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Olive stone an attractive source of bioactive and valuable compounds

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Abstract

The olive stone and seed are an important byproduct generated in the olive oil extraction and pitted table olive industries. As a lignocellulosic material, the hemicellulose, cellulose and lignin are the main components of olive stone as wells as protein, fat, phenols, free sugars and poliols composition. The main use of this biomass is as combustion to produce electric energy or heat. Other uses such as activated carbon, furfural production, plastic filled, abrasive and cosmetic or other potential uses such as biosorbent, animal feed or resin formation have been cited. In this article, an overview of the characterization and main uses of olive stone and seed are described for the first time. Also, this review discusses the potential use of this material based on each component. In this way, a new approach to the olive stone and seed by pretreating with a steam explosion followed by chemical fractionation is described.

1. Introduction

Olive oil extraction and olive table represent an economic and social industrial activity that is highly relevant in the Mediterranean countries. The extraction process has quite a large environmental impact due to the production of highly polluted wastewater and/or solid residue, depending on the olive oil extraction or table olive process. The solid wastes generated in the olive oil extraction are alperujo, from the two-phase system, and orujo from the three-phase system. In the olive oil industry only the olive stone without seed (stone) can be recovered by filtration of solid waste. From the pitted table olive industry, the whole olive stone (stone and seed) is recovered by separation of the pulp. In the 2005/2006 season, the world olive oil and table olive production were estimated to be 2.58 and 1.73 million tons/year, respectively (International Olive Oil Council, 2007). Spain, the principal world producer, produced approximately 30 thousand tons/year and 400 thousand tons/year of stone from table olives and olive oil industries, respectively. Therefore, the stone and whole stone comprise the majority and more commercial interest of the waste produced in the olive fruit industrial sector. Olive stone is a lignocellulosic material, with hemicellulose, cellulose and lignin as main components. Many current studies aim to develop methods of recovering the lignocellulosic material or biomass in order to produce solid, liquid or gas biofuel. Therefore, widespread olive stone use is directed towards its use as a solid fuel or its derivatives fuel as renewable source of energy. Despite the environmental benefits of using this biomass as fuel, some problems remain, such as air pollution (carbon monoxide, nitrogen oxides, and particulates such as soot and ash produced by combustion). The whole olive stone is a rich source of valuable components due its chemicals and physical properties in addition to its combustion heat. There are many ways for its utilization, one of which is fractionation, a method for obtaining each component to increase the value of the stone.

A large number of research articles have been published dealing with the chemical composition of olives and olive oil. However, only a few studies have been dedicated to analyzing the components and uses of the olive stone. The aim of this article is to review the characterization and current, past or potential uses of the whole olive stone. The potential uses center on the fractionation method as a future tool to obtain all of the stone's components. The components isolated could then be utilized in old and new uses. Steam explosion appears to be a promising pretreatment for converting low-value biomass (lignocellulosic material) into commercially useful products (Fernández-Bolaños et al., 2001). To combine this pretreatment followed by a fractionation could facilitate the future approach of isolating olive whole stone components.

2. Characterization

The olive fruit can structurally be separated into the following three parts: (1) the skin, called epicarp (1.0–3.0% of the drupe weight), which contains the chlorophyll, carotenoids and anthocyanins that account for the color; (2) the pulp or flesh, called mesocarp (70–80% of the whole fruit), is the major part of the olive and is the reserve supply of all the constituents; (3) and the stone, called the woody endocarp (18–22% of the olive weight), which contains the seed (Bianchi, 2003).

The whole stone consists of the wood shell (stone) and the seed. The stone is obtained by filtration of byproducts from the olive oil extraction, and the whole stone is obtained from the olive table industry.

The chemical composition of olive seed husks and whole stones have been studied (Table 1). Cellulose, hemicellulose and lignin are the main components of this lignocellulosic biomass, although fat and protein are present in considerable quantities.

2.1. Fat

The olive seed contains a considerable amount of oil (22–27% of the weight), 1% of which remains on the seed husk. Percentage of CHCl3–EtOH extractable compounds of stone and seed are showed in Table 2. Alkanes present are a mixture of C23–C33, with C25, C27 and C29 being the main component (Bianchi, 2003). Seed oil is rich in total polyunsaturated acids (PUFA) because of high contents of linoleic acid (Ranalli et al., 2002a), higher than its wild variety

(Eromosele and Eromosele, 2002). 1,2-Dilinoleoyl-3-oleoyl-glycerol (LLO) is the major triacylglycerol in seed, but not in olive oil, and the triacylglycerol species acylated with the linoleoyl chain are also more abundant in seed oil (Ranalli et al., 2002a). Seed oil is poor in total aliphatic long-chain and triterpene alcohols (Ranalli et al., 2002b).

2.2. Free sugars and poliols

The reducing power of the extracts of the seed has been attributed to the presence of glucose. Studies about sugars in the olive stone began with paper chromatography and gas–liquid chromatography (Rivas, 1983). Sucrose, glucose, fructose, arabinose, xilose, mannitol and myoinositol were determined.

Fernández-Bolaños et al., 1983 studied oligosaccharides in the olive seed and described the extraction and characterization of trisaccharide planteose by chromatography system.

2.3. Proteins in seed

In the seed, the level of protein is higher than the rest of the olive fruit. Protein content is an important part of the nutritional value of the olive seed. Protein extraction was studied using assays of solubility and precipitation, with concentrates reaching 75% proteins by weight (Fernández, 1960a,b,c,d). Furthermore, the amino acid composition was also determined by the same author by paper electrophoresis. All essential amino acid were present.

Recent studies have demonstrated that the most abundant proteins in the mature olive seeds belong to the 11S proteins family (storage protein), accounting for approximately 70% of the total seed proteins (Alché et al., 2006). In this work, the basic or acid character, solubility and localization of 11S proteins was verified by two-dimensional polyacrylamide gel electrophoresis, transmission electron microscopy and solubility experiments.

The same authors have demonstrated that the amino acid content in the alperujo is similar to that which exists in the mature olive seeds (Jime´nez et al., 2005); therefore, the seed protein content remains in the alperujo after the olive oil extraction process.

The high level of proteins verifies the seed as a good nutritional complement for the animal food formulation (Martín et al., 2003).

2.4. Phenols

The olive fruits contain a wide variety of phenolic compounds that are potent antioxidants and play an important role in the chemical, organoleptic and nutritional properties of the virgin olive oil and the table olives. The positive effect of olives and olive-derived products consumption on human health is well documented by a large number of epidemiological studies (Owen et al., 2000; Visioli et al., 2000, 1999; De la Puerta et al., 1999; Auroma et al., 1998). Their presence both in olive stone and seed are also significant.

Three glucosides including salidroside (tirosol–glucose), nüzhenide (glucose–elenolic acid–glucose–tyrosol) and nüzhenide-oleoside, and two secoroiridoid glucosides with tirosol, elenolic acid and glucose moieties with differences in sequence were isolated from the olive seeds (Maestro-Durán et al., 1994). The isolated glucosides were similar to the presents in other oleaceae and it is supposed that they are involved in the germination of the seed.

Nüzhenide is found only in the seed, as a predominant phenol, and verbascoside only appears in significant quantities in the seed and pulp (Table 3) (Ryan et al., 2003). Tyrosol, hydroxytyrosol, oleuropein and diadehydic form of decarboxymethyl oleuropein (3,4 DHFEA-EDA) were present in all the investigated olive tissues including the pulp, leaves, seed and stone. Tyrosol and hydroxytyrosol were identified for the first time in the olive stone by Fernández-Bolaños et al. (1998), and its presence as a structural component was suggested.

2.5. Fiber and polysaccharides

Fiber is the one component that determines the texture and digestibility in the olive fruit. In the olive stone and seed, the fiber is the major component. Despite the abundance of methods to determine fiber content, not all of them are appropriate for the olive, due to its high oil and polyphenols contents (Guille´n et al., 1992). The composition of the whole olive stone (stone and seed) has been investigated for several varieties of olive fruit using a neutral detergent fiber method (NDF) (Heredia et al., 1987). The fiber fraction ranged for different varieties and shows a certain variability in stone and high variability in seed (Table 4). The main components are cellulose in the stone, and hemicellulose in the seed.

Cell wall polysaccharides of olive stone were isolated and characterized by Coimbra et al. (1995). This dry material contains 62% of the total carbohydrates, which are rich in xylose and glucose, resulting from hemicellulose and cellulose, respectively. After exhaustive delignification treatment, the extraction of polysaccharides from cell wall was possible, with glucuronoxylans as the major non-cellulosic polysaccharides present. Xylo-oligosaccharides were obtained by partial acid hydrolysis and identified by MALDI-MS (Reis et al., 2002). The spectra showed that

Xylo-oligosaccharides from olive stone were predominantly constituted by XylnGlcA and XynGlcA2 oligosaccharides (Xyl = xylopyranose, GlcA = glucuronic acid).

3. Utilization of olive stone and seed

With an environmental and economic point of view, this byproduct can be considered to be a renewable energy source. In addition, further high added-value compounds may be obtained that may have other uses depending on specific chemical and physical properties. Table 5 outlines the most important uses of the whole stone or olive stone and other contributing factor. Each of these uses will be explained in further detail later in the text.

3.1. Real uses of olive stone and seed

In this paragraph, the current uses of olive stones and seeds will be described (Table 5).

3.1.1. Combustion of stone and whole stone

Nowadays, it is necessary to ensure that new types of biomass fuel have minimal environmental impact and cover new energy demands. From this viewpoint, the olive stone is an interesting fuel due its low N and S percentages (González et al., 2003). This fact minimizes the NOx and SO2 emissions that are found in acid rain and contribute to the destruction of the ozone layer. It can be mixed with the vegetation water concentrated as an efficient fuel to reduce the environmental impact of this waste (Vitolo et al., 1999). The heat of combustion of stone is 4.075 Kcal Kg1 (Durán, 1985), which is near the carbohydrate heat of combustion (4.10 Kcal Kg1) and higher than dry alperujo. The heating power of stone is used for power generation in the electricity sector and for space heating in residential and commercial buildings.

Stone is used as a biomass for power generation in combustion-turbine cycle, gas turbine-based solution or hybrid solutions. Gas turbine-based solutions are the most often used system in byproducts, with an average price as biomass in Europe of 0.05 €/Kg (European Bioenergy, 2003). A more detailed study regarding the uses of thermally treated olive stone was realized by Arvanitoyannis et al. (2007). Thermal processes such as pyrolysis, combustion and gasification with its products, were clearly described as real uses of this byproduct.

3.1.2. Activated carbon from olive stone

The use of activated carbons for adsorption is of great interest and has expanded into many fields as diverse as food, chemical, petroleum, nuclear, mining, or pharmaceutical industries (Stavropoulos and Zabaniotou, 2005; El-Sheikh et al., 2004). Activated carbon is a microporous carbonaceous material with high surface area materials due to its high degree of porosity that depends on activation system. Several studies were performed to determine the effects of the activation process with chemicals and physical techniques from olive stone (Stavropoulos and Zabaniotou, 2005; El-Sheikh et al., 2004; Ubago-Pe´rez et al., 2006; Molina-Sabio et al., 2006; Sa´nchez et al., 2006; Martınez et al., 2005) and to improve its adsorption properties.

Activated carbon from olive stone is used extensively for the removal of unwanted colors, as dyes (Najar-Souissi et al., 2005), odors, tastes or contaminants such as arsenic (Budinova et al., 2006) or aluminum (Ghazy et al., 2006).

3.1.3. Liquid and gas products from olive stone pyrolysis

In spite of the current use of pyrolysis in the activation carbon process, it can also be useful to obtain interesting liquid and gas products. For example, a product called Bio-oil is useful as a fuel and similar to petroleum due to its n-pentane fraction (Pütün et al., 2005).

3.1.4. Olive seed oil

During the extraction of olive oil, part of the seed oil is included. There are systems that extract olive oil without the olive stone or seed (Gurguc, 2006), several of them also recover the seed oil after its release and extract its oil (Kourtzis, 1999; Artacho, 1999). The stone removal seems to improve the organoleptic quality and oxidative stability of the olive oil, although the olive seed contributes to the olive oil aroma during the virgin olive oil extraction (Luaces et al., 2003). However, the major source of seed is the whole stone produced from the pitted table olive industry. The seed is released by breaking the whole stone. From 100 kg of fresh olives (22 kg of olive stone contain approximately 4 kg of seeds), it is possible to obtain 2 kg of olive seed oil as well as 2 kg of flour (Artacho, 1999).

Comparative analysis among olive oil and olive seed oil were carried out (Ranalli et al., 2002a,b). The seed oil was richer in individual sterols (2.3-fold higher), mainly in bsitosterol, which has important effects on absorption of cholesterol and bile acid (Hakala et al., 1997). It was also richer in total polyunsaturated fatty acids (PUFA), due its higher contents of linoleic acid. On the other hand, it had less triterpene dialchols (3.5-fold lower) than the olive fruit.

3.1.5. Furfural production

The worldwide furfural production is approximately 300.000 Mt/yr. Furfural has many industrial uses as a solvent or as a base for synthesizing its derived solvent. Furfural is produced by dehydrating pentoses present in lignocellulosic material. Furfural is produced by acid hydrolysis of xylose, the main pentose present in this kind of material. There are several processes to obtain furfural, some of which present the olive stone as a lignocellulosic biomass from which 135 kg/t of furfural can be produced (Montané et al., 2001). Even studies using the hydrolyzed olive stone from the production of furfural to obtain a humic fertilizer were performed (Riera et al., 1990).

3.1.6. Olive stone as a plastic filled

In order to minimize the negative effects on the environment of certain plastic structures, promoting clean technologies and recycled products, the use of olive stone as a plastic filler was studied. The preparation of composite samples by mixing olive stone and polypropylene to produce a new thermoplastic polymer was performed (Siracusa et al., 2001). In this study, the use of dehydrated stone and a control range of temperatures (180–200 °C) were necessary to avoid the production of volatile compounds or weight loss due to humidity.

There are industrial films that have developed a homogeneous polymer compound incorporating olive stone as a natural and biodegradable raw material (Natraplast, 2007; Flextron, 2007). Products such as panels, pipes, tubes or profiles amongst others, have been elaborated by extrusion and injection technologies (Cristofaro, 1997).

3.1.7. Olive stone as an abrasive

The use of olive stone protects worker health and the environment and is not aggressive with the surface preparation. Unlike other abrasives, it does not produce contamination through its residues. These qualities and its resistance to rupture and deformation are the main reasons for its abrasive use in a wide industrial sector (Dawson, 2006).

3.1.8. Olive stone in cosmetic

Due to exfoliation qualities of olive stone, there are many market products that include this material as a component to aid in skin exfoliation (Cosmoliva, 2007; Korres, 2007). These products use an olive stone granules combine with hydrating components, and even heating agent (Mohammadi et al., 2005).

3.2. Potential use of olive stone

This paragraph describes studies on the possible uses of olive stone and seed, including different research levels.

3.2.1. Olive stone as a metal biosorbent

Olive stone may be used as a sorbent solid for heavy metal ion removal from aqueous effluents. Studies to determinate the effect of some parameters on the sorption of Cd(II) (Bla´zquez et al., 2005; De Castro et al., 2004; Calero et al., 2006; Fiol et al., 2006) and other ions including Pb(II), Ni(II) and Cu(II) have been investigated (Fiol et al., 2006). Results showed that the smaller the particles size (0.355 and 0.250 mm) and higher temperature (80 °C) improved the metal ion sorption and minimized the time of contact, reaching values of 9.72 mg/g of dry olive stone and 20 min in the case of cadmium (Calero et al., 2006).

3.2.2. Olive stone as a dietary animal supplementation

The prevention of digestive troubles in growing rabbits has also been studied (Carraro et al., 2005). The effect of this low-digestive fiber source was not negative, but no differences were detected between assays performed with and without olive stone.

3.2.3. Obtain of phenol–formaldehyde resins

Olive stone can be used as a source of phenols for phenol–formaldehyde resins after treatment in a liquefaction reactor (Tejeda-Ricardez et al., 2003). It is the thermosetting phenolic resin manufactured that can be used in moldings for electrical and mechanical parts, due its properties (low cost, strength and chemical resistance).

After pyrolysis treatment of novolac-resin and olive stone mixing under high temperatures, the final material can be used for electrochemical applications due its optical properties (Theodoropoulou et al., 2004).

4. Fractionation

The fractionation interest is due to the presence of attractive components such as cellulose, hemicellulose and lignin, usually from lignocelullosic material, in the whole stone. The possible alternative to combustion could be fractionation to obtain its components. Physical and chemical barriers impede the direct fractionation. Thus, drastic pretreatment conditions are necessary. This fact is supported by a large number of papers that have studied the need of steam explosion as a pretreatment of several lignocellulosic materials to obtain a liquid source of fermentable glucose for the production of bioethanol (Tabka et al., 2006; Ballesteros et al., 2004; Varga et al., 2004; Tucker et al., 2003). In fact, steam explosion was the only pretreatment useful to prepare this raw lignocellulosic to an effective fractionation (Fernández-Bolaños et al., 1999). This system combines physical and chemical methods, using high-pressure steaming and temperatures (10–40 kg/cm2 and 160–240 °C), during a short period of time (2–10 min) with a rapid decompression or explosion. As a consequence, autohydrolysis occurs. Depending on the conditions used, there is a depolymerization of polysaccharides (mainly of hemicelluloses) and a breaking of the lignin-carbohydrate bonds, resulting in the solubilization of lignin fragments of low molecular weight, giving rise to sugars and phenolic compounds that are soluble in water. Thus, the steam explosion system is the most successful and real option for fractionating olive stone into its three major components: hemicellulose, cellulose and lignin. Currently, this steam explosion reactor (Stake Technology) is used by the fuel industry to obtain the above-mentioned bioethanol (Sunopta, 2007).

In this work, whole olive stone (stone and seed) and olive stone were treated by steam explosion reactor after a previous impregnation with or without a dilute solution of strong mineral acid to improve the efficiency. Next, the hemicellulose was solubilized, leaving the lignin and cellulose insoluble material. The major part of hemicellulose and a small part of lignin becomes soluble in the aqueous phase. The fractionation (Fig. 1) begins with an aqueous alkaline-extraction of the insoluble material in order to remove the depolymerized lignin, resulting in a cellulose fraction. The soluble lignin was precipitated by acidification to obtain the lignin fraction (light brown powder). For example, under medium treatment conditions of whole stone or stone, the percentage values of the different fraction recoveries are shown in Table 6. The acid impregnation had an effect on the whole stone. The water-soluble substances were primarily phenols and hemicellulose, and the insoluble fraction after alkali-extraction consisted of cellulose and the remaining hemicellulose.

This study successfully separated and characterized three fractions (Fernández-Bolaños et al., 2001). The possible uses of each fraction are described later in the text.

4.1. Water soluble substances

After phenol extraction, the soluble carbohydrates from hemicellulose were the main components (25–55%), and protein was also present in whole stone. This fraction could be used in a variety of ways including animal food, as a source of unicellular proteins, to obtain furfural, xylitol and low molecular weight oligosaccharides or as a source of fermentable sugar to obtain ethanol, acetone or butanol. In this fraction, the main phenols present (hydroxytyrosol and tyrosol) are used in the industry as a natural antioxidant (Fernández-Bolaños et al., 1998).

4.2. Water insoluble substances

The water insoluble fraction consisted of cellulose and partially degraded lignin with a slight insoluble hemicellulose residual. The lignin recovered by alkaline-extraction followed by acid precipitation from steam exploded olive stones is a de-etherified lignin with an extensive cleavage of the b-aryl ether linkage (Fernández-Bolaños et al. 1999). This polymeric lignin could be used as fuel or as prepolymers in engineering materials, resins (phenol–formaldehyde) or as an adhesive resin. Also, could be attractive for therapeutic uses, which have been investigated through its anti-inflammatory effect (Kim et al., 2006; Suzuki et al., 2002; Sorimachi et al., 2002) and antiviral activity in humans (Sakagami et al., 2005; Yamamoto et al., 1997) or avians (positive action on threat of AVIAN flu). From the lignin monomer, it is possible to obtain vanillin, which has a wide range of application in food, chemical and pharmacy industry, or antioxidant compounds.

Cellulose was the major component in the insoluble alkali-extraction from insoluble water fraction, in which the rest of lignin (30–40% of lignin) was present. The steam explosion system is effective in making the recalcitrant cellulose more accessible to an enzymatic post-hydrolysis in order to release glucose as an alcoholic fermentable sugar. This post-hydrolysis was carried out enzymatically using commercial cellulase. The remaining lignin was limited to the enzymatic action and only when it was treated with sodium chlorite a complete saccharification was obtained. The best sugar yield obtained by hydrolysis of cellulose from this fraction was 87% of the theoretical yield and 100% after sodium chlorite treatment. The cellulose fraction has a wide range of industrial uses besides saccharification in ethanol production. These uses include an anticake agent, emulsifier, stabilizer, dispersing agent, thickener, gelling agent and holding on to water, depending on the crystalline degree of cellulose. Also, different reaction studies have been performed from this cellulose source to get new applications (Vaca-Garcia and Borredon, 1999).

5. Conclusions

The olive whole stone characterization showed an important source of sugar from hemicellulose and cellulose material beside its high content of simple phenols and lignin. Its high heat of combustion and easy managing makes this product as excellent direct or indirect fuel to be widely used in many industries. In spite of this, many uses may be performed due to its physical and chemical properties, but its valuable content must be considered. The only way that it has been possible to fractionate it involved a pretreatment with steam explosion system followed by chemical fractionation to obtain simple phenols, sugar from hemicellulose, lignin and cellulose, all of which are suitable for the same uses as the whole stone or other valuables uses. Seed oil is used on the basis of its major content in compounds such as a PUFA or individual sterols compared to virgin olive oil.

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Tables

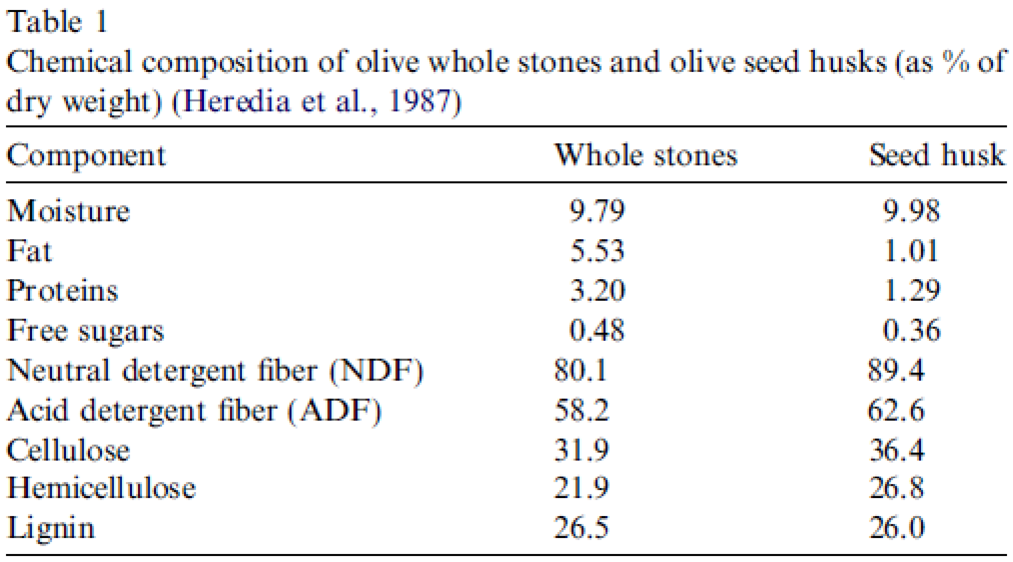

Table 1
Chemical composition of olive whole stones and olive seed husks (as % of dry weight) (Heredia et al., 1987)

Component	Whole stones	Seed husk
Moisture	9.79	9.98
Fat	5.53	1.01
Proteins	3.20	1.29
Free sugars	0.48	0.36
Neutral detergent fiber (NDF)	80.1	89.4
Acid detergent fiber (ADF)	58.2	62.6
Cellulose	31.9	36.4
Hemicellulose	21.9	26.8
Lignin	26.5	26.0

Table 2
Percentage of $CHCl_3$–EtOH extractable compounds of stone and seed of "Coratina" (Bianchi, 2003)

	Stone	Seed
Alkanes	1,7	tr
Squalene	–	tr
Alkyl esters	–	0.3
triacylglycerols	78	80
Free fatty acids	7	8
Aliphatic alcohols	0.1	0.2
Aldehydes	–	–
Triterpene alcohols	1.5	0.4
Triterpene acids	0.6	4
Free sterols	tr	tr
Steryl esters	1,1	2
Unidentified	10	5

Table 3
Range of phenols values in stone and seed olive for two seasons (phenols are expressed as grams per 100 g of dry matter) (Ryan et al., 2003)

Phenol	Stone	Seed
Tyrosol	0.1–0.8	0.5–4
Hydroxytyrosol	0.4–1.9	0.1–1
3,4 DHFEA-EDA	0.3–1.0	0.1–0.6
Oleuropein	0.1–0.2	0.1–0.2
Verbascoside	–	0.4–0.8
Nüzhenide	–	2.8–7.6

Table 4
Fractional composition of the fiber in stone and seed olive for several varieties of olive (the fiber fraction ranged are expressed as grams per 100 g of dry matter) (Heredia et al., 1987)

	Stone	Seed
Cellulose	29.79–34.35	2.36–3.91
Lignin	20.63–25.11	2.19–4.60
Hemicellulose	21.45–27.64	4.02–8.95
Ash	0.01–0.68	0.03–0.13

Table 5
Actual and future stone and seed uses

Application	Raw material	Pretreatment	Raw transformed	Bases in properties	Application sector	Uses	Useful Byproduct and uses	Ref.
Combustion	Stone and seed	Dried	Electric or heat	Physical (heat of combustion)	All industries residential and commercial	Nowadays in use	Ash/cement industries	González et al. (2003), Durán (1985), European Bioenergy (2003)
Activated carbon	Stone and seed	Pyrolysis activation	Activated carbon	Physical (adsorption)	Food, chemical, petroleum, nuclear, mining, pharmacological industry	Nowadays in use	–	Stavropoulos and Zabaniotou (2005), El-Sheikh et al. (2004), Ubago-Pérez et al. (2006), Molina-Sabio et al. (2006), Sánchez et al. (2006), Martínez et al. (2005)
Bio-oil	Stone and seed	Pyrolysis	Liquid and gas production	Physical (combustion heat)	Wide field of industries	Nowadays in use	–	Pütün et al. (2005)
Olive seed oil	Seed	Separation extraction refining	Olive seed oil	Chemical	Food, pharmacological and cosmetic industry	Nowadays in use	–	Gurguc (2006), Kourtzis (1999), Artacho (1999), Luaces et al. (2003), Ranalli et al. (2002a, b), Hakala et al. (1997)
Furfural	Stone and seed	Acid hydrolysis	Furfural	Chemical (Solvent)	Wide field of industries as solvent	Used in the past	Hydrolyzed/ fertilizer	Montané et al. (2001), Riera et al. (1990)
Plastic filled	Stone	Grinding	Composite	Physical	Plastic and construction	Nowadays in use	–	Siracusa et al. (2001), Natraplast (2007), Flextron (2007), Cristofaro (1997)
Abrasive	Stone	Grinding	Powder	Physical (hardness)	Cleaning	Nowadays in use	–	Dawson (2006)
Cosmetic	Stone	Grinding	Cosmetic products	Physical (abrasive)	Cosmetic	Nowadays in use	–	Cosmoliva (2007), Korres (2007), Mohammadi et al. (2005)
Biosorbent	Stone	Grinding	Granulated or powder stone	Physical, chemical	Metallurgy and food	Potentially in use	–	Blázquez et al. (2005), De Castro et al. (2004), Calero et al. (2006), Fiol et al. (2006)
Animal feed	Stone and seed	Grinding	Animal food	Physical	Food	Potentially in use	–	Carraro et al. (2005)
Resins	Stone and seed	Pyrolysis or liquefaction	Phenol–formaldehyde	Chemical	Electrochemical	Potentially in use	Fuel	Tejeda-Ricardez et al. (2003), Theodoropoulou et al. (2004)
Fractionation	Stone and seed	Steam explosion and fractionation	Soluble phenols and hemicellulose, lignin and cellulose	Chemical	Food, cosmetic, pharmaceutical, alcohol	Potentially in use	Source of protein and sugar/animal feed or fertilizer	Fernández-Bolaños et al. (1998, 1999, 2001)

Table 6
Recovery yields (g/100 g dry weight of initial material) after pretreatment of olive whole stone and olive stone by steam explosion (215 °C, 2 min and with or without H_2SO_4 0.1% (w/w) impregnation) (Fernández-Bolaños et al., 2001)

Substrate	Recovery yield (%)		
	Water soluble substances	Water insoluble substances	
		Lignin alkali-extracted	Insoluble
Whole stone with acid	19.5	16.6	45.5
Whole stone without acid	10.8	6.29	67.6
Stone with acid	26.9	19.8	40.1
Stone without acid	27.5	13.3	40.8

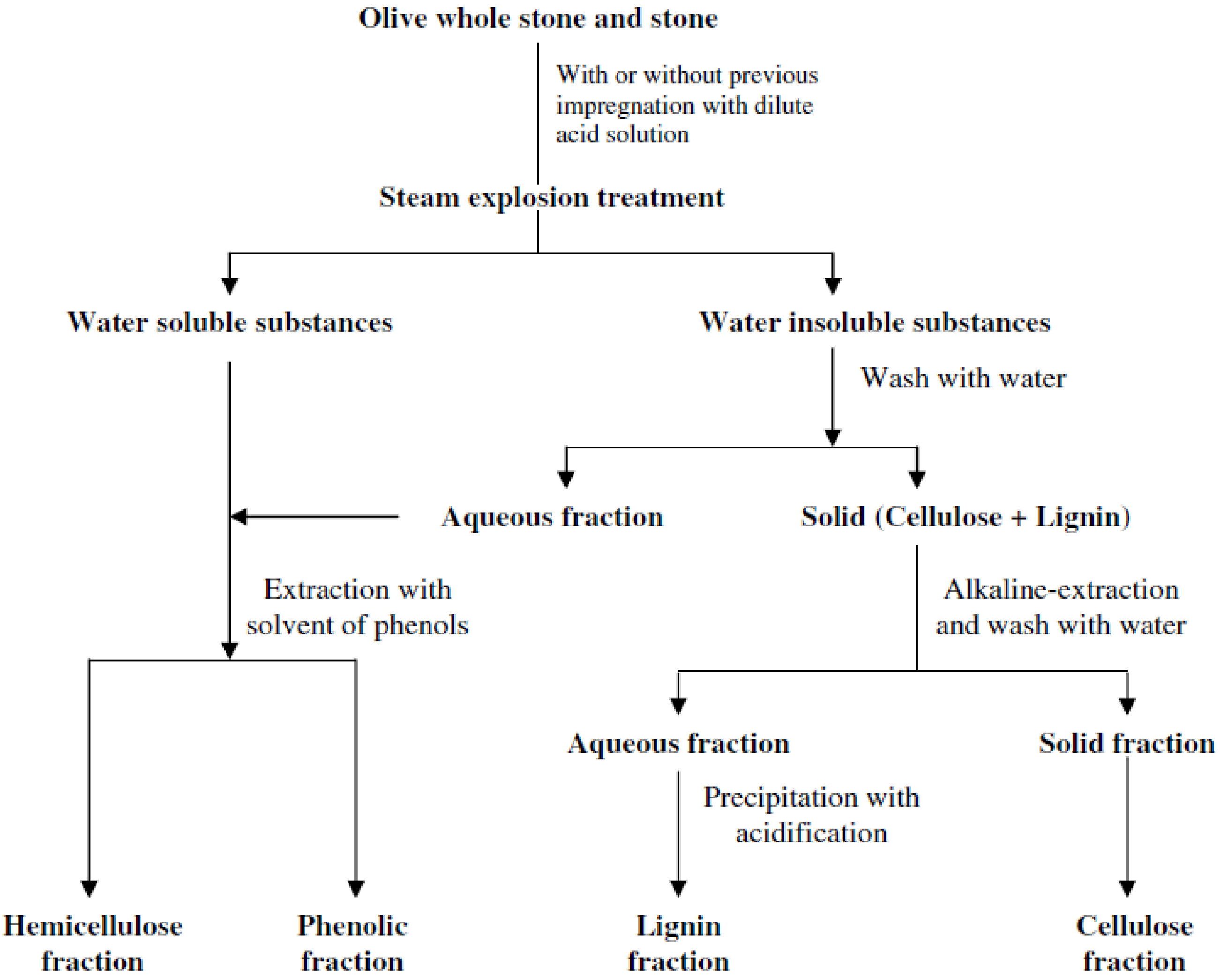

Fig. 1. Scheme of the fractionation treatments of olive whole stone (stone and seed) and stone after steam explosion pretreatment.