions) obtained by wet fraction processed were considered as the targeted references in order to evaluate the efficiency of the different dry fractionation alternative routes proposed in the present study. The first

parameter indicating the efficiency of the separation was the color, the pulp being very dark (almost black) and the stone yellow/brown. The other characteristics were the biochemical composition, the thermal stabilityand polarity of powders. In addition to the evaluation of the dry fractionation efficiency, results have also been useful topropose potential routes of valorization for all olive pomace fractions.

3.1. Wet fractionation

Color is an intrinsic characteristic of the olive fruit. Literature reports that the pigment concentration greatly differs according to the variety, ripeness state, moment of picking and chloroplast pigment distribution through the tissues of the fruit [24]. In contrast to the stone, whose growth stops after about two months, the pulp continues to grow through ripening. Olive contains greater amounts of chloroplasts in skin and pulp that are able to carry out photosynthesis, explaining that these two tissues retain chlorophylls and carotenoids pigments more than the stone.

A change in the color of the obtained fractions was thus considered as a first indicator of fractionation efficiency. Washing the crude olive pomace with water allowed to obtain two contrasted fractions, *i.e.* a dark brown (almost black) fraction corresponding to the pulp-rich fractionand a yellow/brown fraction corresponding to the stone-rich fraction (Figure A-Supplementary information). These visual observations were confirmed by the measurement of the color parameters (L*, a*, and b*). According to the Commission International de l'Eclairage [21], L* representing the luminance, ranges from 0 (black) to 100 (white) while the two chromatic components, a* (from green to red) and b* (from blue to yellow), range from -120 to +120. The starting biomass (F0), corresponding to a mixture of pulp and stone, exhibited L*, a* and b* values of respectively 43.6, 9.4 and 15.7 (Table

1). The stone-rich fraction (wS) was significantly clearerthan F0, with a higher value of L* (65.8), and more yellow, with a slightly lower value of a* (5.3) and higher value of b* (18.6). On the opposite, the pulp-rich fraction (wP) was considerably darker, with a lower L* value (34.9), and browner with a higher value of a* (9.2) and lower value of b* (11.6) (Table 1). It can be concluded, as expected, that washing in water is an efficient treatment to produce contrasted fractions, what justifies its applicationby several authors to remove the pulp from the stone [11, 12, 13].

Table 1.

The biochemical composition was a second quantitative parameter to evaluate the separation efficiency of the two main tissues of olive pomace (Table 2). The starting biomass (F0) used in this study recorded a concentration of 14.8% in cellulose, 14.7% in hemicellulose and 37.8% of lignin. These values are in agreement with those found by Haddadin et al. [25], which are about 18.3% for cellulose, 15.7% for hemicellulose and 38.5% for lignin. However, they differ from those registered by Gharbi et al. [4], who found values of 25% in cellulose, 35% in hemicellulose and 35% in lignin. Concerning proteins and ashes, contents of 4.5% and 3.5% were respectively recorded for F0. These results are not far from those reported by Haddadin et al. [25], which ranged from 5.5 to 6% for proteins and between 7.7 and 15% for ashes. As it was already reported, slight discrepancies between values are due the fact that the composition of olive pomace is variable, mainly depending on the fruit variety, growing region, and process of oil extraction [7].

Concerning the powders produced by wet fractionation, results showed that the stone-rich fraction was characterized by higher celluloseand hemicellulose contentswith a total value

of 33% d.b. against 18% d.b. for the pulp-rich fraction. The two fractions could also be distinguished by their lignin concentration, with a significant lower lignin content in the stone-rich fraction (37 % d.b.) than in the pulp-rich fraction (43 % d.b.) (Table 2). These results are concordant withvaluesreported in literature. Several authors agree that the stone containshigher contents in cellulose as compared to the pulp, with values ranging from 15 to over 70% [26, 27]. For Matos et al. [28], the main components in stone arecellulose (28.1–40.4%), hemicelluloses (18.5–32.2%) and lignin (25.3–27.2%). On the other hand, lignin together with polyphenolsis known to be more abundant in the pulp [29].

Important differences were also noticed concerning the protein content, with a higher content in the pulp-rich fraction (12 % d.b.) and only traces in the stone-rich fraction (0.43%) (Table 2), in accordance with already published values [10, 27, 30].

Finally, results showed that the stone-rich fraction was also characterized by a significant lower ashes content (around 2 % d.b.) as compared to the pulp-rich fraction (around 7% d.b.) (Table 2). This tendency was previously demonstrated by Maymone et al. [27] who reported an ashes content of 0.8% for the stone against 4% for the pulp, whereas Ghanbari et al. [31] reported values ranging from 0.01 to 0.68% for the stone. However, it is worth noting that the ashescontent recorded for our stone-rich fraction was slightly higher than values reported for the stone. This can be ascribed to an incomplete separation of the stone from the pulp following our wet fractionation, or also to a bad washing of the olives at the mill and, consequently, to the persistence of soil in the olive pomace resulting from the presence of fruits collected at ground during the harvest. On the other hand, there is no work in the literature focusing on olive pulp indicating characteristic values concerning its

biochemical composition, most publications transmit mainly composition of the crude olive pomace and only some of them, reporting data about the stone composition.

Table 2.

Different characteristics for the pulp-rich and stone-rich fractions obtained after washing the crude OP in water confirmed the efficiency of this treatment for the separation of OP in fractions richer in different tissues. Indeed, soaking the olive pomace into distilled water for 24 hours allows weakening the pulp tissue owing to water absorption, thus making easier the peeling of the pulp from the stone upon the second step of stirring. Furthermore, after sieving the stone sample is abundantly washed with water to remove any trace of residual pulp, allowingobtaining a purer fraction.

However, despite theefficient separation, this process presents some disadvantages. First, it is necessary to note the consumption of a large quantity of water (5 volumes of water per 1 volume of biomass), which is accompanied by the generation of a liquid effluent (Figure 1), whose composition seems to be similar to that of olive wastewater. This effluent, presenting an additional environmental problem, must be treated or co-valorized. Secondly it is likely that a prolonged contact of olive pomacewith water (48 hours in this study) would promote the loss of some interesting hydrophilic substances (including carbohydrates, organic acid, phenols, polyphenols) in the aqueous phase [29], which can reduce the valorization fields of the obtained fractions. Additionally, the loss of matter upon the wet fractionation process is not negligible, with ayield of about 82 %. Finally, obtained lignocellulosic fractionswill require a drying step before further treatments such as grinding and then, incorporation as fillers in a polymer matrix. This is the reason why dry fractionation has recently emerged as a sustainable alternative to conventional wet

treatments for the valorization of the lignocellulosic biomass stemming from agro-food industries.

3.2. Dry fractionation

Theselected dry fractionation routeshave been applied to the raw biomass in order to separate the pulp from the stone with the highest yield and lowest consumption of energy while preserving the integrity of the fractions. First, crude OP wasbeforehandsubjected to two successive grindings in a knife mill in order to reduce the size of the particles from the cm down to the mm.This obtained powdersfollowedthen two different dry fractionation routes: (A1) sorting by sieving and (A2) electrostatic separation. Considering the crumbly nature of crude OP another fractionation route has been investigated, *i.e.* (B) friction mode, using mild conditions of ball milling without preliminary grinding (Figure 1). In this latter process the coarse particles correspond to the stone-rich fraction (particle size higher than 1 mm), which resist to the low friction forces due to its richness in cellulose. In contrast, the fine particles of the pulp-rich fraction are more brittle and consequently crumbly under the influence of applied frictions, owing to its low cellulose content. Indeed, according to Ciolacu et al. [32], the crystallinity of the cellulose is at the origin of its resistance. The resulting fractions were compared to both the starting biomass (F0) and the reference fractions obtained by wet fractionation, in terms of color and biochemical composition in order to assess the efficiency of the applied dry fractionation routes.

Colorimetric parameters (L*, a*, and b*) varied according to the fraction and applied treatment. As previously observed for the wet fractionation, stone-rich fractions (dS1, dS2 and dS3) were globally clearer than F0, with higher L* and b* values and lower a* values. For stone-rich fractions, L* ranged from 51 to 56.7,

values of b* between 14.6 and 19.4, and a* of 5 and 8.6. On the opposite, pulp-rich fractions (dP1, dP2 and dP3) were darker (lower L* and b* values and higher a*) than F0, with L* values ranging from 29.1 to 44.9, b* around 12-13, and a* around 7-10 (Table 1). Considering the results of ΔE, it can be noted that the most contrasted pulp and stone-rich fractions in term of color were obtained by wet fractionation with values of 9.6 and 22.7 respectively. For the dry fractionation, the pulp powder produced by friction (dP3) showed the greatest difference in the color compared to F0 with ΔE of 14.8. On the other hand, the stone-rich fraction (dS3) showed the lowest difference with starting biomass compared to dS1 and dS2 fractions, with a value of 8.3 (Table 1). For the fractions obtained by sieving and electrostatic sorting, the obtained results did not allow to estimate the efficiency of separation at this stage of analysis.

The biochemical composition was also determined for different fractions. The analysis of the biochemical composition confirmedthus recorded for the wet process and also in accord with the literature [26] for OP composition. Indeed, the stone-rich fractions exhibited globallya higher cellulose-hemicellulose concentration, with about 16% of cellulose and 17% of hemicellulose in the fractions of stone, and 9-13% of cellulose and 7-11% of hemicellulose in the fractions of pulp. On the opposite, the pulp- rich fractions were richer in lignin (38-44%), proteins (5-10 %) and ashes (until 7 %) with regard to the stone-rich fractions which exhibitconcentrations of 34-39 %,1-3 % and 3-5 % for lignin, proteins and ashes respectively. The most contrasted pulp-stone couple differing from the other fractions was obtained by friction, with lignin, protein and ashes contents of 44.3, 10.9 and 7.6% respectively for dP3, and cellulose-hemicellulose concentrations exceeding 32% for dS3.

These results confirmed that the fractionation process significantly affects the characteristics of the produced powders. The differences in the biochemical composition are related to the origin of the plant tissues and their localization in the cell wall of the olive fruit. Thus, the intensity of the color depends on the ratio between the stone and the pulp tissues in each fraction and consequently on its composition, which are the product of the solicitation and forces of applied processes.

The best results were obtained by sorting using friction solicitations in a ball milling owing to the crumbly nature of crude olive pomace. Indeed, applying a low vibration force during a short time (15 Hz / 2 min) was sufficient to remove the superficial layers of the pulp tissue that adhered to the stone, without grinding and thus avoiding mixing it with the pulp. A subsequent sieving step was necessary to separate the two constituents. Though, these operating conditions was very efficient to isolate analmost pure pulp-fraction but were not sufficient to completely purify the stone. Indeed, the applied frequencies did not allow removing the final layer of pulp which is strongly adhered to the stone. This explains the ΔE and the composition values obtained for the fraction (dS3), which showed the highest rate of lignin (39%) and ashes (more than 5%) (Table 2), as compared to other stone-rich fractions obtained by dry and wet processes.

The composition values obtained for fractions dS3 and dP3 closed to those obtained for wS and wP suggested that the friction process allowed the separation of the pulp from the stone with a greatest efficiency. However,the higher value of ΔE indicated that the applied frequencies did not allow removing the thin final layer of pulp, which was strongly adhered to the stone.

It was shown that dP1, dS1, dP2 and dS2 fractions displayed intermediate results in terms of color and composition (Tables 1 and 2). The reason of poor separation in the case of sieving and electrostatic sorting may be related to the two successive grinding operations applied to the crude OP before fractionation. Indeed, the knife milling steps destroyed the initial organization of the tissues in the raw biomass, reduces the size of particles and consequently, promotes mixing between the two compartments of the fruit *i.e.* pulp and stone. This effect is even more accentuated with the electrostatic process due to an additional grinding step (impact milling) before sorting (Figure 1). In the case of electrostatic sorting, this effect could be hindered by making successive passages of the biomass in the electrostatic system, as suggested in the works of Chuetor et al. [17] for rice straw and by Basset et al. [20] for rapeseed oil cakes. It should be noted that given the range of particle sizes, it is very less probable that agglomeration/aggregation phenomena could occur because cohesion forces are very weak as compared to the weight of particles.

On the other hand, yields of production were also strongly affected by the selected processes. The highest yield was recorded for the friction fractionation with only 0.6% of losses, followed by electrostatic sorting and sieving with losses of 4% and 22.2% respectively, against 17.9% for the wet fractionation (Table 2). These results were directly related to the applied treatment and depend on the number of grinding and separation steps. Indeed, friction was the shortest route (Figure 1). For thetwo other dry fractionation routes, losses were due to the biomass that remained adhered to the equipment in the multiple stages of the process. In addition, the results showed that the stone-rich fraction represents the most important part of the olive pomace used in this study. The recorded yields of stone and pulp-rich fractions varied according to the applied process. Rates of 16 to 28%

were recorded for the pulp-rich fractions, and between 59-71% for the stone-rich fraction. As reported by Theriez and Boule (1970) [29], this is one of the characteristics of olive varieties intended for the production of oil.

Based on the obtained results of OP-base fractions and the literature data, it can admit that on the whole, both wet and dry fractionation processes applied in this study allow to separate the pulp and stone tissues but, at different degrees of purity. Fractionation routes were classified in terms of separation efficiency in the decreasing following order: in the first one the wet and dry fractionation by friction with a similar efficiency, followed by sieving sorting and electrostatic separation, which are less efficient than the first processes. Therefore, in the perspective to reduce the environmental impact of OP, it is clear that for an ecological and long-term solution that may be applied at industrial scale, dry fractionation by friction is more relevant option.

3.3. Potentiality of using OP-based fractions as raw resources for the production of fillers

In response to the growing environmental awareness, concepts of sustainable development and eco-friendly materials have become a necessity in order to preserve the environmental resources while improving economic activities [33]. In this context, the conversion of OP into reinforcing fillers for the production of biocomposites would allow transforming an abundant waste into anadded-value product. The thermal stability of the constituents is of great importance for biocomposites manufacturing, since it affects their processability and their physical and mechanical behaviors [13]. For this reason, the thermal stability of produced olive pomace-based powders was evaluated under both oxidative and inert conditions by thermal degradation analysis (TGA) in the temperature range from 20°C to

900°C. The degradation temperatures in oxidative conditions of each fraction are summarized in Table 3. The thermograms of weight loss (ATG) and derivative weight loss (DTG) of olive pomace powders obtained by wet process (wS, wP), and thus produced by dry process with sieving (dS1, dP1) compared to crude OP (F0), were illustrated in Figure 2.

During the thermal degradation in inert conditions, olive pomace base samples exhibited a two main steps decomposition (Figure 2a). The first step between 40 and 130 °C, corresponded to the evaporation of water entrapped into the molecular structure of each fraction particles. The moisture content of F0 is more than 6%, the produced samples are somewhat drier and exhibited moisture levels between 3 and 4% (Table 2). These results can be attributed to the drying of the powders, as a result of the heating of the apparatus with which they are in contact during the different steps of the process (grinding, friction and sieving). Furthermore, the fractions produced by wet process were dried at 50°C for 24h (Figure 1).

The second step starts round 150°C and extends to 500°C. In the first, the degradation of hemicellulose between 150 and 300°C followed by degradation of cellulose up to 400°C with a maximum around 343°C displayed by the stone-rich fraction (wS) due to its high cellulose content. As for lignin, its degradation takes place over a wide temperature range and extends to 500°C. The solid residue remaining after the thermal degradation of the main constituents of the biomass is estimated to be 19% for F0 and the fraction wS, and more than 22% for the wP fraction. These results were in perfect correlation with those obtained by Benavente and Fullana [34], who also studied the thermal stability under nitrogen of the olive pomace produced by the two-phase extraction system. These authors noted a thermal degradation of the hemicellulose between 220-315°C, and cellulose

thermal degradation ranges from 315 to 400 °C. They also recorded 20% of solid residue at the end of degradation. On the other hand, other authors also report that lignin is thermally more stable and its degradation slowly happens under a wide temperature range from 100 to 900°C [35].

During the thermal degradation in oxidative conditions, the DTG curves show three consecutive degradation steps of olive pomace based samples. As in inert conditions, the first step corresponded to water loss. Then, between 130 and around 200 °C, the olive pomace samples were relatively thermally stable (Figure 2b-c and Table 3), even if the degradation of lignin may have begun. Indeed, as has already been reported, lignin is known to start at relatively low temperatures, proceeding over a wide range of temperatures. The 130-200°C range can be thus considered as the optimal interval of temperatures for the process of olive pomace, as mentioned by Koutsomitopoulou et al.[13]. When the temperature increased beyond 200°C, *i.e.* once hemicellulose and then cellulose degradation has started, the degradation was very fast and gave rise to a characteristic sharp peak on the DTG curve. Hemicellulose is known to be the least thermally stable of lignocellulose components due to the presence of acetyl groups [36]. This is in agreement with already published results demonstrating that the decomposition of hemicellulose and cellulose occurred on average between 220 and 380°C [37]. The stone-rich powders prepared by washing (wS) or obtained by friction (dS3) exhibited the same degradation temperature (276°C, measured at the maximum rate of degradation), which corresponds to a 20% of mass loss. An increase of more than 10°C is noted as compared to the crude pomace (262°C) (Table 3). This is due totheir higher content in cellulose, about 32% for the stone-rich fractions against 29% for F0 (Table 2). Indeed, an increase in the thermal degradation temperature is known to be correlated to an increase in

cellulose composition. Yang et al. (2007)[36], report that cellulose is characterized by high thermal stability, seen is consisted of a long polymer of glucose without branches, its structure is in a good order and very strong. Koutsomitopoulou et al. [13] reported that surpassed 300 °C, hemicellulose is essentially converted into gasses and acetic acid. When the hemicellulose is already decomposed, the contribution on the increase in weight loss rate is attributed to the cellulose decomposition.

For the stone-rich fraction produced by wet process, the peaks associated respectively to the degradation of hemicellulose and cellulose are distinguished, unlike the stone fraction obtained by sieving (Figure 2 b2 and c2). This result indicates that the stone produced by washing is cleaner. In the case of sieving, the absence of these two peaks may be masked by the presence of the pulp, as it can be attributed to a loss of part of the stone in the pulp fraction after sieving. OP-based fractions exhibited peaks of maximum degradation at different values of temperature. From Table 3, the highest peaks are recorded for the fractions of the pulp obtained by wet fractionation (wP) and friction (dP3) with very close values at 286 and 288°C respectively, which also display the highest lignin content 44% (Table 2). The recorded results are close to the values recorded by Nabinejad et al. [38], which report a degradation of lignin from 230 to 500 °C. These results may also reveal a similar purity rate of these two fractions. The third step of degradation, recorded at temperatures above 400°C (Figure 2b-c), corresponds to the oxidation of the partially decomposed hemicellulose, cellulose and lignin [36].

Referring to the results shown in Table 3, it can too be noted that overall degradation temperatures of the stone-rich fractions (228-309°C) were higher than those recorded for the pulp-rich fractions (208-288°C) with variations depend of the content in lignocellulose of each of them (Table 2). An exception was observed for the fractions obtained by

electrostatic sorting (dS2 and dP2). The latter exhibit almost identical thermal degradation values ($T_{5\%}$, $T_{20\%}$ and T_{max}), certainly explained by their similar composition.

On the other hand, by comparing the values of the thermal degradation of the sample produced by dry process with those produced by wet process, it was noted that wS, wP, dS3 and dP3 fractions displayedalmost similar thermal degradation profile. These results confirm, the influence of the powder composition on its thermal stability, which depends on the nature and content tissues of each sample and therefore, depend on the applied fractionation treatment. The recorded values may be another indicator parameter of the fractions purity and thus, the efficiency of the separation. They demonstrate clearly that the least contrasted pulp-stone powders are produced by electrostatic sorting (similar thermal degradation temperatures) and the most contrasted correspond to the fractions obtained by washing in water followed by those produced by friction (different temperatures of degradation) (Table 3). So, this result allows confirming the possibility of substituting wet fractionation by dry fractionationwith friction milling mode.

Table 3.

It is worth noting that a weight loss of 5% at temperatures higher than 200°C was recorded both for the crude OP and all obtained fractions (Table 3), which corresponds to temperatures higher than the melting point (T_m) of maythermoplastic conventional polymers such as polyethylene (PE) (T_m=130-170°C), polypropylene (PP) (T_m=165°C) and polyvinyl chloride (PVC) (T_m=160-170°C), or biosourced polymers such as poly(3-hydroxybutyrate-co-3 hydroxyvalerate) (PHBV) (T_m=165°C), polylactic acid (PLA) (T_m=160-190°C). It makes OP-based fractionssufficiently thermally stable to be used as reinforcing fillers in several thermoplastic polymers for the production of biocomposites.

Properties of composite materials stronglydepend on the intensity of the affinity between the fiber and matrix. In general, the interphase in polymer matrix composites can be formed by four basic mechanisms that can vary in magnitude and occur simultaneously: molecular segregation, chemical bonding, van der Waals bonding and mechanical interlocking [39]. However, the main problem of natural fiber/polymer composites is the incompatibility between the hydrophilic nature of vegetal fibers that contrasts with the hydrophobic nature of most thermoplastic matrices, leading to poor Van der Waals interactions. According to Berthet et al. [40], the lignocellulosic biomass displays various physical and chemical structures, leading to a wide range of possible interactions with the polymer matrix. Considering a given filler with a given morphology and surface topography, the strength ofinteractions between the filler and the polymer, which can will be further called ‘‘affinity”, mainly depends on the surface energy of the constituents since the interaction mechanisms of polymer with fillers is an adsorption process [19]. Surface free energy is increasingly often used as a measure of adhesive properties [40].

This is why the estimation of the solid surface free energy of the constituents from contact angle measurements can be useful to predict a work of adhesion and thus tailor new polymer-based composites [42]. For that purpose, five reference liquids with different surface energies were used. First, the contact angle formed between a drop of each liquid on the surface of pellets of compressed particles was measured. Then, the surface free energy (γ) (polar (γ^p) and dispersive (γ^d) components) were estimated from the Owens-Wendt model [23] for all samples (Table 4). The surface energy values recorded for all obtained fractions ranged from 29 to 36 $mJ.m^{-2}$. This range of valued is in agreement with those of Berthet et al. [39], who reported thatthe surface energy of lignocellulosic fibers varies from 30 to 50 $mJ.m^{-2}$ depending on botanical origin. It can be observed that the

pulp/stone couples produced by either the electrostatic or sieving sorting showed similar γ values, *i.e.* 35 $mJ.m^{-2}$ for dS1 and dP1 and 32 $mJ.m^{-2}$ for dS2 and dP2 (Table 4). On the contrary, the pulp/stone couples produced by either wet fractionation or dry friction recorded slightly but significantly different γ values, *i.e.* 30.6 $mJ.m^{-2}$ and 32.4 $mJ.m^{-2}$for wS and wP against 34.5 and 29.9 for dS3 and dP3 respectively (Table 4). It can also be underlined that these two last fractionation processes produced the most contrasted powders in terms of polarity, as revealed by polar component values and contact angles recorded with water. The highest the γ^p value and/or the lowest the contact angle with water, which implies the highest the polarity. For example, γ^p were 14.1 and 0.3 $mJ.m^{-2}$ for wS and wP, and 1.7 and 0.8 $mJ.m^{-2}$ for dS3 and dP3 respectively, while contact angle with water were 75.2 and 96.4° for wS and wP, and 82.4 and 93.7° for dS3 and dP3 (Table 4). These results clearly demonstrated the polar character of stone-rich fractions and apolar character of pulp-rich fractions, which is dependent on their chemical compositions and hence, on the applied fractionation process. The polar character of the stone is due to its high content in cellulose and hemicellulose as compared to the pulp, which contains higher levels of lignin (Table 2) and also to its heterogeneous and porous structureallowing the penetration of water [12]. The apolar character of pulp-rich fractions is attributed to the low amount of cellulose and hemicellulosesand also to the presence of a high level of lignin, whose main function is to bring rigidity and impermeability to water for the plant [43].

It is worth noting that the stone-rich fraction obtained by washing in water was the most polar of all the fractions, with the highest γ^p value (14.1 $mJ.m^{-2}$) as compared to all the other stone-rich fractions which presented values between 1.4 and 1.7 $mJ.m^{-2}$ (Table 4).

This certainly justifies the necessity of applying post-treatments in order to modify its surface properties and thus improve its affinity with apolar polymer matrices [2, 4, 11, 12].

Table 4.

Predicted values of adhesion work indicated that the affinity between the filler and the polymer matrix depends on the nature of each constituent (Table 5). Adhesion work was predicted to be greater with PP and PLA polymers for all OP-based fractions (around 56-78 $mJ.m^{-2}$), these two polymers exhibiting the highest polarity (γ^p of 2 and 11 $mJ.m^{-2}$ respectively). On the opposite, adhesion work was predicted to be less important in the case of PE and PHBV polymers (between 46 and 65 $mJ.m^{-2}$) that corresponded to the less polar polymers under consideration (γ^p of 0 and 0.5 $mJ.m^{-2}$ respectively). It is worth noting that OP-based fractions expressed different affinities towards a given polymer. For all polymers, the highest values of work of adhesion were predicted for dS3, leading to conclude that stone-rich fractions obtained by dry fractionation should be preferred to improve the interfacial adhesion with these kinds of polymer. It is interesting to note that a wet fractionation process is clearly in detriment of a high work of adhesion, especially in highly apolar polymer matrices such as PE and PHBV. In the case of apolar matrices such as PE and PHBV, the difference of behavior between pulp-rich and stone-rich fractions was clearly reduced. Finally, not a so marked difference was observed between F0 and dS3. Based on these results, it is supposed that a range of biocomposites could be developed without adding coupling agents nor modifying the surface of fillers by appropriately choosing the filler/matrix couple. However, to date, no work does report the use of pulp-rich fractions nor F0 as raw ressources for the production of reinforcing fillers

in biocomposites. It would therefore be interesting in the future to also exploit these two latter fractions in this field of application.

Table 5.

The production of a range of pulp-rich and stone-rich fractions by dry fractionation can be useful in other fields of applications than biocomposites. Concerning the pulp-rich fractions, given their high content of chlorophyll pigment demonstrated by colorimetric analyzes, they can present a natural source for the extraction of dyes which could be used as an additive in either agro-food industry or textile industry. This last application already exists for olive mill wastewater but not yet for OP [44]. Regarding the potential application in food industry, the additional advantage of chlorophylls is their antioxidant propertiesthat give the ability to reduce the oxidative damages associated to many human diseases [45].

Concerning the stone-rich fractions, one valuable use could be their incorporation in cosmetic formulations as an exfoliating agent [46]. Additionally, given thehigh amounts of cellulose and hemicellulose present in stone-rich fractions (Table 2), they may act as functional ingredients in cosmetic formulations, by improving physical and structural properties of hydration, oil holding capacity, emulsion and oxidative stability, viscosity, texture, sensory characteristics, and shelf-life of products [47]. These fractions could also find applications in animal feeding. Indeed, numerous experiments have reported a "poor digestive use" of olive pomace when incorporated into animal feed rations due to its high content in lignin that may reduce the activity of the rumen flora [30]. Thus, the incorporation of pulp-poor fractions in animal feeding instead of crude OP could be interesting. Finally, the use of stone-rich fractions instead of crude OP could be proposed in the case of bioconversion processes for the production of biofuels or for composting.

Indeed, the importance of lignin elimination by pre-treatments of the lignocellulosic biomass has been frequently suggested in these fields of applications due to its low decomposition rate [45].

4. Conclusion

Olive pomace is a lignocellulosic biomass displaying a complex composition, characterized by a heterogeneous distribution of its constituents through the different tissues of the fruit. With the prospect of a complete exploitation of this olive oil by-product, a treatment allowing the separation of the pulp from the stone while maintaining the integrity of components contained in the biomass constitutes the first step of its recycling and takes a major importance for potential valorizations. In the present work, different dry fractionation routes have been successfully investigated to produce contrasted and pure stone-rich and pulp-rich fractions from crude olive pomace. Results revealed that the separation of the pulp from the stone using friction solicitations in a ball mill operating in very mild conditions (only 2 min at a frequency of 15 Hz) on a raw sample was the most efficient dry fractionation route. This highlights that it was not necessary to finely grind samples to separate the stone-rich fraction from the pulp-rich fraction. Obtained powders displayed similar biochemical composition, surface free energy, color and thermal stability as those obtained by wet fractionation. It was also demonstrated that dry fractionation allowed achieving a higher total yield than wet fractionation (99.4% against only 82.1% in the case of the wet fractionation followed in the present study). Finally, dry fractionation did not require the use of water while a water:biomass ratio of 5:1 was required in the case of wet fractionation. All these results support the conclusion that dry fractionation is a very sustainable process to efficiently separate the stone-rich from the pulp-rich fraction.

Results demonstrated that it would be advantageous to exploit the stone-rich fraction, but also the crude OP and the pulp-rich fraction as raw ressources for the production of fillers to develop a wide range of biocomposites for targeted applications. It is worth noting that further grinding steps would be necessary to obtain fillers with controlled sizes. To conclude, this work opens a new and promising route for converting this agro-food residue into added value products either as fillers or other applications, through a clean technology for a better eco-friendly valorization.

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Figure Captions.

Figure 1. Fractionation process of crude olive pomace investigated to obtain stone (S) and pulp (P) rich fractions.

Figure 2. TGA (a1, b1 and c1) and DTG (a2, b2 and c2) curves of stone and pulp rich-fractionsproduced either by wet fractionation (a1 and b1 under nitrogen; a2 and b2 under air) or dry fractionation with sieving (a3 and b3 under air).

Tables

Table 1. Color parameters (L*, a*, b* and ΔE) of OP-based fractions

	L*	a*	b*	Δ *E*
F0	43.6±0.2	9.4±0.0	15.7±0.1	-
wS	65.8±0.9	5.3±0.1	18.6±0.1	22.7±0.9
wP	34.9±0.6	9.2±0.0	11.6±0.1	9.6±0.6
dS1	55.4±0.7	8.0±0.0	17.8±0.1	12.1±0.7
dP1	37.8±0.0	9.7±0.0	13.2±0.0	6.3±0.1
dS2	56.7±1.5	5.5±0.0	14.6±0.0	13.7±1.5
dP2	44.9±1.1	7.3±0.0	12.2±0.3	4.3±0.1
dS3	51.0±0.5	8.6±0.0	19.4±0.2	8.3±0.6
dP3	29.1±0.8	9.5±0.1	13.0±0.3	14.8±0.9

Table 2. Biochemical composition (dry basis) of different olive pomace fractions produced by wet and dry process

	F0	Wet fractionation		Dry fractionation					
		wS	wP	dS1	dP1	dS2	dP2	dS3	dP3
Yield (%)	100	65.5	16.6	59.9	17.9	71.2	24.8	70.6	28.8
Humidity (%)	6.2±1.5	4.1±0.0	4.3±0.0	4.6±0.0	4.7±0.0	4.9±2.0	3.9±0.0	3.5±0.0	4.2±0.1
Ashes (%)	3.5±1.3	1.9±0.1	7.2±0.4	4.7±0.4	6.6±0.0	3.9±1.8	6.1±0.1	5.5±0.0	7.6±0.1
Cellulose (%)	14.8±1.3	14.2±1.0	11.5±0.4	15.1±1.3	13.0±1.0	15.7±1.1	10.2±1.6	15.7±0.8	9.2±0.0
Hemicellulose(%)	14.7±1.3	18.1±0.5	6.9±0.3	16.2±1.2	11.2±2.4	15.4±0.7	11.5±1.7	17.1±0.5	6.9±0.1
Lignin (%)	37.8±2.1	37.1±2.6	43.5±3.5	34.1±2.9	38.9 ±3.2	35.7±1.4	41.5±5.1	39.2±3.5	44.3±4.4
Glucose (%)	16.4±1.5	15.8±1.1	12.7±0.4	16.8±1.5	14.5±1.1	17.4±1.3	11.4±1.8	17.4±0.9	10.2±0.1
Xylose (%)	16.6±1.4	20.5±0.5	7.9±0.3	18.3±1.4	11.5±1.0	17.4±0.8	13.0±2.0	19.4±0.6	7.8±0.1
Proteins (%)	4.5	0.4	12.4	1.6	7.8	3.0	5.6	1.1	10.9
C (%)	47.91	47.10	49.82	47.20	48.64	48.12	48.95	46.98	50.14
H (%)	6.11	5.91	6.33	6.03	6.22	6.42	6.48	6.33	6.77
N (%)	0.72	0.07	1.98	0.25	1.25	0.48	0.90	0.18	1.75

Table 3. Degradation temperatures (°C) of olive pomace-based fractions (tests recorded under air atmosphere at a heating rate of 10 °C.min^{-1}). $T_{5\%}$, $T_{20\%}$ and T_{max} correspond to the temperatures of 5%, 20% and maximum mass loss rates of dry matter.

	$T_{5\%}$	$T_{20\%}$	T_{max}
F0	222±2	262±1	274±0
wS	250±0	276±1	309±1
wP	208±1	254±1	286±2
dS1	238±0	265±1	271±1
dP1	211±0	257±0	277±0
dS2	228±5	270±1	279±0
dP2	226±2	270±1	281±1
dS3	247±1	277±1	278±1
dP3	217±1	259±2	288±3

Table 4: Contact angle measurements and solid surface free energy of different fractions (γ: solid surface free energy, γ^d: dispersive component of the solid surface free energy, γ^p polar component of the solid surface free energy, *nd*: not determined)

	Contact angle ɵ (°)					Surface energy (mJ.m^{-2})		
	Water	**Ethylene glycol**	**Diiodomethane**	**Formamide**	**Glycerol**	**γ**	**γ^p**	**γ^d**
F0	91.1 ± 3.6	71.9 ± 3.6	48.1 ± 1.8	58.7 ± 2.3	90.78 ± 0.6	33	0.8	32.2
wS	75.2 ± 2.0	53.7 ± 4.9	nd	nd	nd	30.6	14.1	16.4
wP	96.4 ± 2.4	68.8 ± 5.3	52.8 ± 4.4	61.9 ± 0.3	94.8 ± 1.5	32.4	0.3	32
dS1	83.4 ± 2.9	69.4 ± 2.3	40.7 ± 4.5	47.6 ± 0.5	92.3 ± 1.1	35.5	1.5	33.9
dP1	95.4 ± 4.0	68.1 ± 2.1	44.1 ± 1.6	62.5 ± 2.5	91.8 ± 3.6	35.5	0.2	35.3
dS2	86.3 ± 3.3	66.2 ± 5.5	45.2 ± 3.4	62.8 ± 1.6	95.1 ± 6.1	32.2	1.4	30.8
dP2	87.2 ± 3.7	67.2 ± 1.3	41.6 ± 3.9	66.8 ± 3.0	94.3 ± 1.6	32.5	1.1	31.4
dS3	82.4 ± 3.3	63.9 ± 1.8	42.3 ± 1.7	48.7 ± 1.2	99.2 ± 1.6	34.5	1.7	32.8
dP3	93.7 ± 3.8	71.3 ± 1.2	56.7 ± 0.6	59.2 ± 1.8	97.6 ± 2.9	29.9	0.8	29.2

Table 5. Polar component (γ^p) and dispersive component (γ^d) of some polymer matrices and the predicted work of adhesion (W) between thesepolymer matrices and the olive pomace-based fractions produced by wet process and dry process with friction.

	Surface energy of some polymer matrices ($mJ.m^{-2}$)		**Work of adhesion (W) ($mJ.m^{-2}$)**				
	γ^p	**γ^d**	**F0**	**wS**	**wP**	**dS3**	**dP3**
PE	0[(a)]	33[(a)]	65.2	46.5	65.0	65.8	62.1
PP	2[(a)]	32[(a)]	66.7	56.4	65.5	68.5	63.7
PLA	11[(a)]	37[(a)]	75.0	74.2	72.5	78.3	71.7
PHBV	0.5[(a)]	27[(a)]	60.2	47.4	59.6	61.4	57.4

[(a)]: data from [39]

Figure 1.

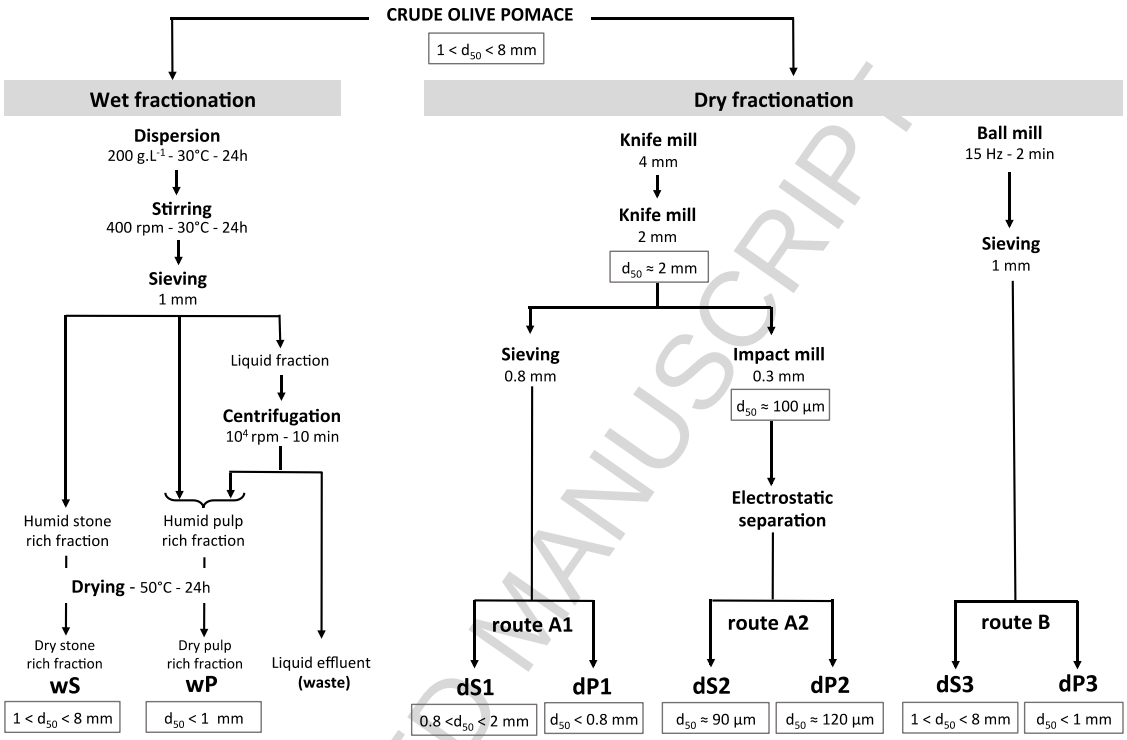
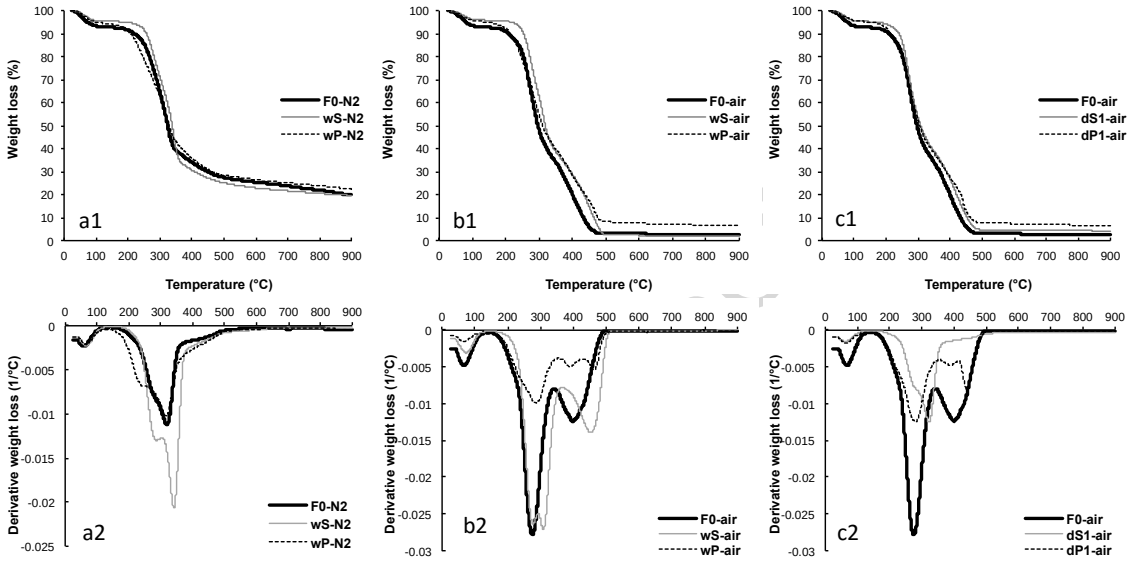
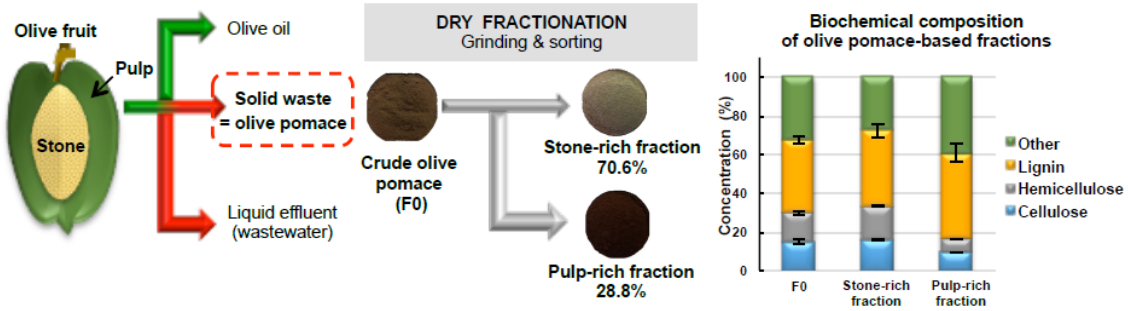


Figure 2.





Graphical abstract

Highlights

- Olive pomace is currently exclusively treated using wet and polluting processes
- Fractionation processes are chosen based on the heterogeneity of the crude biomass
- Pulp-rich and stone-rich fractions can be produced by dry fractionation
- Dry fractionation is a promising technology for substituting wet pre-treatments
- A high purity of the produced fractions results in contrasted characteristics