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Potential Applications of Green Technologies in Olive Oil Industry

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1. Introduction

Conventional olive oil production methods create large amounts of waste and by-products. Most production plants do not invest in purification and utilization of those by-products. Purification or conversion methods may add value to those by-products and prevent the environmental pollution.

Global trends show that "green" products and technologies are needed. Increasing environmental concerns, government measures and population drive the search for green processes to replace the conventional ones. This search is essential to achieve sustainable processing and to reduce commercial energy use (Clark, 2011). There are several applications for green technology in the olive oil industry.

This chapter reviews the potential applications of major green processes such as supercritical fluid extraction, membrane technology, bioconversions and molecular distillation in the olive oil industry.

2. Supercritical fluid technology

Supercritical Fluid Technology (SFT) has received growing interest as a green technology, with extraction being the main application in the food industry. Fluids become supercritical by increasing pressure and temperature above the critical point. Supercritical fluids have liquid-like solvent power and gas-like diffusivity. These physical properties make them ideal clean solvents for extraction of lipids.

Carbon dioxide (CO_2) is the most widely used supercritical fluid due to a lack of toxicity and flammability, low cost, wide availability, tunable solvent properties, and moderate critical temperature and pressure (31.1°C and 7.38 MPa) (Black, 1996). Because of the relatively low viscosity, high molecular diffusivity and low surface tension of the system, mass transfer is improved in supercritical CO_2 (SC-CO_2) in comparison to liquid organic solvents (Oliveira & Oliveira, 2000). Moreover, separation of CO_2 from the product can easily be achieved by reduction of pressure, because the products do not dissolve in CO_2 at atmospheric pressure.

Another unique property of supercritical fluids is their selectivity. The density of a supercritical fluid is higher than that of a gas, making them better solvents. Extraction selectivity of supercritical fluids can be changed altering density which is done by adjusting pressure and temperature. Selectivity can also be changed by the addition of a co-solvent such as ethanol, methanol, hexane, acetone, chloroform and water to increase or decrease the polarity. Ethanol is the most preferred co-solvent because it is non-toxic and meets green technology criteria (GRAS status) (Dunford, 2004).

SC-CO_2 processing adds value because products obtained may be considered as natural. Although SFT is used for extraction of plants and vegetables of different sources (Table 1), applications in the olive oil industry have been limited. SFT can be used in olive oil processing for extraction and deacidification, as well as separation, purification or concentration of minor components.

Sample	Analyte	Reference
Carrot	Carotenes	Vega et al. (1996)
Tomato skin	Lycopene	Ollanketo et al. (2001)
Mushrooms	Oleoresins	del Valle & Aguilera (1989)
Tea	Caffeine	Calabuig Aracil (1998)
Grape skin	Anthocyanins	Blasco et al. (1999)
Cottonseed	Lipids	Bhattacharjee et al. (2007)
Hops	Humulone, lupulone and essential oils	Langezaal et al. (1990)
Rosemary	Oil	Bensebia et al. (2009)

Table 1. Supercritical fluid extraction of different plants and vegetables.

2.1 Extraction

SC-CO_2 has been used to replace hexane in the olive oil industry and meets the growing demand for natural products (Temelli, 2009). The most common applications are extraction of total lipids from olive husk or minor lipid components from olive oil. Extraction of high value minor components without degradation led industry and researchers to focus on SC-CO_2 extraction. Fig. 1 represents a typical lab scale SC-CO_2 system used for extraction of lipids.

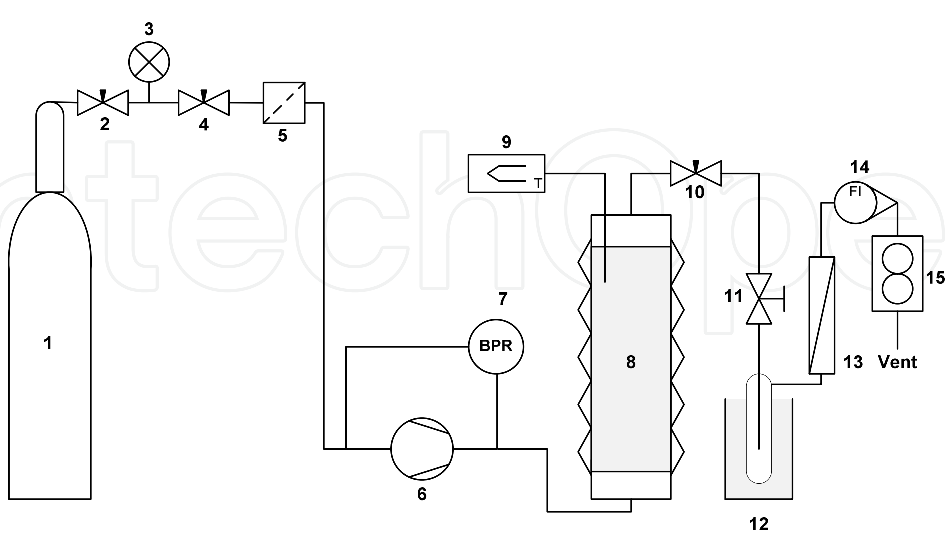

Fig. 1. Schematic diagram of a lab scale SC-CO_2 extraction system: 1, CO_2 tank; 2,4,10, shut-off valves; 3, pressure gauge; 5, filter; 6, compressor; 7, back pressure regulator; 8, extraction vessel; 9, thermocouple; 11, micrometering valve; 12; sample collector; 13, oil and moisture trap; 14, flowmeter; 15, gas meter.

SC-CO_2 extraction of olive husk oil is superior compared to conventional hexane extraction because the oil is also deacidifed and deodorised during the extraction process, and the resulting extract is free of residual solvent (Esquivel & Bernardo-Gil, 1993). Esquivel and Bernardo-Gil (1993) extracted olive husk oil using SC-CO_2 under pressures of 12 to 18 MPa and temperatures of 35 to 45 °C.

2.2 Deacidification

Crude olive oil contains free fatty acids (FFA) and other impurities which must be removed, yielding a triacylglycerol (TAG) rich fraction. A high FFA content decreases the oxidative stability of the oil and leads to rancidity. A reduction in FFA content in virgin olive oil results in an increase in commercial value (Vázquez et al., 2009).

Supercritical fluid extraction has been proposed as an alternative technology for deacidification of oils and has been used for deacidification of olive pomace oil, an important by-product of olive oil industry. Crude olive pomace oil is often very acidic, darkly colored and highly oxidized. Intensive refining is thus required to make it suitable for human consumption. Neutralization is currently applied, but there are drawbacks to this process. Product yield is very low and neutralization increases the cost per unit. Therefore, it is necessary to reduce the FFA content before refining (Fadiloglu et al., 2003). Supercritical deacidification is actually a selective supercritical fluid extraction process. During the process, FFAs preferentially extracted with minimum neutral oil (TAGs, tocopherols, phytosterols) loss (Vázquez et al., 2009). A schematic diagram of a supercritical fluid extraction system for deacidification of oils is shown in Fig. 2. The oil is fed to the extraction column by a pump. The extraction column consists of two sections: an enriching (above of the oil feeding point) section, and a stripping section (below the oil feeding point). Raffinate is first separated from the extract and sent to the stripping section. Then, in the stripping section, the extract is separated from raffinate and transported to the enriching section. Extract rich in minor lipid compounds and CO_2 is separated in the separator. A specified amount of the extract is transferred to the top of the column as reflux (Brunner, 2009). CO_2 can be purified and recycled into the system. Raffinate is collected at the bottom of the column.

Deacidification of different oil sources using supercritical fluids have been performed at laboratory scale by several researchers. Turkay et al. (1996) achieved a selective and quantitative (90%) FFA extraction for deacidification of high acidic black cumin seed oil using SC-CO_2 at relatively low pressure (15 MPa) and relatively high (60 °C) temperature. Ooi et al. (1996) decreased the FFA content of palm oil to 0.1% in a continuous SC-CO_2 extractor.

Brunetti et al. (1989) obtained deacidification of high acidic olive oil with SC-CO_2 at pressures of 20 and 30 MPa, and temperatures of 40 and 60 °C. They reported that the selectivity for FFAs was highest at 20 MPa and 60 °C. Bondioli et al. (1992) studied the supercritical fluid deacidification of olive oil in the pressure range of 9–15 MPa and 40–50 °C. The acidity was reduced from 6.3% to values less than 1% at 40 °C and 13 MPa. In another application, Vázquez et al. (2009) used SC-CO_2 as an extraction solvent to remove FFAs from cold-pressed olive oil in a packed column. The acidity was reduced from 4 to 1.43% at 25 MPa and 40 °C.

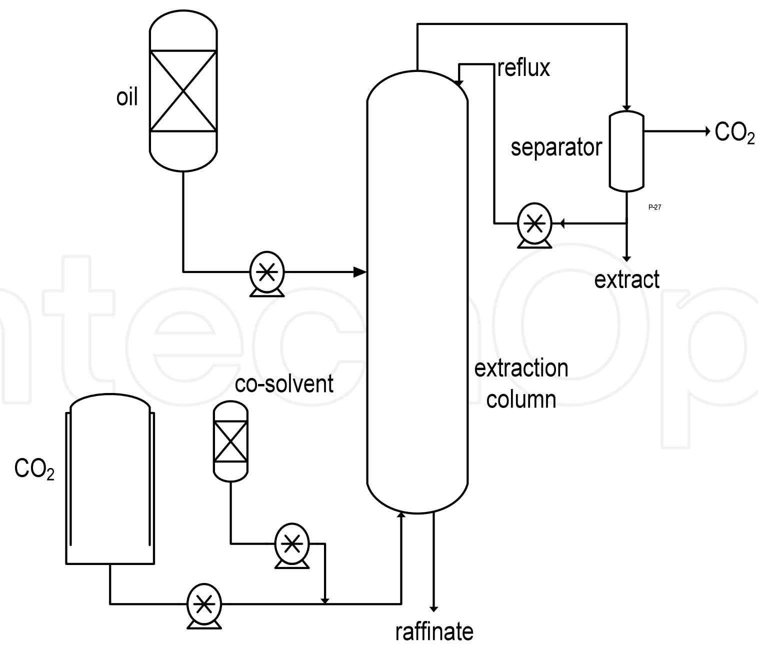

Fig. 2. Schematic diagram of supercritical fluid extraction pilot plant used for deacidification, separation, concentration and purification of oils.

2.3 Separation, concentration and purification of minor lipid compounds

Extraction of high value minor components from natural products is of great interest to food industry. SFT has been applied for purification, separation or concentration of several compounds from vegetable oils, essential oils and deodorizer distillates. These applications include purification of monoacylglycerols (MAGs) and lecithin, removal of cholesterol and limonene, and separation of squalene, tocopherols and fatty acid esters (Brunner, 2009).

Products of the olive oil industry are important sources of high value components such as tocopherols, phytosterols, squalene and fatty acids. The system used for separation of minor lipid compounds is the same as shown in Fig. 1. Fornari et al. (2008) purified squalene from a by-product obtained after distillation, esterification and transesterification of olive oil deodorizer distillates. They obtained 89.4% squalene purity and 64.2% yield at 70 °C and 18 MPa, and obtained a raffinate concentrated in TAGs and sterol compounds.

Dauksas et al. (2002) extracted tocopherols from olive tree leaves using SC-CO_2. They obtained a high value extract of 97.1% (w/w) tocopherol at 25 MPa and 40 °C after 1 h of extraction, and 74.48 % at the same pressure and temperature after 2 h. Le Floch et al. (1998) used supercritical fluid extraction for isolation of phenols from olive leave samples using SC-CO_2 modified with 10% methanol at 33.4 MPa and 100 °C.

2.4 Use of supercritical fluids as reaction media for enzymatic modification of lipids

Enzymatic interesterification in organic solvents leads to very important modifications of lipids. However, the use of organic solvents in these reactions is a disadvantage. Therefore, biosynthesis in supercritical fluids is attracting much attention. Replacement of organic solvents by supercritical fluids makes the process green and eliminates the need of solvent separation. The lower viscosity and the higher diffusivity of supercritical fluids allow easier transport of substrates to the catalyst and, in the case of enzyme within the pores of enzyme support, this results in an easier access to the enzyme sites leading to higher reaction rates. In addition to the previously mentioned advantages of supercritical fluids, the finding that enzymes can retain their biocatalytic activity at high pressures has also encouraged the use of enzymes under supercritical condition (Rezaei et al., 2007b; Rezaei et al., 2007a).

In general, expansion of the substrates in CO_2 seems to be the main advantage of enzymatic lipid reactions in SC-CO_2. Expanded substrates have better diffusivity, low surface tension and low viscosity. In addition, a lesser amount of substrate available per unit amount of enzyme per unit time will increase the reaction rate (Ciftci & Temelli, 2011). However, at very high pressures, mass transfer properties of the substrates may be affected negatively. High CO_2 densities at high pressures lead to a decrease in enzymatic conversions. It has been reported that diffusion coefficients of fatty acids, fatty acid esters and glycerides in SC-CO_2 may also decrease at high pressures due to increase in the density of CO_2 (Rezaei & Temelli, 2000). Therefore, optimization of the process in terms of pressure and temperatures is crucial. Esmelindro et al. (2008) produced MAGs from olive oil in compressed propane. Their results showed that lipase-catalyzed glycerolysis in compressed propane might be a potential replacement for conventional methods, as high contents of reaction products, MAG and diacylglycerol (DAG), were achieved at mild temperature and pressure conditions (30 °C and 3 MPa) with a low solvent to substrates mass ratio (4:1) in short-reaction times (1 h). Lee et al. (2009) produced biodiesel from various oils, namely, olive, soybean, rapeseed, sunflower and palm oil, using lipase in SC-CO_2. The highest yield (65.18%) was obtained from olive oil at 13 MPa, 45 °C and 20% of lipase concentration (based on weight of oil).

3. Membrane technology

Membrane technology is becoming increasingly important as a green processing and separation method in food processing and waste water treatment Membranes are used as filters in separation processes and have a wide variety of applications Membrane technology is now competitive compared to conventional techniques such as adsorption, ion exchangers and sand filters.

The main advantage of membrane processing is that it avoids the use of any chemicals that have to be discharged. It works with relatively high efficiency and low energy consumption (Mulder, 1996). It also has the advantage of operating at ambient temperature, resulting in preservation of heat-sensitive components and nutritional value of food products (Dewettinck & Le, 2011).

Membrane separation processes differ greatly in the type of membranes and driving forces used for separation, the process design, and the area of application. There are many different membrane processes, including reverse osmosis, micro-, ultra- and nanofiltration, dialysis, electrodialysis, Donnan dialysis, pervaporation, gas seperation, membrane contactors, membrane distillation, membrane based solvent extraction, membrane reactors, etc. Among them, the innovative methods preferred by the food industry are pressure driven separation processes such as reverse osmosis, nanofiltration, ultrafiltration and microfiltration. These preferred methods facilitate the separation of components with a large range of particle sizes. The obtained products are generally of high quality and less post-treatment procedures are required (Baker, 2004).

3.1 Applications of membrane technology in the olive oil industry

Membrane technology has been used in the edible oil industry for degumming, deacidification, waste water treatment, recovery of solvent from micelles, condensate return, catalyst recovery and hydrolysis or synthesis of structured lipids with two-phase membrane reactors, involving pigment removal, separation and concentration of minor compounds in the oil. Despite its use in other sectors of the edible oil industry, this technology has not been broadly extended to olive oil processing.

3.1.1 Deacidification

Conventional chemical and physical deacidification methods have some drawbacks such as use of large amount of water and chemicals, and loss of neutral oil (Kale et al., 1999). Membrane technology may be proposed as a new alternative deacidification process for edible oils (Bhosle & Subramanian, 2005).

A membrane-based process for deacidification of lampante olive oil was undertaken by Hafidi et al. (2005a). Their objective was to deacidify, while also preserving the sensitive and bioactive components in the oil by operating at ambient temperature. The results showed that oils were obtained almost FFA- and soap-free in a single step. In another study, the impact of this process on some minor components and on the organoleptic characteristics of the purified olive oils was investigated (Hafidi et al., 2005b). It was reported that, while a complete deacidification was achieved, some desirable components, mainly phenolics, were eliminated during the filtering process. Thus, it was suggested to focus on reducing the elimination of phenolic compounds and the improvement of the organoleptic characteristics of the filtered oils.

3.1.2 Wastewater treatment

Olive mill wastewater (OMW), a by-product of olive oil extraction, is one of the most contaminated effluents. The polluting load is due to organic substances such as sugars, tannins, polyphenols, polyalcohols, pectins, lipids, proteins and organic acids, (Cassano et al., 2011). Phenolic compounds can act as phytotoxic components, inhibiting microbial growth as well as plant germination and vegetative growth (Morillo et al., 2009).

Biochemical oxygen demand (BOD5) and chemical oxygen demand (COD) of OMW may be as high as 100 and 200 g L^{-1}, respectively (de Morais Coutinho et al., 2009). Besides, OMWs are considered as a potential source for the recovery of antioxidant, antiatherogenic and anti-inflammatory biophenols (Obied et al., 2005). Detoxification and recovery of valuable components from wastewater are among the most useful treatments based on membrane technology.

In the study of Paraskeva et al. (2007), combinations of different membrane processes were used for the fractionation of OMW. Ultrafiltration in combination with nanofiltration and/or reverse osmosis were found to be very efficient for this process. It was shown that better efficiency of the OMW treatment was achieved by applying reverse osmosis after ultrafiltration. The ultrafiltration concentrate was found to contain the largest portion of fats, lipids, solids, etc. Further processing with nanofiltrationmay be employed for the separation of a greater part of phenols.

In another study, OMW was used to investigate the variation of COD and total organic carbon (TOC) removal efficiencies together with permeate fluxes for ultrafiltration process (Akdemir & Ozer, 2009). Two types of ultrafiltration membranes which are JW (polyvinylidine-difluoride) and MW (ultrafilic) gave close removal efficiencies. Ultrafiltration membranes with bigger molecular weight cut-offs for OMW were suggested to increase flux value and decrease efficiency loss. In their previous work, observed COD removal efficiency by ultrafiltration without pretreatment was found higher than 80% by promising value for OMW (Akdemir & Ozer, 2008). El-Abbassi et al. (2009) studied the treatment of OMW to obtain high value-added compounds such as sugar and polyphenols, by membrane distillation. Two types of commercial membranes, polytetrafluoroethylene (TF200) and polyvinilydene fluoride (GVHP), were compared and the effects of membrane parameters on direct contact membrane distillation (DCMD) performance (i.e. permeate flux and polyphenols retention) were investigated. Their results demonstrated that TF200 had a better separation coefficient (99%) after 9 h of DCMD operation than that of GVHP (89%). OMW concentration factor was found to be 1.72 for TF200, whereas it was only 1.4 for GVHP after 9 h.

Another OWM treatment was tested by Dhaouadi and Marrot (2008). Diluted solutions of OMW were treated in a ceramic membrane bioreactor with biomass specially acclimated to phenol. It gave stabilized permeate flux with zero suspended solid and no phenolic compounds. No fouling problems occurred during the experiments. OMW treatment in a membrane bioreactor can be used as a pre-treatment stage for the removal of phenolic compounds before a conventional biological process.

Recently, Coskun et al. (2010) studied the treatment of OWM using nanofiltration and reverse osmosis membranes. They reported that overall COD removal efficiencies were 97.5%. It was shown that reverse osmosis membranes are capable of producing a higher quality effluent from OMW than nanofiltration membranes. NF270 membranes were found to be most applicable among nanofiltration membranes due to their higher fluxes and higher removal efficiencies. In addition, it was found that centrifugation alone can be used as a promising option for primary treatment of OMWs with nanofiltration process.

In summary, there appears to be a potential for the use of membrane technology in the olive oil industry. Membranes can provide an opportunity to develop alternative environmentally friendly processes for the refining of olive oils and treatment of OWM. Despite promising results, further studies must be done on this new approach, namely, to evaluate the effect of the process on the oil composition, to improve flow rate, to reduce fouling inclusions and to assess economic viability.

4. Bioconversions

Lipids require modification in order to be used for special purposes or production of value added products. Lipids can be modified by hydrogenation, blending, fractionation and chemical or enzymatic reactions such as hydrolysis, direct esterification and interesterification.

4.1 Enzymatic conversions

Interesterification reactions are widely studied to produce margarines and shortenings with zero-*trans* fatty acids, cocoa butter equivalents, structured lipids with specific nutritional properties, partial glycerides and biodiesel. Chemical interesterification uses metal alcoholate catalysts to incorporate fatty acids randomly. This reaction produces a complete positional randomization of acyl groups in TAGs. In enzymatic interesterification the final structure of TAGs is controlled and a desired acyl group can be guided into TAGs using nonspecific, regiospecific (*sn*-1,3- or 2- specific) and fatty acid specific lipases as catalysts. This results in products with predictable composition. Enzymatic interesterification is becoming a more attractive method to convert cheap oils such as olive pomace oil, soya bean oil, rape seed oil, lard, tallow, etc. to high-value-added products and modified fats (An et al., 2007; Liua et al., 1997; Macrae, 1983; Miller et al., 1991; Pomier et al., 2007; Xu, 2003). Furthermore, enzymatic interesterification has milder reaction conditions and produces less waste than the chemical alternative. In addition, the same immobilized enzyme can be used many times (Akoh et al., 1998; Marangoni & Rousseau, 1995; Willis et al., 1998; Willis & Marangoni, 2002). Therefore, intensive research has aimed at replacing chemical interesterification with enzymatic interesterification.

There are three types of interesterification reactions: acidolysis, which is the reaction between an ester and a fatty acid, alcoholysis, the reaction between an ester and an alcohol, and transesterification, the reaction of an ester with another ester, also called ester-ester exchange (Macrae, 1983; Xu, 2003). Production of structured lipids and biodiesel has been the major topics of enzymatic interesterification studies.

4.1.1 Structured lipids

Structured lipids are novel modified TAGs produced by the incorporation of desirable fatty acids at specific positions or by changing the position of the fatty acids on the glycerol backbone. These processes allow for specific characteristics to be obtained such as melting behavior, functionality, and metabolism. Lipases, especially those which are *sn*-1,3 specific, are used for this purpose because these enzymes can make changes at *sn*-1 and *sn*-3 positions by keeping *sn*-2 ester group position unchanged.

Cocoa butter (CB) has a narrow melting range due to its unique TAG composition. This melting behavior is critical. The steepness of the melting profile (% solid fat as a function of time) has an impact on flavor release and crystallization. The high price of cocoa butter has prompted the industry search for CB alternatives. CB equivalents (CBEs) can be produced from palm oil and exotic fats by means of fractionation. Enzymatic synthesis of CBEs from cheap oils and fats using *sn*-1,3 specific lipases is also an alternative method. CB-like fats could be produced which have even more desirable properties than natural CB. Ciftci et al. (2010) used olive pomace oil for the production of CB-like fat using *sn*-1,3 specific lipase. They interesterified refined olive pomace oil, palmitic acid and stearic acid at a molar ratio of 1:2:6, respectively, at 45°C using a pack bed reactor filled with *sn*-1,3 specific lipase. They reported that the CB-like fat could replace CB up to 30% without significantly changing the physical and chemical properties of the product. Chang et al. (1990) also produced CB-like fat by enzymatic interesterification of fully hydrogenated cotton seed and olive oils. The melting point of their CB-like fat was 39°C; close to 36°C, the melting point of CB.

Any lipid containing medium-chain and long-chain unsaturated fatty acids might be useful for certain applications and functionalities. Nunes et al. (2011) produced structured lipids containing medium-chain fatty acids at *sn*-1,3 position and long-chain unsaturated fatty acids at the *sn*-2 position by acidolysis of virgin olive oil and caprylic or capric acids using

1,3-selective *Rhizopus oryzae* heterologous lipase (rROL) immobilized in Eupergit C and modified sepiolite. These structured lipids are low caloric and and have dietetic properties for controlling obesity and malabsorption. They showed that rROL immobilized in Eupergit C was able to catalyze the incorporation of 21.6 and 34.8 mol% of caprylic or capric acid into virgin olive oil, after 24 h at 40 °C in solvent-free media. Fumoso and Akoh (2002) also used lipase-catalyzed acidolysis of olive oil and caprylic acid to produce structured lipids. They used a *sn*-1,3-specific lipase from *Rhizomucor miehei* in a bench-scale packed bed bioreactor. They studied the effect of solvent, temperature, substrate mol ratio, and flow rate/residence time. The optimal solvent-free production of structured lipid was obtained at a substrate flow rate of 1 ml/min, a residence time 2.7 h, 60 °C, and a mol ratio 1:5 (olive oil/caprylic acid). The structured lipid produced at optimal conditions had 7.2% caprylic acid, 69.6% oleic acid, 21.7% linoleic acid and 1.5% palmitic acid at the *sn*-2 position. Another structured lipid used as a constituent of infant formulas, consisting mainly of UPU triglycerides (U=unsaturated acyl chains, P=palmitic acyl group), can be prepared by lipase catalyzed reactions of fractionated palm oil, rich in tripalmitin, and oleic acid from olive oil (Schmid et al., 1998).

4.1.2 Biodiesel

Biodiesel can be obtained from vegetable oils, animal fats, recycled grease, or algae and can be produced by the reaction of TAGs with methanol (methanolysis). Lipase-catalyzed methanolysis is more attractive than conventional base-catalyzed method since the glycerol produced as a by-product can easily be recovered and the purification process for fatty acid methyl esters (FAMEs) is relatively simple. In the oil and fat industry, conversion of waste edible oil and soapstock (a by-product generated in alkali refining of vegetable oils) to biodiesel has attracted a great deal of attention (Azócar et al., 2010; Safieddin Ardebili et al., 2011; Singaram, 2009). Unlike the conventional chemical routes for synthesis of diesel fuels, biocatalytic routes permit one to carry out the interesterification of a wide variety of oil feedstocks in the presence of excess FFAs.

Olive pomace oil was used by Yucel (2011) for enzymatic production of biodiesel. Yucel (2011) immobilized microbial lipase from *Thermomyces lanuginosus* on olive pomace by covalent binding, and then used this immobilized lipase for the methanolysis of olive pomace oil. Under the optimized conditions for solvent-free reaction, the maximum yield was reported to be 93% at 25 °C after 24 h. Sanchez and Vasudevan (2006) produced biodiesel by transesterification of olive oil triolein with methanol using lipase. They studied the effects of the molar ratio of methanol to triolein, semibatch (stepwise addition of methanol) vs batch operation, enzyme activity, and reaction temperature on overall conversion. Because of the inactivation of the enzyme by insoluble methanol, stepwise methanolysis with a 3:1 methanol to triolein molar ratio and an overall ratio of 8:1 gave the best results.

4.2 Enzymatic deacidification

One method to reduce the FFA content in fats and oils is to convert the FFAs to TAGs. This is carried out by direct esterification of fatty acids with glycerol.

A reported application of enzymatic deacidification of olive pomace oil is the enzymatic glycerolysis of highly acidic (32%) olive pomace oil (Fadiloglu et al., 2003). FFAs of olive pomace oil were esterified with glycerol using a nonspecific immobilized lipase, reducing the acidity of the oil to 2.36%. In another study, the FFA content of high acidic (31.6%) degummed and dewaxed olive oil was reduced to 3.7%.

4.3 Bioremediation

Bioremediation, generally classified as *in situ* or *ex situ*, is the use of microorganism metabolism to remove pollutants. *In situ* bioremediation involves treating the contaminated material at the site, while *ex situ* involves the removal of the contaminated material to be treated elsewhere. Some examples of bioremediation technologies are phytoremediation, bioventing, bioleaching, landfarming, composting, bioaugmentation, rhizofiltration, and biostimulation (Shukla et al., 2010). Besides being cost effective, bioremediation can result in the complete mineralization of the pollutant, considered a permanent solution of the pollution problem. Furthermore, it is a non-invasive technique, leaving the ecosystem intact. Bioremediation can deal with lower concentrations of contaminants where cleanup by physical or chemical methods would not be feasible. Unfortunately, it presents some major drawbacks which still limit the application of these techniques, including long processing times and less predictable results compared to conventional methods (Perelo, 2010).

The disposal of OMW is predominantly carried out via land spreading or by means of evaporation ponds, although a wide number of chemical and biological decontamination and valorisation technologies have been reported. The two-phase centrifugation system, as an alternative ecological approach for olive oil production, drastically reduces the water consumption during the process. This system generates olive oil plus a semi-solid waste, known as the two-phase olive-mill waste (Morillo et al., 2009).

Ramos-Cormenzana et al. (1996) performed aerobic biodegradation on OMW by using bacterium *Bacillus pumilus* to reduce the phenol content. They reported 50% reduction in phenol content using *Bacillus pumilu*s. The detoxification of OMW following inoculation with *Azotobacter vinelandii* (strain A) was performed for two successive 5-day-period cycles in an aerobic, biowheel-type reactor, under non-sterile conditions by Ehaliotis et al. (1999). The authors indicated that the phytotoxicity of the processed product was reduced by over 90% at the end of both cycles. However, aerobic bacteria cannot generally biodegrade complex phenolic compounds which are responsible for the dark color of OMW. Fungi, compared to bacteria, are more effective at degrading both simple and complex phenolic compounds presenting in olive mill wastes. This is due to the presence of compounds analogous to lignin monomers, which are more easily degraded by wood-rotting fungi (García García et al., 2000).

Demirer et al. (2000) generated biogas containing about 77% methane by anaerobic bioconversion of OMW (57.5 L methane per liter of wastewater). Ammary (2005) treated OMW using a lab scale anaerobic sequencing batch reactor, achieving more than 80% COD removal at 3 d hydraulic retention time. Anaerobic bioconversion has some advantages compared to aerobic processes: (a) high organic load feeds are used, (b) low nutrient requirements are necessary, (c) small quantities of excess sludge are usually produced, and (d) a combustible biogas is generated. However, the nutrient imbalance of OMW, mainly due to its high C/N ratios, low pH and the presence of biostatic and inhibitory substances, cause a problem. Not quite clear Rephrase An additional problem of two-phase olive-mill waste is its high consistency making its transport, storage and handling difficult (Morillo et al., 2009).

Olive mill wastes can be treated with other methods such as composting to produce fertilizers (Ntoulas et al., 2011); using as a culture medium to produce useful microbial biomass (de la Fuente et al., 2011); using as a low-cost fermentation substrate for producing microbial biopolymers for production of polysaccharides and biodegradable plastics (Ntaikou et al., 2009); and as a base-stock for production of biofuels (Rincon et al., 2010).

5. Molecular distillation

Molecular distillation, also called short path distillation, has become an important alternative for separation of heat sensitive compounds or substances with very high boiling points. Molecular distillation is characterized by a short time exposure of the distilled liquid to elevated temperature and high vacuum, with a small distance between the evaporator and the condenser (Lutišan et al., 2002). The small distance between the evaporator and the condenser and a high vacuum in the distillation gap results in a specific mass transfer mechanism with evaporation outputs as high as 20–40 $gm^{-2}\ s^{-1}$ (Cvengroš et al., 2000). Due to short residence time and low temperature, distillation of heat-sensitive materials is accomplished without thermal decomposition. Another advantage of the process is the absence of solvents. Therefore, molecular distillation is considered as a promising method in the separation, purification and concentration of natural products (Martins et al., 2006).

Vegetable oil deodorization process produces a distillate rich in high value components such as phytosterols, tocopherols, and fatty acids, depending on the oil or fat. Martins et al. (2006) separated FFAs from soybean oil deodorizer distillate to obtain a tocopherol concentrate, which contained only 6.4% of FFA and 18.3% of tocopherols (from a raw material containing 57.8% of FFA and 8.97% of tocopherols.) The specific processing conditions were an evaporator temperature of 160 °C and a feed flow rate of 10.4 $gmin^{-1}$. Under these conditions, they achieved 96% FFA elimination and 81% tocopherol recovery.

Although molecular distillation is a promising separation and purification method, it is not commonly applied in the olive oil industry. One relevant application is the purification of the structured lipids enzymatically produced from olive oil and caprylic acid (Fomuso & Akoh, 2002). If the advantages and efficiency of the system are further considered, it may be used in the olive oil industry for deacidification and separation of nutraceuticals. The cost of the system and possible alterations in the structure of the oil during the process seem to be serious disadvantages. Therefore, optimization of each particular system is necessary for a successful industrialization.

6. Use of by-products of olive oil industry for waste treatment

The use of by-products of the olive oil industry for waste treatment is another green approach. Solid olive wastes were used for water purification by El-Hamouz et al. (2007). The solid olive residue was processed to yield relatively high-surface area active carbon after extraction of the oil from the residue. The resulting carbon was used to reversibly adsorb chromate ions from water, aiming at a purification process with reusable active carbon. In another study, olive pomace was used as reactive dye biosorbent material for the removal of RR198 textile dye from aqueous solutions (Akar et al., 2009).

Vlyssides et al. (2004) developed an integrated pollution prevention method which decreased wasterwater production 50% from the 3-phase olive oil extraction process. The process included mechanical separation, crushing, mixing, composting, malaxation, 3-phase centrifugation, coagulation flocculation, chemical oxidation, biological treatment, and reed beds steps. Furthermore, a Fenton oxidation process was used to detoxify the wastewater, with the possibility of extracting commercially valuable antioxidant products. They also produced high-quality compost from the solid residues.

7. Conclusions

Current trends show that future oil processing technologies will be based on green processes. Laboratory and pilot scale applications of such processes in the olive oil industry show that they can be used as alternatives to conventional processes. Further optimization studies are necessary for more successful applications. In spite of the high first capital investment, these processes are advantageous considering the market value of the natural products obtained and remediation of environmental pollution.

8. References

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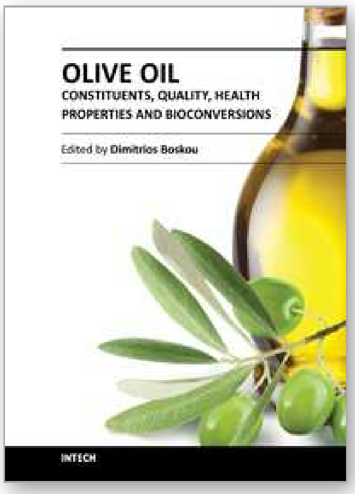

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The health-promoting effects attributed to olive oil, and the development of the olive oil industry have intensified the quest for new information, stimulating wide areas of research. This book is a source of recently accumulated information. It covers a broad range of topics from chemistry, technology, and quality assessment, to bioavailability and function of important molecules, recovery of bioactive compounds, preparation of olive oil-based functional products, and identification of novel pharmacological targets for the prevention and treatment of certain diseases.