

1. Definition of olive

The olive fruit is a drupe, but it differs from other drupes because it contains much lower sugar content and a higher concentration of oil. Drupe size and shape depend on the cultivar and growing conditions, with a weight at physiological maturity ranging from 1.5 to 4.5 g. The olive tree's fruit is composed of three parts (Figure 1): an external part called the epicarp or skin; a middle part, the mesocarp or pulp, which is more or less colored and represents 70-80% of the weight of the whole fruit to physiological maturity, from which we obtain about 70% of oil; and an internal part called the endocarp, or stone, which represents 15–25% of the fruit and contains the seed (2.5–4%) and produces the remaining 30% of oil.

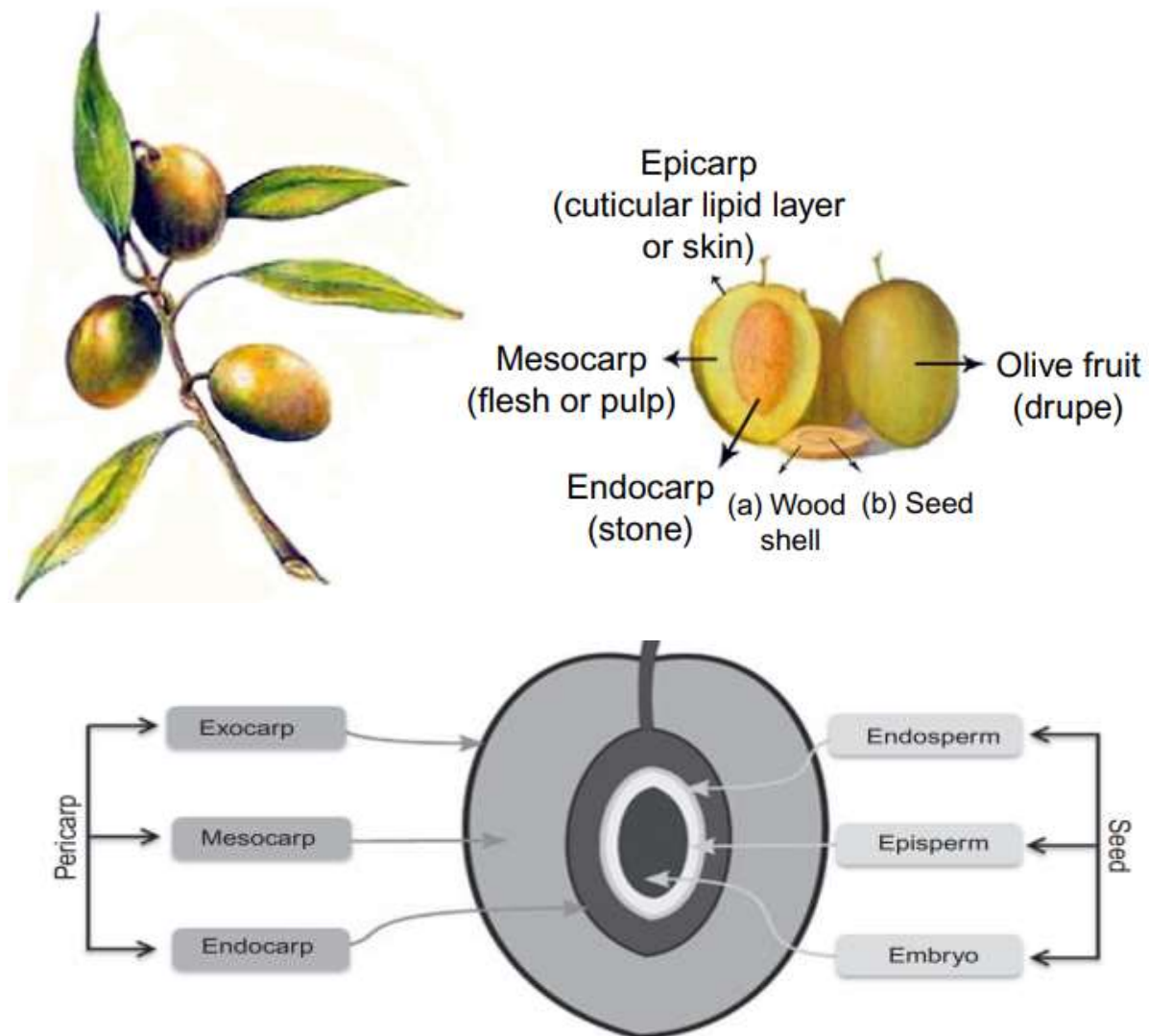


Figure 1. Cross-section of an olive and seed fruit.

2. Definition of olive oil

Olive oil is the oil obtained solely from the fruit of the olive tree (*Olea europaea*. L). olive oil can be considered an example of a functional food, containing a variety of compounds that contribute to its overall therapeutic properties.

3. Olive oil classification

The quality and authenticity parameters of olive oil are influenced by several factors, namely: the variety, the environment, cultivation techniques, and the extraction technology. However, the influence of the varietal factor remains the most important on the quality and chemical composition of olive oils produced under suitable production and processing conditions.

3.1. Classification parameters

The different categories of olive oil, as well as characteristics of types of olive oil, including acidity, peroxide index, and K232 and K270 parameters established by the IOC (2013), are shown in Table 1. Acidity, peroxide value, and UV absorbance characterize the category of an olive oil. Different categories of olive oil as well as the limits quality records published by COI (2013) are: Extra virgin olive oil, virgin olive oil, ordinary virgin olive oil, lampante virgin olive oil, refined olive oil, olive oil, refined olive pomace oil, olive pomace oil.

3.1.1. Acidity

The level of acidity of olive oil is a measure of the free fatty acids, and it is conventionally expressed as a percentage of oleic acid. Acidity is influenced by olive ripeness and harvest systems. Increased acidity changes the oil quality and decreases its commercial value.

3.1.2. Peroxides index

The peroxides index is an important indicator of good conservation of olive oil. Indeed, unsaturated fatty acids react with oxygen to form peroxides, releasing volatile compounds that give the characteristic rancid off-flavors. Therefore, oil is good if the number of peroxides is low.

3.1.3. Spectrophotometric indices

Spectrophotometric indices of olive oil, K232 and K270, determined according to The Commission of the European Communities, allow an understanding of whether oil is altered.

3.1.4. Sensory or organoleptic parameters

Sensory or organoleptic analysis of olive oil has a significant importance in judging the quality of the final product.. Sensory or organoleptic analysis are carried out by specialized organizations. The committees are made up of a panel leader and a minimum of 8 and a maximum of 12 tasters. The set of different sensory perceptions allows these members to formulate a final judgment, which takes into account of the overall harmony of sensations. At the end of the assessments, each taster completes the data sheet and assesses the presence and the intensity of the good qualities (fruity, bitter, and spicy) and the defects (rancid, mold, heating, winey, metal, etc.). Fruity is an important sensory characteristic that is derived from healthy, fresh, green or ripe fruit.

3.2. Olive oil types

- **Virgin olive oils suitable for consumption**
 - **Extra virgin olive oil**

Four criteria should be satisfied for an olive oil to be certified as extra-virgin olive oil: it must contain no more than 0.8% oleic acidity; it must be produced by mechanical extraction methods without chemicals and hot water; it must come from first cold pressing; and it must have a perfect taste. Virgin olive oil with a free acidity expressed as oleic acid of no more than 0.8 g/100 g of oil (IOC, 2013).

- **Virgin olive oil**

Virgin olive oil with a free acidity expressed as oleic acid of no more than 2 g/100 g of oil (IOC, 2013).

- **Ordinary virgin olive oil**

Virgin olive oil with a free acidity expressed as oleic acid of no more than 3.3 g/100 g of oil (IOC, 2013).

- **Virgin olive oils not suitable for consumption**
 - **Lampante virgin olive oil**

This is called lampante olive oil; oils with an acidity greater than 3.3% are submitted to a refining process (IOC, 2013) in which some components, mainly phenolic compounds and, to a lesser degree, squalene, are lost.

- **Refined olive oil**

This is olive oil obtained from virgin olive oils using refining techniques that do not alter the initial glyceride structure. Its free acidity, expressed as oleic acid, must not exceed 0.3 g/100 g. (IOC, 2013).

- **Refined olive pomace oil**

Refined olive pomace oil is the oil obtained from crude olive pomace oil by refining methods, which do not lead to alterations in the initial glyceridic structure. It has a free acidity, expressed as oleic acid, of not more than 0.3 grams per 100 grams and its other characteristics correspond to those fixed for this category in the IOC standard.

- **Olive pomace oil**

After virgin olive oil production, the rest of the olive drupe and seed is processed and submitted to a refining process. Olive pomace oil is the oil comprising the blend of refined olive pomace oil and virgin olive oils fit for consumption as they are. It has a free acidity of not more than 1 gram per 100 grams and its other characteristics correspond to those fixed for this category in the IOC standard.

Table I. The different categories of olive oil and their quality criteria (IOC, 2013).

Type	Free acidity(% oleic acid)	Peroxides index (m Eq O ₂ /kg)	K232	K270
Extra Virgin Olive Oil	≤ 0.8	≤ 20	≤ 2.50	≤ 0.22
Virgin olive oil	≤ 2.0	≤ 20	≤ 2.60	≤ 0.25
Ordinary Virgin Olive Oil	≤ 3.3	≤ 20	N/A	≤ 0.30
Lampante virgin olive oil	>3.3	No limit	N/A	N/A
Refined olive oil	<0.3	≤ 5	N/A	≤ 1.10
Olive oil	1.0	≤ 15	N/A	≤ 0.90
Refined olive pomace oil	<0.3	≤ 5	N/A	≤ 2.00
Olive pomace oil.	< 1.0	≤ 15	N/A	≤ 1.70<

4. Biochemical composition of olive oil

Like all vegetable oils, olive oil is composed of two fractions: saponifiable and unsaponifiable. A wide diversity can be found in composition among different varieties of olive oils. Also, environmental and seasonal effects, as well as the olive oil processing methods, have been reported to affect olive oil composition.

4.1. Saponifiable fraction

This fraction represents 99% of the oil and is mainly composed of triglycerides (98-99%) and fatty acids. The main fatty acid in olive oil is oleic acid (C18:1), a monounsaturated fatty acid, and represents 65 to 80% of the fatty acids in olive oil. The limits for fatty acid composition set by the IOC (2013) are summarized in **Table 2**.

Table 2. Fatty acid composition of olive oil.

Fatty acid	Symbol	Composition
Myristic acid	C14:0	<0.03
Palmitic acid	C16:0	7.5-20.00
Palmitoleic acid	C16:1	0.3-3.5
Heptadecanoic acid	C17:0	<0.3
Heptadecanoic acid	C17:1	<0.3
Stearic acid	C18:0	0.5-5.00
Oleic acid	C18:1	55.00-83.00
Linoleic acid	C18:2	3.5-21.00
Linolenic acid	C18:3	<1.00
Arachidic acid	C20:0	<0.60
Gadoleic acid	C20:1	<0.40
Behenic acid	C22:0	<0.20
Lignoceric	C24:0	<0.20

4.2. The unsaponifiable fraction

This fraction represents 1% of olive oil and contains a variety of components, also called minor compounds. These minor compounds, such as alcohols, phenolic compounds, chlorophylls, carotenoids, sterols, and tocopherols, contribute to the organoleptic quality, taste, flavor, and

nutritional value of olive oil, which can distinguish oils from different production regions and varieties.

4.2.1. Sterols

Sterols are present in olive oil in both free and esterified forms with fatty acids. Their quantity is approximately 100 to 300 mg/100 g of oil. The main sterols in olive oil are β -sitosterol, campesterol, and stigmasterol. The action of sterols is quite considerable as it prevents cholesterol absorption.

4.2.2. Hydrocarbons

In general, hydrocarbons are represented by squalene, a triterpene, the amounts of which vary between 500 and 780 mg/100g of oil.

4.2.3. Aromatic compounds

These compounds contribute to the distinctive aroma and flavor of olive oil. Among these are aldehydes and ketones, which are degradation products of unsaturated fatty acids, and aliphatic and aromatic hydrocarbons.

4.2.4. Tocopherols

Tocopherols are important compounds in olive oil due to their contribution to oxidative stability and nutritional qualities. The tocopherol content of virgin olive oil varies from 100 to 300 mg/kg. 90% of the tocopherols are in the α form, which has the highest vitamin activity. α -Tocopherol is present at concentrations of 170 to 590 mg/kg, while the concentration of other isoforms does not exceed 100 mg/kg.

4.2.5. Pigments

The color of olive oil results from the solubilization of two types of lipophilic pigments: chlorophylls and carotenoids present in the source fruit. The levels of these pigments depend on the variety, the degree of fruit ripeness, environmental conditions, extraction conditions, and especially storage conditions.

4.2.6. Chlorophylls

Chlorophylls belong to the tetrapyrrol family; they are photosensitizers and acquire pro-oxidant activity through the formation of singlet oxygen, thus causing the degradation of the organoleptic properties of the oil. The chlorophyll content of olive oil generally varies from 0

to 20 ppm. Chlorophylls a and b occur naturally in fresh olives; pheophytins a and b constitute 40 to 80% of the total chlorophyll in the oil and are formed during the crushing and malaxation of the fruit following the release of acids.

4.2.7. Carotenoids

Virgin olive oil has variable carotenoid content ranging from 5 to 10 mg/kg, of which 5 to 15% is β -carotene. The main carotenoids present in olive oil are lutein, β -carotene, and xanthophylls.

4.2.8. Phenolic compounds

Phenolic compounds encompass a wide range of diverse substances that give olive oil its distinctive taste compared to other oils. However, they are currently the focus of numerous studies, primarily due to their potential for promoting human health. A high phenolic compound content appears to be a nutritional advantage and therefore could favor one olive variety over another. Typical levels in olive oil generally range from 75 to 700 mg/kg. The most quantitatively significant polyphenols in olive oil are tyrosol, hydroxytyrosol, oleuropein, and ligstroside. Olive oil also contains other, more complex molecules such as lignans.

5. Olive oil production techniques

Oil is a vegetable oil that can be obtained directly from olive fruit using only mechanical extraction and that can be consumed without further treatments. The steps of the olive oil production process include collecting, washing, and crushing olives, malaxation of olive paste, centrifugation, storage, and filtration. The preliminary operations to which the olives must be subjected before extraction are defoliation and washing. The different stages allowing oil extraction are as follows:

5.1. Collecting

The olives begin to appear towards the end of May, and they arrive at their full ripening in September. In this period the harvesting phase occurs, which can be manual or mechanical. The harvesting phase is crucial because the final oil quality is directly linked to olive quality. Premature or late harvesting and prolonged or incorrect storage are aspects that negatively influence olive oil quality parameters.

5.2. Defoliation and washing

After harvesting, preliminary operations prepare the olives for subsequent processing, such as defoliation and washing. The olives must be harvested without breaking the fruit skins, and fruit should be processed within 12-24 h of harvest. Olives are washed only if they have been harvested from the soil or have spray residues on the skin. The extra moisture can reduce extraction efficiency because water-oil emulsions form. Oils produced from washed olives are usually less desirable due to a reduction in bitterness (amertume) and pungency (gout piquant) and a less fruity flavor (saveur).

5.3. Crushing

Crushing olives is a physical process used to break the fruits' tissues and release the oil contained in the vegetable cell vacuoles. The clean olives are subjected, without heating or cooking, to a thorough grinding (broyage) process which aims to burst (éclater) the oil-filled, pulpy drupe (la drupe pulpeuse repmplie d'huile), crush the pit and crush the contents of the kernel (écrasez le noyau et broyez le contenu de l'amande). The olive paste (pâte) is currently prepared in industrial oil mills (moulins industriels) with either a traditional discontinuous stone mill or traditional muller (moulin à pierre discontinue) or a continuous hammer or disc crusher (broyeur à marteaux continu).

5.3.1. Stones mills

Stone mills, the oldest method for crushing olives, consist of a stone base and upright stone enclosed in a basin. The slow movement of the stone crushers does not heat the paste and results in less emulsification, so the oil is easier to extract. The disadvantages of this method are the slowness of machinery and its high cost, and its inability to be continuously operated. Most stone mills have been replaced during the past 20 years because of their inefficiency.



Figure 2. Stones mills

5.3.2. Hammer mills

Hammer mills generally consist of a metal body that rotates at a high speed, hurling the olives against a metal screen. The major advantage of hammer mills is their speed and continuous operation, which translate into high rate and low cost. The rapid crushing of the fruit, however, creates more emulsification of the oil and water within the paste and higher temperatures. Oil produced from a hammer mill generally has a stronger flavor because the pulp is broken up more.



Figure 3. Hammer or disk mills.

5.4. Malaxation of olive paste

This operation aims to perfect the grinding, give the paste a homogeneous appearance, and increase the percentage of free oil. Malaxation of the olive paste is carried out with a stainless steel device made of a semi cylindrical vat with a horizontal shaft, rotating arms, and blades of different shapes and sizes. This vat is equipped with a heating jacket, circulating hot water to warm the olive paste. Malaxation prepares the paste for separation of the oil. It is done to reverse the emulsification that occurs during the crushing process and is particularly important if the paste was produced in a hammer mill. The mixing process optimizes the amount of oil extracted through the formation of larger oil droplets and a reduction of the oil water emulsion. The paste is slowly stirred for 30 to 60 min. The temperature of the paste during malaxation is very important. It should be warm (26.6 – 30°C), which is still cool to the touch, to improve the

viscosity of the oil and improve extractability. Temperatures more than 30°C can cause problems such as loss of fruit flavors, increased bitterness, and increased astringency.



Figure 4. Malaxation tank

5.5. Separation

The oil extraction is carried out by separating the liquid phase (must oil) from the solid one (pomace). Different types of machines can be used depending on the separation principle used. The oil extraction from the paste can be carried out by pressure (pressing), using a hydraulic press, or by centrifugation, using three- or two-phase centrifuges (centrifugal decanters). The oil can be extracted also by selective filtration, or through combinations of the different methods.

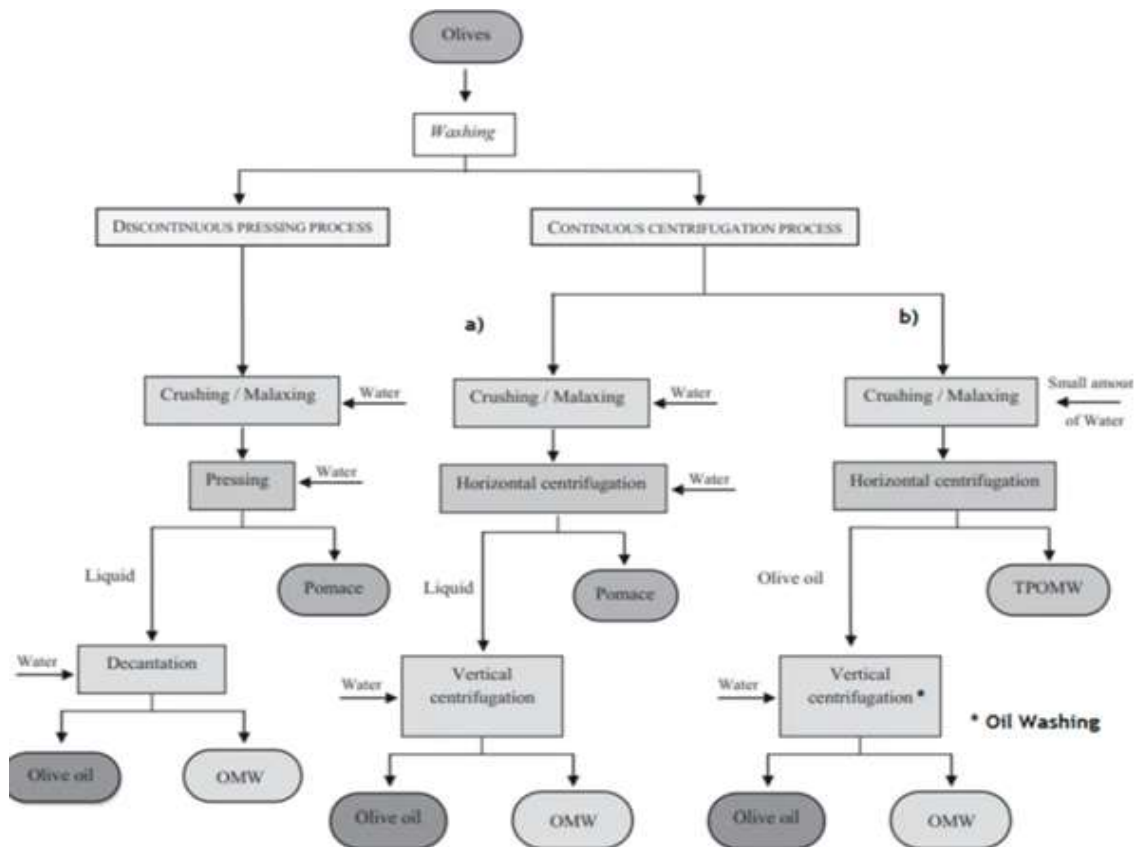


Figure 5. Main processes of olive oil production. Traditional (pressing) method, (a) three-phase centrifugation method and (b) two-phase centrifugation method.

5.5.1. Pressing

Pressing is one of the oldest methods (traditional methods) of oil extraction. This method remains cold hydraulic pressing. The paste is spread in quantities of 2 to 5 kilos onto round mats, called scourtins, which must be both very strong and permeable. The scourtins, covered with a layer of paste, are stacked in groups of twenty-five or thirty to be pressed. They retain the solid part of the paste and allow the liquid, composed of a mixture of oil and water called olive mill wastewater, to flow out. This process requires more labor than other extraction methods, the cycle is not continuous, and the filter mats can easily become contaminated, introducing fermentation and oxidation defects into the oil. Consequently, the use of traditional presses is becoming obsolete.



Figure 6. Pressing methods

5.5.2. Centrifugation

Centrifugation is usually applied for a primary separation of the olive oil fraction from the solid vegetable material and vegetation water. This step may be carried out using the combination of two different systems: horizontal centrifugation (three- and two-phase decanters) and vertical centrifugation. Horizontal centrifugation using a three-phase decanter requires the addition of warm water to dilute the olive paste to facilitate the separation described above, whereas the two-phase decanter consists of “no-water” centrifugation plants for separating the oily phase from malaxed pastes without requiring the addition of warm water. It should be considered that the two-phase decanter requires a minimal moisture value in the olive paste (50%) to facilitate the separation process. When this value is not reached, a small amount of water is loaded into the decanter. A vertical centrifugation system is used to separate the oily must obtained from horizontal centrifugation.

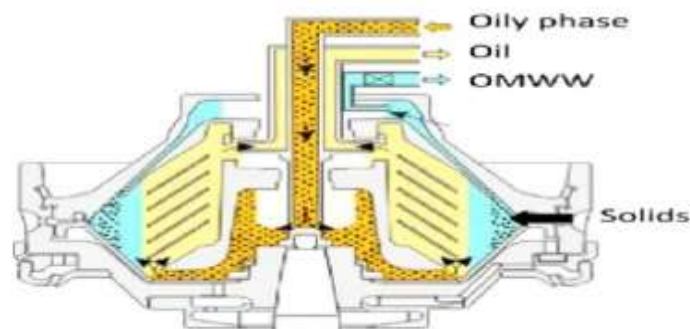


Figure 7. Vertical centrifuge system of olive oil extraction.

5.6. Bottling and storage

Bottling is one of the most delicate stages of the processing process because it is necessary to reduce contact with air during the transfer. Olive oil containers must be made of material that avoids contact with light as much as possible, as light can be a cause of degradation. As an alternative to the widely used dark glass. In fact, it must be quick in order to preserve the organoleptic properties of freshly pressed olives. After storage for 9 months, the peroxide values increase and the total phenol content and oxidative stability of olive oil decrease.

6. Refining lampante olive oil

6.1. Refining process

Refining is the term applied to the process of neutralizing the free fatty acids present in oil by treatment with alkali and the separation of the resulting insoluble material (e.g., phospholipids, color compounds, and soluble and insoluble impurities). The term refining is used with both **physical** and chemical processes. Table displays the chemical or alkali refining process.

Table 3. Basic steps in refining process

Alkali or chemical refining	Main of groups of compound removed
Washing /degumming	Phospholipids
Neutralizing	Free fatty acids
Bleaching	Pigments/metals/soaps
Winterization	Waxes/saturated triacylglycerols
Deodorization	Volatiles/free fatty acids

6.1.1. Degumming

The objective of this step is to eliminate phospholipids, also called gums. These compounds consist of a glycerol molecule esterified at the 1 and 2 positions with fatty acids and at the 3 position with phosphoric acid normally linked to a polar group of varying nature. Phospholipids are strongly emulsifying compounds that are normally associated with prooxidative metals, which diminish stability and result in murky oil due to the appearance of precipitates. In addition, if phospholipids are present, the oil produced will develop a darker color, showing poor organoleptic characteristics and stability. To achieve a complete elimination of these compounds, it is necessary to transform nonhydratable

phospholipids into their hydratable forms by breaking metal/phospholipid complexes down with a strong acid, namely, phosphoric acid or citric acid

6.1.2. Neutralizing

The neutralization step is aimed at eliminating fatty acids (prooxidants) and adding an alkali. The oil is treated with an excess of 10-20% of the calculated amount of NaOH to promote the saponifying reaction or the formation of soaps insoluble in the oil by which minor compounds (sterols and tocopherols) are removed together with other toxic compounds. This soap is then separated by washing with water, reducing the acidity to a level close to zero. One or two washings are carried out using 8–10 % hot water (90–95 °C).

6.1.3. Bleaching

The oil is treated with activated earth or activated carbon at approximately 100°C to absorb the pigments responsible for the color (carotenes, chlorophyll) and oxidized substances. The result is a clear, pale yellow oil. Bleaching clay also facilitates decomposition of oxidation products, and consequently, the peroxide value diminishes. Primary and secondary oxidation compounds are adsorbed during bleaching, along with metals, detergents, phospholipids, pesticides, and polyaromatic substances. Bleaching earth, whether activated or not, consists of bentonites and montmorillonites (aluminum-magnesium silicate) with a particle size in the range of 20–80 µm.

6.1.4. Winterization

The crystallization step, which is carried out by cooling down the oil, is called winterization. The objective is the elimination of any compound that might cause the final product to appear cloudy or murky and, hence, unacceptable to consumers. Winterization involves a cooling of the oil at around 5-8 °C that allows the margarine (solid portion, mainly constituted by waxes and saturated triglycerides) to crystallize in 24-48 h. The process is followed by separation into two phases through filtration or centrifugation.

6.1.5. Deodorization

In addition to triglycerides, all olive oils contain a large amount of minor compounds in much smaller quantities. Among them are volatiles that contribute not only to its appreciated sensory perceptions (fruity, green) but also to undesirable odors (rancid, fusty, and

vinegary). Deodorization, which allows removing those undesirable odors, consists of distillation under vacuum with stripping gas. In the physical refining process, as fatty acid were not previously removed during neutralization with alkali, they are also eliminated during deodorization.

7. Olive pomace oil

The production of olive pomace oil begins with the solid residues obtained after extracting virgin olive oil. This residue, known as olive pomace, consists of pieces of pulp, fragments of pits, residual water, and a small amount of remaining oil. First, the pomace is collected from olive mills, and then it is dried to reduce moisture content and ground to obtain a homogeneous material that facilitates the extraction process.

Next, the remaining oil is extracted using chemical solvents, most commonly hexane. The solvent dissolves the residual oil contained in the pomace, forming a mixture that is later separated. This mixture is then heated to remove the solvent through distillation, allowing the solvent to be recovered and reused. The crude oil obtained at this stage is not suitable for direct consumption, so it undergoes a refining process that includes neutralization, bleaching, and deodorization in order to make it edible.

In some cases, the refined oil is blended with a small quantity of virgin olive oil to improve its characteristics, and it is then marketed as olive pomace oil. This oil is characterized by a light color and a neutral taste. However, it has lower nutritional value compared to virgin olive oil, as it contains fewer beneficial compounds such as antioxidants.

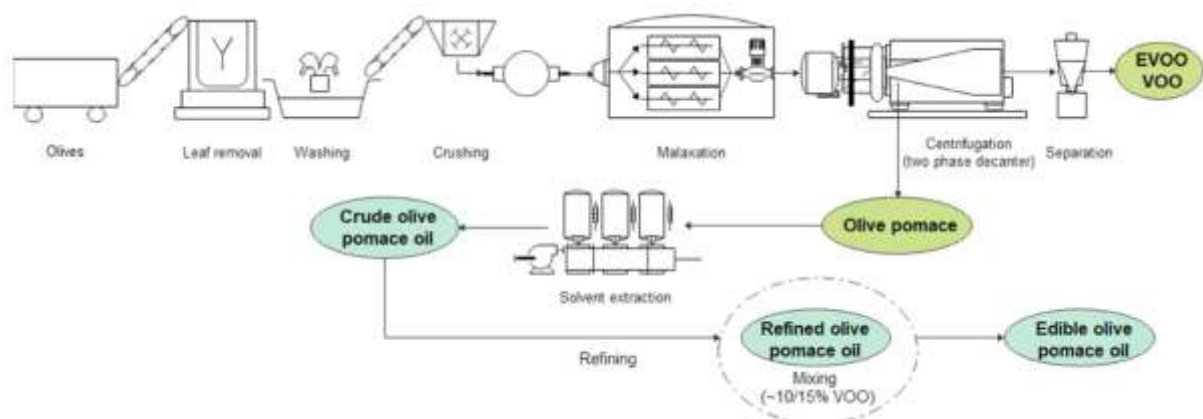


Figure 8. Olive oil and olive pomace oil production process. EVOO: Extra virgin olive oil, VOO: Virgin olive oil.

References

1. IOC **2013**. Classification of olive oils. International standards applicable to olive oil and olive pomace oil. International Olive Council.
2. Rocha, C; Soria, M A; Madeira, L M. **2022**. Olive mill wastewater valorization through steam reforming using multifunctional reactors: challenges of the process intensification. *Energies*, 15:920.
3. Aparicio R and Harwood J. **2013**. Handbook of olive oil: analysis and properties. Victoria Ruiz-Méndez M ; Aguirre-González M R ; Susana Marmesat. Chapter 19. Olive oil refining process.