Valorization of Solid Waste Residues from Olive Oil Mills: A Review

Dimitrios Kalderis[1] • Evan Diamadopoulos[2*]

[1] Department of Natural Resources and Environment, Technological Educational Institute (TEI) of Crete, Branch of Chania, 73100 Chania, Greece
[2] Department of Environmental Engineering, Technical University of Crete, 73100 Chania, Greece

Corresponding author: * diamad@dssl.tuc.gr

ABSTRACT

The solid waste residues from olive oil mills constitute an environmental threat if disposed of in the natural environment, as it is common practice in many areas. This review summarizes the efforts of the scientific and technical community to develop appropriate technologies for the valorization of these wastes. The majority of the research towards this purpose focuses on the recovery of high-added value compounds, the production of adsorbents, the production of compost or soil amendment products, and applications related to energy generation either through biotechnological processes or through advanced thermal processes.

CONTENTS

INTRODUCTION

Olive oil production is an important agricultural sector in Europe, mainly located in countries and areas bordering the Mediterranean Sea. Long known to many generations in the Mediterranean world as essential to their health and diet, it is now widely appreciated in Europe and around the world for its nutritional properties. The European Union is the leading world producer, accounting for 80% and consuming 70% of the world's olive oil. In 2000, the area under olive groves in the EU was approximately 5,163,000 ha, roughly 4% of the utilizable agricultural area, of which 48% were in Spain and 22.5% were in Italy (European Union-Directorate General for Agriculture and Rural Development 2003). Approximately 2.5 million producers – roughly one third of all EU farmers – are involved, with 1,160,000 in Italy, 840 000 in Greece, 380,000 in Spain, and 130,000 in Portugal. France, the fifth producing country in the EU, has 50,000 growers. Olive oil production in 2007 is estimated to have reached 2.14 million tones, 85% of which was produced in Spain, Italy and Greece (European Union-Directorate General for Agriculture and Rural Development 2007). **Table 1**

Table 1 The main olive oil producing and consuming countries in the world (United Nations (UNCTAD), Market Information in the Commodities Area – Olive oil, 2005).

	World production (%)	World consumption (%)	Annual per capita consumption (kg)
Spain	36	20	13.6
Italy	25	30	12.4
Greece	18	9	23.7
Tunisia	8	2	11.1
Turkey	5	2	1.2
Syria	4	3	6
Morocco	3	2	1.8
Portugal	1	2	7.1
United States	1	8	0.6
France	1	4	1.3
Lebanon	<1	3	1.2

shows the main olive oil-producing and -consuming countries. Olive cultivation is important for the rural economy, local heritage and the environment. Additionally, it is the
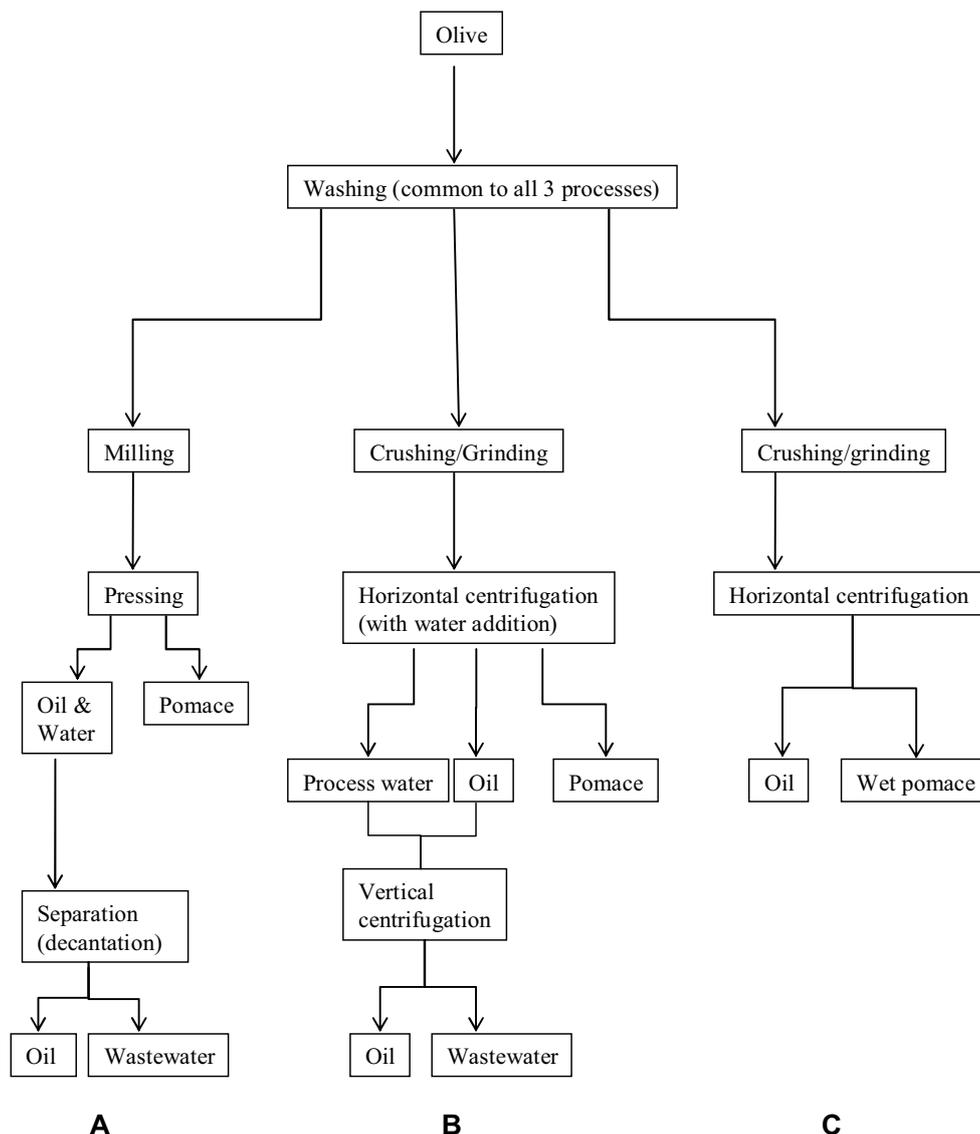
Fig. 1 Flow diagram of the three olive oil extraction processes. (**A**) Traditional method, (**B**) three-phase extraction process, (**C**) two-phase extraction process

main source of employment and economic activity in many producing regions, and it has shaped the landscape in these areas over many centuries.

OLIVE OIL EXTRACTION PROCESS AND WASTE STREAMS

Olive oil extraction is the process of separating and collecting the oil from the olives. Olive oil quality is equally dependent on the quality of the olives themselves, on the time of harvest as well as the extraction method itself. Today, three different extraction processes are commonly used:

- The traditional process
- The 2-phase decanter process
- The 3-phase decanter process

The traditional and 3-phase decanter processes generate one stream of olive oil and two streams of waste, a wastewater and a wet solid, called olive cake or olive pomace, which consists of the seed and the spent olive mass (skin). The 2-phase decanter process generates a stream of olive oil and a mixed stream of wastewater and olive cake. The olive oil yield of these processes is essentially the same, however the amount and composition of the waste streams differs significantly. A brief diagram of the steps involved in each

of these processes is presented in **Fig. 1**. The advantages and disadvantages of each method, as well as other details can be found elsewhere (Borja *et al.* 2006; Boskou 2006; Niaounakis and Halvadakis 2006).

The composition of the waste streams is not constant qualitatively or quantitatively and it varies according to soil cultivation, harvesting time, degree of ripening, olive variety, climatic conditions, use of pesticides and fertilizers and duration of aging (Niaounakis and Halvadakis 2006). **Table 2** shows the typical values for the main properties of the solid and liquid waste streams.

The olive mill waste streams, especially the wastewater (OMW), are a significant source of environmental pollution in the olive oil-producing countries. The uncontrolled disposal of the waste streams is a serious environmental problem, due to their high organic content and the high level of microbial growth-inhibiting compounds, such as phenolic compounds and tannins. The solid fraction has little economic value and only occasionally may be utilized in pomace treatment plants for recovery of pomace oil (a lower grade oil). Most commonly the solid fraction is burned for heating purposes, thus contributing negatively to atmospheric pollution by releasing gaseous and particle emissions to the atmosphere, or disposed of in sanitary and unsanitary landfills.

Due to the current lack of complete management stra-

Table 2 Typical values of the main properties of the olive processing cake and wastewater.

	Wastewater	Olive cake	Reference
pH	4 - 6.7	4.8 - 5.6	Borja *et al.* 2003b, 2006
Redox potential (mV)	-80 to -330	-	Borja *et al.* 2006
Moisture (%)	-	52	Borja *et al.* 2003b
Total volatile fatty acids TVFA (g acetic acid/l)	-	0.7 - 2.20	Borja *et al.* 2003b
Alkalinity (g CaCO$_3$/l)	-	0.73 - 0.35	Borja *et al.* 2003b
Conductivity (mS)	8 - 16	-	Borja *et al.* 2006
Density (g/l)	1 - 1.1	-	Borja *et al.* 2006
Turbidity (NTU)	42000 - 62000	-	Borja *et al.* 2006
Suspended solids (g/l)	1 - 9	35 - 106	Borja *et al.* 2003b, 2006
Biochemical oxygen demand,BOD$_5$ (g/l)	35 - 110	-	Borja *et al.* 2006
Chemical oxygen demand COD (g/l)	45 - 170	34 - 113	Borja *et al.* 2003b, 2006
Total bacteria (10^6 col/ml)	5	-	Borja *et al.* 2006
Total phenolic compounds (g caffeic acid/l)	-	0.6 - 1.8	Borja *et al.* 2003b
Lignin (g/kg)	-	426.3	Alburquerque *et al.* 2004
Hemicellulose (g/kg)	-	350.8	Alburquerque *et al.* 2004
Cellulose (g/kg)	-	193.6	Alburquerque *et al.* 2004
Fats (g/kg)	-	121.0	Alburquerque *et al.* 2004
Protein (g/kg)	-	71.5	Alburquerque *et al.* 2004

tegies, the olive mill wastes pose a potential threat to surface and groundwater resources. Both the liquid and the solid fraction can degrade the soil physical and chemical properties, such as porosity, acidity, salinity and heavy metal content. Additionally, they may have a detrimental effect on the growth of plants and crops, through the phytotoxic properties of some organic compounds present (Niaounakis and Halvadakis 2006; Kapellakis *et al.* 2008).

The main effects of olive mill wastes on natural water bodies are related to their concentration, composition and seasonal production. The most visible effect of OMW pollution is the discoloring of the body water. This change in color is due to the oxidation and subsequent polymerization of tannins giving darkly colored polyphenols, which are difficult to remove from the effluent (Niaounakis and Halvadakis 2006 and references therein). The lipids in OMW form an impenetrable film on the surface of water, which blocks out sunlight and oxygen to microorganisms in the receiving water, leading to a reduction in plant growth and increasing erosion (Kapellakis *et al.* 2008). Other deteriorating effects include eutrophication due to the high phosphorus content and toxicity to aquatic species. Solid mill wastes with high moisture are also a source of odor nuisance, especially during warm and dry weather. These odors are attributed to volatile fatty acids, particularly butyric, caproic, valeric and isobutyric acid (Niaounakis and Halvadakis 2006). Various treatment methods have been applied to olive mill wastewater. Most notably, aerobic and anaerobic processes, electrochemical and Fenton oxidation methods, ozonation, flocculation, adsorption of the waste pollutants on to activated carbon and membrane processes such as reverse osmosis and ultrafiltration (Mantzavinos and Kalogerakis 2005; Sarika *et al.* 2005; Paraskeva and Diamadopoulos 2006; Kapellakis *et al.* 2008).

OLIVE MILL SOLID WASTE VALORIZATION OPTIONS

The targets set out in the Biomass Action Plan (European Union 2005) and Commission Green Paper for "A European strategy for sustainable, competitive and secure energy" (European Union 2006), call for exploitation of the agricultural wastes and the development of integrated waste management schemes. Article 5 of the Landfill Directive states that, by 2016 only 35% of the biodegradable waste produced in 1995 will be allowed to be landfilled (European Union 1999). This practically means that alternative management options are required for olive cake in order to reduce the quantities disposed of in landfills and at the same time protect the environment.

Many solutions have been suggested for the valorization of olive mill wastes but several factors should be considered

when selecting the optimum valorization method, for instance, total amount of waste, investment required to perform the treatment, available land, industrial or agronomic environment, legal framework and last but not least, the local needs. Of all the valorization options examined so far, the following technological solutions appear to be the most promising: isolation and recovery of added value compounds, production of high quality adsorbents, conversion to biofuels for energy production and use in compost mixtures for subsequent land applications. These solutions are examined below.

Recovery of high-added value compounds

Olive fruits contain a wide variety of phenolic compounds that play an important role in the chemical and nutritional properties of olive oil and table olives. These compounds prevent the deterioration of food by inhibition of lipid oxidation and improve the health-promoting properties when they are added. After the mechanical processing of olives for olive oil extraction, less than 1% of the phenolic compounds are found in the olive oil with over 98% being located in the olive-mill wastes (Rodriguez *et al.* 2009) Therefore, the solid residue could be considered a promising source for these compounds. Rodriguez *et al.* (2008) has thoroughly reviewed the characterization and the current, past or potential uses of the whole olive stone. Additionally, the antioxidant, antimicrobial and molluscicidal properties of the total phenolic extract have been well established (Obied *et al.* 2005a, 2005b, 2007, 2008).

An insight into the phenolic composition of the solid residue was brought by Mulinacci *et al.* (2005). The authors tested several extraction methods to determine the optimum process for phenols recovery. The results showed that Soxhlet extraction with ethanol was the optimum method for the recovery of verbascoside, tyrosol and caffeic acid, both in terms of yield and scale-up potential. However, the long extraction times (15 h) of this method was a disadvantage. Suarez *et al.* (2009) studied several methods for preparing antioxidant phenolic extracts from the olive mill solid residues. Through accelerated solvent extraction (ASE), the authors recovered many phenolic compounds, including the known antioxidants tyrosol, hydroxytyrosol, oleuropein and ligstroside in 10 min. After establishing the antioxidant activity of the extracts, the authors claimed that ASE is a feasible process for industrial scale production of antioxidant fractions from olive mill residues.

Using a hydrothermal process, researchers managed to obtain mixtures of monosaccharides and oligosaccharides from wet olive cake (Fernández-Bolaños *et al.* 2004). Through a simple purification process, they were successful in obtaining mannitol, a low-calorie sweetener in the food

industry, in highly pure form. The treated solids were rich in cellulose and residual oil, which allowed for the application of further valorization methods. Under the same methodology, Ghoreishi *et al.* (2009) recovered mannitol from the olive leaves at a yield of 76.7% (w/w).

Instead of the total phenolic fraction, many authors have focused their work in recovering specific substances. Anti-oxidant compounds that have been successfully isolated and obtained in pure form, include hydroxytyrosol (Fernández-Bolaños *et al.* 2002), 3,4 dihydroxyphenylglycol (Rodrí-guez *et al.* 2009), hydroxytyrosyl acyclodihydroelenolate and *p*-coumaroyl-6´-secologanoside (Obied *et al.* 2007).

Production of adsorbents

Activated carbon (AC) is a well known material used in ever increasing numbers of environmental applications, in environment protection, in water and wastewater treatment, in gas filters, etc. AC can be produced theoretically from any carbonaceous material rich in elemental carbon. Typical precursors for AC production were coal, peat and lignite. In the recent years, there is growing interest in the production of ACs from agricultural by-products and residual wastes, including those from olive oil processing.

Depending on the impregnation agent, type and temperature of activation, residence time and reactor design, many ACs have been prepared for a wide range of applications. The preparation of ACs from olive mill residues involved either physical activation using steam, CO_2, N_2 or a mixture of these, or chemical activation using a dehydrating agent such as $ZnCl_2$, H_3PO_4, KOH, $CaCl_2$ or K_2CO_3 (Al-jundi *et al.* 2008; Zabaniotou *et al.* 2008; Silvestre-Albero

Table 3A Carbon preparation and adsorption test parameters.

Impregnating agent	Pyrolysis temperature/°C	Pyrolysis time/min	Activation temperature/°C	Activation time/min	Reference
none	500	60	850	30	Demiral *et al.* 2008
none	600	-	950	-	Rogério-Pereira *et al.* 2006
none	850	120	850	60	El-Sheikh *et al.* 2004a
none	-	-	800	90	Al-Khalid *et al.* 1998
none	600	-	800	-	Plaza *et al.* 2009
none	850	-	800	-	Pala *et al.* 2006
none	850	120	800	40	Galiatsatou *et al.* 2001
none	600	60	800		Schröder *et al.* 2007
none	850	120	850	60	El-Sheikh *et al.* 2004b
none	600	60	850	60	Román *et al.* 2008
none	850	60	825	-	Alvim-Ferraz *et al.* 2003, 2005
none	-	-	300	-	El Bakouri *et al.* 2009
none	-	-	600-800	120	Girgis *et al.* 2002
none	-	-	-	-	Gharaibeh *et al.* 1998
none	600	60	850	30	González *et al.* 2009
none	800	-	-	-	Gañán *et al.* 2006
none	800	120	900	240	Mameri *et al.* 2000
none	1000	60	840	960	Haydar *et al.* 2003
none	750	15	750	240	Moreno-Castilla *et al.* 2003
none	850	90	850	90	Galiatsatou *et al.* 2002
none	850	15	850	240	Pérez-Cadenas *et al.* 2003
none	510	-	800	-	Rodríguez-Valero *et al.* 2001
none	1000	30	850	-	Salas-Peregrín *et al.* 1994
none	-	-	850	1020	Rivera-Utrilla *et al.* 1986
none	850	120	825	-	González *et al.* 1995
none	600	-	800	-	Guiza *et al.* 2004
none	850	120	585-655 (SCW), 800 (steam)	60-660 (SCW)	Molina-Sabio *et al.* 2006
none	-	-	750-850	30-80	Baçaoui *et al.* 2002
none	-	-	-	-	Lòpez *et al.* 2003
none	-	-	700	60	Cimino *et al.* 2005
none	-	-	500	30	El-Hamouz *et al.* 2007
none	-	-	700	30	Nebili *et al.* 2008
KOH	800	60	900	240	Stavropoulos *et al.* 2005
KOH	-	-	800	60	Spahis *et al.* 2008
KOH	600	60	900	60	Martinez *et al.* 2006
KOH	350	60	800	120	Moreno-Castilla *et al.* 2001
KOH	840	60	800	120	Ubago-Pérez *et al.* 2006
KOH	800	60	800	180	Skodras *et al.* 2007
KOH	800	60	900	180	Michailof *et al.* 2008
$ZnCl_2$	500	180	850	120	Silvestre-Albero *et al.* 2009b
$ZnCl_2$	500	-	725	-	Almansa *et al.* 2004
$ZnCl_2$	-	-	650	120	Kula *et al.* 2008
$ZnCl_2$	-	-	650	120	Uğurlu *et al.* 2008
H_3PO_4	800	60	800	-	Lafi *et al.* 2001
H_3PO_4	450	-	450	120	Baccar *et al.* 2009
H_3PO_4	-	-	500	120	Daifullah *et al.* 2003
H_3PO_4	-	-	500	-	Khalil *et al.* 2001
H_3PO_4	-	-	500	120	Rodríguez-Reinoso *et al.* 2008
H_3PO_4	-	-	450	120	Nakagawa *et al.* 2007
K_2CO_3	800	60	950	60	Petrov *et al.* 2008
K_2CO_3	-	-	950	10	Budinova *et al.* 2006
$CaCl_2$	-	-	800	360	Juárez-Galán *et al.* 2009

-: data not performed or not reported

Table 3B Carbon preparation and adsorption test parameters.

Activating agent	BET Surface area (g/m²)	Substance(s) adsorbed	Loading (mg/g)	Reference
Steam	718	Cr	136.6	Demiral *et al.* 2008
Steam	855	Cr	7.8	Rogério-Pereira *et al.* 2006
Steam/N_2	750	-	-	El-Sheikh *et al.* 2004a
CO_2	-	-	-	Al-Khalid *et al.* 1998
CO_2	1079	CO_2	107	Plaza *et al.* 2009
Steam/N_2	800	Remazol GelB 3RS, Remazol RB133, Remazol Schwarz, textile wastewater	-	Pala *et al.* 2006
Steam/N_2	940	-	-	Galiatsatou *et al.* 2001
Steam	850	-	-	Schröder *et al.* 2007
CO_2	677	-	-	El-Sheikh *et al.* 2004b
CO_2/steam	1187	-	-	Román *et al.* 2008
CO_2	1190	-	-	Alvim-Ferraz *et al.* 2003, 2005
-	479	Aldrin	19.5	El Bakouri *et al.* 2009
		Dieldrin	23.7	
		Endrin	43.7	
Steam	515	-	-	Girgis *et al.* 2002
-	-	NH_3; tetrachloroethene; benzothiazole; 1,2-dihydro-2,2,4-trimethylquinoline *N*-dimorpholinyl-ketone; methyl-sulphyl- benzothiazole; methyl-2-benzothiazole sulphone	-	Gharaibeh *et al.* 1998
Steam	813	-	-	González *et al.* 2009
-	489	-	-	Gañán *et al.* 2006
Steam	1813	Phenol	11.2	Mameri *et al.* 2000
CO_2	1696	p-nitrophenol	500	Haydar *et al.* 2003
CO_2	789	-	-	Moreno-Castilla *et al.* 2003
Steam/N_2	914	Zn	31.3	Galiatsatou *et al.* 2002
CO_2	691	-	-	Pérez-Cadenas *et al.* 2003
CO_2	-	-	-	Rodríguez-Valero *et al.* 2001
Steam	1475	CO_2	14.2 (cm³/g)	Salas-Peregrín *et al.* 1994
CO_2	1156	Pb	17.5 (μg/g)	Rivera-Utrilla *et al.* 1986
CO_2	1426	-	-	González *et al.* 1995
Steam	920	O_3	1800 (decomposition)	Guiza *et al.* 2004
Supercritical water, Steam	-	-	-	Molina-Sabio *et al.* 2006
Steam	1145	2,4-dichlorophenocyacetic acid	532.6	Baçaoui *et al.* 2002
		MCPA	469.4	
-	915	Vinegar colour	-	Lòpez *et al.* 2003
-	-	Phenol	19.8	Cimino *et al.* 2005
		Methylene blue	19.2	
		DBSNa	20.9	
		Ag^+	31	
N_2	-	Chromate ions	1.2	El-Hamouz *et al.* 2007
Water vapour	290	Benzene	0.29 (cm³/g)	Nebili *et al.* 2008
		I_2	686.9	
		Methylene blue	145.1	
-	3049	Methylene blue	262	Stavropoulos *et al.* 2005
N_2	1541	-	-	Spahis *et al.* 2008
N_2	-	-	-	Martinez *et al.* 2006
N_2	1768	-	-	Moreno-Castilla *et al.* 2001
N_2/steam	1484	Toluene	720	Ubago-Pérez *et al.* 2006
N_2	1690	Hg	0.87	Skodras *et al.* 2007
N_2	1880	Caffeic acid	259.7	Michailof *et al.* 2008
		Vanillin	182.3	
		Vanillic acid	94.7	
		π-hydroxybenzoic acid	57.1	
		Gallic acid	70.7	
N_2	2127	Ethanol	47.8	Silvestre-Albero *et al.* 2009b
CO_2	-	CH_4	180 (cm³/g)	Almansa *et al.* 2004
N_2	790	Cd	1.85	Kula *et al.* 2008
N_2	790	Remazol Red B	8.5	Uğurlu *et al.* 2008
-	-	Methylene blue	115	Lafi *et al.* 2001
N_2	1062	I_2	583	Baccar *et al.* 2009
		Methylene blue	312.5	
-	848	BTEX	27.9 (total)	Daifullah *et al.* 2003
-	750	-	-	Khalil *et al.* 2001
N_2	>2000	CH_4	170	Rodríguez-Reinoso *et al.* 2008
N_2	~1900	-	-	Nakagawa *et al.* 2007
N_2	1850	I_2	1720	Petrov *et al.* 2008
		Methylene blue	420	
N_2	1850	As	1.39	Budinova *et al.* 2006
CO_2	670	-	-	Juárez-Galán *et al.* 2009

:- data not performed or not reported

et al. 2009a). ACs from the olive mill solid residues have been tested on the adsorption of heavy metals and metal ions, volatile and other organic compounds, for the removal of dyes, pesticides and gaseous by-products. The details of carbon preparation and adsorption tests are summarized in **Table 3**. It can be seen that in the case of physical activation, the minimum activation temperature is 750°C, whereas most authors selected 800°C for the activation step. On the other hand, temperatures in the range of 450–600°C are not uncommon in the case of chemical activation. Large differences are noted in the activation times, these ranging from 10 min to as high as 6400 min. However, statistically it appears that the optimum residence period is 60-120 min.

Instead of AC, Bouzid *et al.* (2008) incinerated olive cake at 600°C for 2 h to produce ash and then tested the removal characteristics of copper from aqueous solution. The ash produced had a surface area of 146.4 m^2/g and showed a copper loading of 6.98 mg/g at an optimum pH of 7.2.

The olive cake has also been utilized as a sorbent for metals without prior carbonization and activation. In these cases, after olive-oil extraction, the spent residue is further extracted with an organic solvent, usually hexane, to remove all residual oil. It is then dried and sieved to the desired particle sizes. This sorbent has shown positive adsorption behavior towards dyes and metals.

El Sha'r *et al.* (1999) tested the adsorption of methylene blue and methyl orange on untreated solid olive mill residues and activated carbon prepared from oil shale. Their results showed that although methylene blue adsorption on the mill residues compared well to that on the activated carbon, methyl orange (anionic dye) adsorption on the olive cake was not equally successful. The authors were among the first to prove that it is possible to prepare a low-cost, efficient sorbent from olive mill solid residues. The results of El Sha'r *et al.* agree well with those reported by Banat *et al.* (2007), who studied the bench-scale and packed bed sorption of methylene blue on hexane-extracted olive cake. A loading of 42.3 mg/g was achieved after 7 h equilibrium time.

The biosorption of copper on raw olive cake was studied by Pagnanelli *et al.* (2002, 2005) and Gondar *et al.* (2009). All authors concluded that the biosorption occurred by a general ion exchange mechanism combined with a specific complexation reaction for copper ions. The copper loadings reported reached values up to 15.8 mg/g. Konstantinou *et al.* (2009) studied the chemical affinity of solid natural organic matter (from olive cake) for Cu^{2+} and Eu^{3+} ions. Their results showed that the chemical affinity of the hydrophilic extracts of the olive cake for the Cu^{2+} ion is identical to the affinity of humic acids for the respective metal ion. This indicates that the same type of active sites (e.g. carboxylic groups) is responsible for the metal binding by various types of natural organic matter. These conclusions were supported by Kolokassidou *et al.* (2009) who studied Cu^{2+} complexation by the hydrophilic olive cake extracts. Potentiometric studies showed that hydrophilic olive cake extract and commercial humic acid possess similar "complexation capacity" and show identical chemical affinity for Cu^{2+}.

Martín-Lara *et al.* (2009) evaluated the surface chemistry of olive stone, olive cake and olive tree prunings for the removal of lead from aqueous solutions. These wastes are able to fix lead ions efficiently, however, the release of harmful organic substances from the matrix is a potential threat to the environment. Blazquez *et al.* (2009) studied the effect of pH on the biosorption of Cr^{3+} and Cr^{6+} on olive stones. The authors concluded that the removal of the ions is highly pH sensitive. The percentage of Cr^{3+} removed reached a maximum at a pH range of 4-6, reaching values of 90%. For Cr^{6+}, the maximum removal of 80% was achieved at a pH value of 2 or lower.

Even without removal of the residual oil, the olive cake has shown considerable adsorption capacity. Akar *et al.* (2009) used dried olive cake without any other pre-treat-

ment for the adsorption of RR198, a reactive dye used in the textile industry. The highest dye biosorption capacity was found at pH 2, at an equilibrium time of 40 minutes and a biosorbent concentration of 3.0 g/l.

USE OF OLIVE CAKE AS SOIL AMENDMENT FOR LAND APPLICATION

Characteristics of olive cake composting process

Land application of olive cake could be a promising solution that would prevent environmental pollution through integration of organic waste with soil constituents. Due to its high organic content, olive mills solid waste can improve soil properties and productivity. The percentage of organic matter in the solid residues is about 93% by mass making it an excellent candidate as a soil amendment that would increase soil organic matter. However, solid residue, need to be mixed with ligno-cellulosic materials, due to its sticky texture, to obtain adequate physical conditions of the starting mixtures (Garcia-Gomez *et al.* 2003). Since the physical and chemical properties of the olive cake are rather unsuitable for direct biodegradation, in Mediterranean areas many complementary residues such as animal manures, olive leaves, cereal straw, pruning wastes or horticultural residues are usually utilized in composting processes (Canet *et al.* 2008; Montemurro *et al.* 2009). Additionally, the use of olive-mill solid waste, natural or previously biostabilized, as an organic amendment for environmental remediation is still largely unexplored.

Several researchers have studied the biological characteristics and biodegradability of the olive cake in various composting compositions and designs (Vlyssides *et al.* 1999; Paredes *et al.* 2002; García-Gómez *et al.* 2003; Albuquerque *et al.* 2004; Baeta-Hall *et al.* 2005; Aqeel and Hameed 2007a). Details of these studies can be found in a thorough review on the current and potential uses of composted olive oil waste by Arvanitoyannis and Kassaveti (2007). The maturity of composted solid olive-mill wastes was assessed by Sellami *et al.* (2008b), using UV spectra and humification parameters. The results showed that the time required to reach maturity was dependant on the chemical properties of the initial raw materials used. One of the key parameters was the lignocellulosic content. As this content increased, more time was required for the compost to reach maturity. Using the same spectroscopic method, Droussi *et al.* (2009) studied in depth the transformation of the olive cake during composting. The authors examined the elemental and spectroscopic characterization of humic-acid-like compounds during composting of olive mill by-products. As composting proceeded, the main transformations concerned a relative increase of proteinaceous materials, an extended degradation of carbohydrates likely due to microbial activity, a decrease in molecular heterogeneity, an increase in unsaturated structures, molecular size, level of conjugated chromophores, aromatic polycondensation, and humification degree.

Cegarra *et al.* (2006) and Alburquerque *et al.* (2009) investigated the composting of olive cake in terms of the bulking agent added and the number of mechanical turnings for aeration. The combination of cow manure as a bulking agent, the highest possible number of mechanical turnings (14) and forced ventilation, resulted in a clear reduction in the composting time, higher mineralization of the substrate and better humification indices. As composting advanced, the germination index increased and the concentration of both fat and water-soluble phenols decreased, indicating a progressive detoxification (Alburquerque *et al.* 2006a). In order to reduce operating costs, the use of mechanical turning without forced ventilation was recommended due to its effectiveness and simplicity of implementation for future industrial scale development of olive cake composting. These results come in good agreement with the results reported by Cayula *et al.* (2006), who evaluated forced aeration and mechanical windrow turning for composting of

Table 4A Properties of composts prepared from olive cake.

pH	Moisture (%)	EC(dS/m)	TOC (g/kg)	C/N	Reference
8.06	16.9	1.50	421	23.5	Montemurro *et al*. 2009
8.67	-	4.81	434.8	16.6	Cegarra *et al*. 2009
8.88	14	3.07	491.5	22.7	Alburquerque *et al*. 2006b
8.90	-	3.09	489	22.3	Alburquerque *et al*. 2007
8.78	-	3.71	102.2	19.5	Alburquerque *et al*. 2009
7.75	-	-	468.4	15.5	García-Gómez *et al*. 2003
8.08	44.8	-	-	20.3	Sellami *et al*. 2008a
8.34	-	5.48	22.3 (%)	13.6	Hachicha *et al*. 2008
8.9-9.3	-	5.4	20.3(%)	11.9	Hachicha *et al*. 2009
8.4	-	2.4	233	16	Romero *et al*. 2005
9.67	42	15.4	41.2(%)	15.8	Canet *et al*. 2008 (Pile 1)
8.6	-	6.66	-	26.2	Alfano *et al*. 2008 (Pile 4)
8.4	-	-	329	16	Moreno *et al*. 2008

:- data not performed or not reported

Table 4B Properties of composts prepared from olive cake.

g/kg									Reference
N	K	Na	Fe	P	Zn	Cu	Ni	Pb	
17.9	-	-	-	6.7	0.2	0.16	0.05	0.1	Montemurro *et al*. 2009
150	42.5	4.1	1.5	1.9	0.14	0.04	-	-	Cegarra *et al*. 2009
21.7	24.9	2.6	0.7	1.5	0.04	0.02	0.008	0.004	Alburquerque *et al*. 2006b
194	27.5	-	0.9	1.4	0.04	0.02	-	-	Alburquerque *et al*. 2007
24.1	37.2	2.6	0.9	1.7	0.08	0.03	0.007	0.011	Alburquerque *et al*. 2009
30.2	-	-	-	-	-	-	-	-	García-Gómez *et al*. 2003
-	21.5	-	-	8.1	-	-	-	-	Sellami *et al*. 2008a
1.6(%)	2.6(%)	1.2(%)	-	0.9(%)	-	-	-	-	Hachicha *et al*. 2008
1.7(%)	31.2	-	16.3	7.1	-	-	-	-	Hachicha *et al*. 2009
15	-	-	-	2.1	0.044	-	-	0.006	Romero *et al*. 2005
2.6(%)	4.5(%) as in K_2O	0.5(%)	2.6	2(%) as in P_2O_5	0.19	0.09	0.015	0.004	Canet *et al*. 2008 (Pile 1)
1.3(%)	1.3 (%)	-	-	0.65(%)	-	-	-	-	Alfano *et al*. 2008 (Pile 4)
20	12	-	-	2.9	-	-	-	-	Moreno *et al*. 2008

olive mill solid wastes. The study revealed that during forced aeration preferential pathways can be formed, therefore frequent mechanical turnings are necessary to overcome this problem. The results of Alfano *et al*. (2008) also indicate that mechanical turning of the compost is the optimum solution for adequate aeration. The authors went a step further, by performing an economic evaluation of the composting process. The cost of the complete composting process in the first year amounted to 4200 €, finalizing the cost of the mature compost to 0.63 €/kg. Continuous operations in the subsequent years would reduce the cost to 0.12 €/kg, retail price.

Another important parameter of the composting process is the pH value of the final product. As seen in **Table 4**, the pH range is 7.75–9.67, which means the composts are moderately alkaline. It would be therefore beneficial to develop a mechanism for pH control during the composting process. Roig *et al*. (2004) studied the use of elemental sulphur as an alternative to control pH during composting of olive mill wastes. A concentration of 0.5% in sulphur (dry weight basis) and moisture of 40% were determined as the optimum conditions to decrease the compost pH by 1.1 units without increasing in electrical conductivity to levels that may impose a limitation for its agricultural use. Recently, Sánchez-Arias *et al*. (2008) examined the effect of incorporating an acidic ferrous sulphate waste (SF) over a co-composting process of sewage sludge and olive mill solid wastes. The optimum – in agronomic terms – product, was obtained when a 20% of SF was added, under thermophilic conditions, to a mixture 1: 2 of domestic sewage sludge and olive mill solid waste. The addition of SF resulted in a lower pH value of the compost and higher Fe and S availability to the soil.

Montemurro *et al*. (2009) studied the evolution of the most important parameters (temperature, pH, electrical conductivity, total organic carbon, total nitrogen, and C/N ratio) describing the composting process of olive oil husk with other organic wastes. Of all the composts produced, that

with tree prunings and urea exhibited the best agronomic value. The suitability of the olive cake as a compost ingredient was also confirmed by Vlyssides *et al*. (2008), who investigated the porosity, water content, air pressure drop during the composting process.

Applications of olive-cake amended composts

1. Effects on soil properties and crops

The effects of the direct application of solid olive mill waste to several soil properties have been thoroughly investigated. Abu-Zreig *et al*. (2002) reported that land application of raw olive cake increased water retention and saturated hydraulic conductivity in the soil, which may lead to improved water availability for crops. Tejada and Gonzalez (2007) added that the bulk density, aggregate instability and soil loss under simulated rain were also reduced. Finally, Kavdir and Killi (2008) also noticed an increase in soil aggregate stability and organic nitrogen and carbon content after one month of application.

Composts from the solid olive mill residues have been tested on a variety of crops. Hachicha *et al*. (2008, 2009) assessed the properties and application of composts prepared from olive cake, olive mill wastewater and poultry manure to potato plants. In terms of agronomic value, composting olive cake with poultry manure and watered with OMW lead to a stable and mature product that supplied nutrients to plants. It is important to point out, that compost containing OMW is efficient and free from any phytotoxic elements since no acute effect on the development of potato plants were observed. Furthermore, using compost watered with OMW as soil amendment did not have any short-term negative impact on soil properties after harvesting, notably the pH, electrical conductivity (EC) and soluble phenol content of the soil down to a 0.60 m depth. The same team developed a composting process for olive cake, poultry manure and sesame shells (Sellami *et al*. 2008a). The final

product was characterized by its relatively high organic matter content, and low C/N ratio of 14–17. The application of the obtained compost to soil appeared to significantly improve both soil fertility and crop (potato) yield. Similarly, Alburquerque *et al*. (2006b, 2007) evaluated the application of compost prepared from the olive cake on pepper and ryegrass cultivation. The compost obtained was free of toxicity, rich in organic matter (mainly composed of lignin), and had a considerable potassium and organic nitrogen content but was low in phosphorus and micronutrients. It also demonstrated a considerably greater resistance to soil biodegradation in the harsh thermal conditions of the greenhouse. Brunetti *et al*. (2005) investigated the application of exhausted olive cake on durum wheat fields. This soil amendment affected positively durum wheat yields in Mediterranean conditions by increasing the spike density and especially the kernel number per unit area and kernel weight. The enhanced amount of organic matter in olive pomace-amended soils appeared to play a major role in improving wheat performance. The positive effect of this type of compost was also shown on the growth and productivity of the faba bean (Aqeel *et al*. 2007b). Chemical analyses revealed that after the compost application, the levels of zinc, nitrogen, potassium and iron in the beans had increased. In an effort to minimize the cost of olive-oil production, Altieri *et al*. (2008) applied the solid residues mixed with wheat straw and saw dust to olive tree farms. The results showed significant increases in total organic carbon and humic substances in soil of approximately 40% and 58%, respectively, without negative effects on tree growth and yield. Therefore, the use of olive cake-based composts could be an environmentally-friendly, economic alternative to the use of expensive chemical fertilizers.

Nogales *et al*. (1999) and Benítez *et al*. (2002) have thoroughly investigated the vermicomposting of olive cake, mainly using the earthworm *Eisenia andrei*. This species grew and reproduced favourably in the dry olive cake, especially when the by-product was mixed with municipal biosolids and cattle manure. The vermicompost displayed a high degree of stability, as demonstrated by the complete absence of phytotoxicity. More importantly, this vermicompost was applied to a trichloroethylene-contaminated soil (Moreno *et al*. 2008). Trichloroethylene-inhibited soil enzyme activities are involved in the biochemical cycles of carbon, phosphorus, nitrogen and sulphur. The organic matter released by the vermicomposted olive waste tended to avoid the toxic effect of the contaminant.

Table 4 shows some basic properties of selected composts prepared from olive mill solid waste. It is interesting to note, that regardless of the bulking material used, the aeration process, the time to reach maturity and other parameters, all authors produce composts with very similar physical and chemical properties.

2. Interaction with soil contaminants

Addition of raw or composted olive cake to agricultural soils is becoming a common practice as a disposal strategy and to improve the physical and chemical soil properties. However, in order to optimize the use of organic wastes as soil amendments, their effect on the behaviour of other compounds that are also used in agriculture, such as pesticides, needs to be assessed. Albarran *et al*. (2003, 2004) investigated the behaviour (sorption, degradation, leaching) of simazine in soil amended with olive cake. Using a sandy loam soil as the basis for the experiments, the extent and strength of sorption of simazine was increased, biodegradation was reduced and leaching was retarded compared to the untreated soil. Therefore, amendment with the solid residues may be useful to prolong the residence time of the herbicide in the topsoil and to reduce the risk of ground water contamination as a result of simazine leaching losses. Cabrera *et al*. (2007, 2008a, 2008b, 2009) studied the effects of addition of solid olive mill wastes, either raw or composted, to the fate of herbicides, diuron, terbuthylazine

and atrazine in soil. Their results showed an increase in soil sorption of all herbicides in laboratory studies, as compared to untreated soils. Field studies revealed that the addition of these organic amendments increased the amounts of the herbicides present in the soil. Delgado-Moreno *et al*. (2007, 2009) performed sorption and degradation studies in sterile and microbially active soil to evaluate the effect of the chemical and biological degradation of simazine, terbuthylazine, cyanazine and prometryn. The results of the sorption studies agree well with those obtained by Cabrera *et al*. The hydrophobic herbicides terbuthylazine and prometryn increased their retention on amended soil whereas the more polar herbicides simazine and cyanazine were less affected. Soil application of raw olive cake, resulted in the highest herbicide retention. The addition of compost and vermicompost enhanced the biological degradation rate of the herbicides during the first week of incubation, whilst negligible degradation occurred in non-amended soil during this period. In contrast, olive cake did not significantly modify the degradation of the herbicides. Redondo-Gómez *et al*. (2007) studied the behavior of diuron and simazine in soils from a different point of view. The authors investigated the effect of these herbicides on the photochemistry of the tree *Olea europaea* L., and whether the amendment of soil with the solid residues from the olive oil production industry modified this effect. Soil application of these herbicides reduced the efficiency of Photosystem II photochemistry of olive trees due to chronic photoinhibition, and this effect is counterbalanced by the addition of olive cake to the soil. The olive cake reduces herbicide uptake by the plant due to an increase in herbicide adsorption by the soil. This conclusion comes in good agreement with the results reported earlier by Albarran *et al*. and Cabrera *et al*.

Quite different results were obtained by Undabeytia *et al*. (2004), who studied the effects of olive mill solid wastes on the retention and mobility of the herbicide imazaquin in four different soils. The addition of fresh solid amendments on the soil decreased the adsorption of the herbicide because much of the mineral and organic soil surfaces become blocked, with the exception of the sandy soil, which had originally very few adsorptive surfaces. Based on the results from imazaquin, the authors suggested that the application of the solid olive mill residues to soil cannot be accepted as a general practice to reduce herbicide losses due to leaching processes.

Romero *et al*. (2005) studied the suitability of composted olive-mill solid waste for initial reclamation of a mine tailing with high concentrations of Pb and Zn. Their results showed that the solubility and extractability of the Pb and Zn contained in the mine tailings, was increased. These increases represented an advantage where Pb/Zn-mine tailings are reclaimed by phytoextraction, effectively reducing the metal pollution in these mining wastes.

DIRECT COMBUSTION FOR ENERGY

Traditionally, olive cake is combusted without any control in conventional systems in rural areas of many Mediterranean regions. During this uncontrolled combustion process, CO and hydrocarbons are formed at considerable amounts in the flue gas, which pose a significant environmental threat. Co-combustion of coal and biomass is an attractive alternative for disposing of waste products. Besides, replacing part of coal with biomass such as olive cake reduces the overall cost of energy and heat production.

Fluidized bed technology is a good means for converting a wide range of agricultural residues into energy due to its inherent advantages such as fuel flexibility and low operating temperature (Natarajan *et al*. 1998). Thus, several research efforts have used as-received olive cake in fluidized bed combustors (Cliffe and Patumsawad 2001; Armesto *et al*. 2003; Topal *et al*. 2003; Gayan *et al*. 2004; Al-Widyan 2006; Miranda *et al*. 2007; McIlveen-Wright *et al*. 2007; Varol and Atimtay 2007; Atimtay and Varol 2009). Although in all cases the efficiency of the combustion pro-

cess was slightly reduced, so were the HCl, SOx, CO_2 and hydrocarbons emissions.

BIOFUEL PRODUCTION

According to the technology utilized in olive oil processing, the amount of energy consumption, with reference to one ton of treated olives, is 48,000–65,000 kJ (Caputo *et al.* 2003) However, olive mill wastes are characterized by a significant energy content: in fact, the biogas obtained by treating one cubic meter of OMW through anaerobic digestion contains 60–80 kWh of energy (Schmidt and Knobloch 2000), while exhausted olive cake is characterized by a fairly high heating value (18,000 kJ/kg) and by low nitrogen and sulphur content. Therefore, waste treatment technologies aiming at energy recovery represent an interesting alternative for a sustainable disposal of residues from olive oil production able to reduce the environmental impact and to generate electric energy for sale or satisfy the energy needs of oil mills. The efficient operation of thermochemical conversion systems requires a thorough understanding of the influence of the composition and thermal properties of these byproducts on their behaviour during the conversion process. García-Ibañez *et al.* (2006) studied the thermal behaviour of two olive-oil residue samples (non-leached and water-leached olive-oil residue) at three heating rates (10, 20, and 50°C min^{-1}) in air atmosphere using the technique of thermogravimetric analysis. Their results concluded that the water-leached olive-oil residue sample is more degradable through thermochemical conversion processes in comparison with non-leached olive-oil residue sample. Additionally, the higher the cellulosic content of the sample, the higher is its thermal degradation rate. Researchers have achieved in obtaining various bio-oil and biogas compositions from the dry solid residues mainly through the methods of anaerobic digestion, pyrolysis and gasification. The results obtained with these processes are presented below.

Anaerobic digestion

Biogas production by anaerobic digestion of biomass, in combination with other technologies, can help in partially replacing fossil fuel-derived energy and thereby in reducing environmental impact by providing a clean fuel from renewable feedstock. Anaerobic co-digestion of energy crops and a variety of residual biomasses may be a good integrated solution, particularly with wastes that are unsuitable for direct disposal on land, such as olive mill wastes.

Various anaerobic digesters have been used for the investigation of the biofuel components from the olive cake. Borja *et al.* (2003a) used a stirred tank reactor at mesophilic temperature to study the methane production of olive pomace. The results obtained demonstrated that the rates of substrate uptake and methane production were correlated with the concentration of biodegradable total chemical oxygen demand (COD). The methane yield coefficient was calculated at 0.25 m^3/kg COD removed. Gavala *et al.* (2005) also studied the potential of olive cake for biohydrogen and methane production using a CSTR (continuous stirred tank reactor) anaerobic digester. It was proved that the olive cake is an ideal substrate for methane production with approximately 0.28 m^3 CH_4 produced/kg COD removed. This value is comparable to that obtained by Borja *et al.* It has been also shown that bio-hydrogen production can be very efficiently coupled with a subsequent step of methane production.

Schievano *et al.* (2009) substituted energy crops with organic wastes and agro-industrial residues for biogas production in anaerobic digesters. When energy crops were partially substituted with agro-industrial residues other than olive mill wastes, the initial cost of 0.28 € N/m^3 dropped to 0.18 € N/m^3. Furthermore, when the organic fraction of municipal solid waste and olive cake were used as co-substrates (at the same percentage), the cost was reduced to -0.20 and 0.11 € N/m^3, respectively. The negative value

means that operators earn money by treating the waste. The value of 0.11 € N/m^3 represents a 60% reduction compared to the initial price, therefore the incorporation of olive cake in energy crops is a cost-effective way to provide electric and thermal power.

Pyrolysis

Pyrolysis is the thermal decomposition of materials in the absence of oxygen or when significantly less oxygen is present than required for complete combustion. Mohan *et al.* (2006) provides a critical review on the pyrolysis of nearly 100 types of biomass, including olive cake. The authors present detailed information on conventional and fast pyrolysis reactors, on the mechanisms of cellulose, hemicelluloses and lignin transformation and put emphasis on the bio-oil yield and composition, rather than the char or biogas.

The chemistry and product distribution during pyrolysis of olive cake have been extensively studied (Zabaniotou *et al.* 2000; Demirbas 2001a, 2001b; Blanco-López *et al.* 2002; Çağlar and Demirbas 2002; Demirbas 2002; Taralas and Kontominas 2005; Mehmeti *et al.* 2008). A series of studies have been performed to examine the effects of various physical characteristics of olive cake. Encinar *et al.* (1996, 1998) and Chouchene *et al.* (2010) investigated the influence of temperature, particle size and oxygen concentration during pyrolysis of the olive cake. The first reported that pyrolysis of olive cake lead to three phases (solid, liquid and gaseous) whose yields are strongly dependent on temperature and practically independent of particle size under the conditions of their studies. The experiments of the latter were performed under one inert and two oxidative atmospheres. They found that the loss of humidity and volatiles were independent of the oxygen concentration. However, the initial temperature of char oxidation was decreasing with the increase of oxygen concentration. Weight loss profiles, as well as CO and CO_2 emission rates during the oxidative pyrolysis depended on the particle size of the residues. The temperature range of volatilization and char oxidation as well as the amount of remaining ash also depended on the particle size. Samples having size lower than 0.5 mm, are the most reactive and lead to lower char yields. In contrast to Encinar *et al.*, Chouchene *et al.* suggested that olive solid waste with diameter between 2-2.8 mm had the lowest remaining ash and higher char yield during oxidative pyrolysis under 10% of O_2. This conclusion was also supported by Demirbas *et al.* (2004) who noticed that the bio-char yield increased with increasing particle size of the sample, while the pyrolysis temperature increased, the bio-char yield decreased.

Using a fixed bed tubular reactor, Uzun *et al.* (2007) examined the rapid pyrolysis of the olive mill residue for the production of bio-oil. The authors reported that placing the material into a basket (instead of placing it in direct contact with the reactor), improved the oil yield. The maximum oil yield obtained was 41.4% at a temperature of 500°C. The product had a heating value of 22.6 MJ/kg, which is higher compared to typical bio-oils.

The objective of Encinar *et al.* (2008, 2009) was to characterize the solid, liquid and gaseous phases of the olive cake pyrolysis in terms of their energy content, in the temperature range of 400-900°C. It was determined that the increase in temperature resulted in a decrease in the solid and liquid yields and to an increase in the gas yield. It appears that this is a common conclusion drawn from most researchers that deal with pyrolysis of olive cake. The authors suggested that the appropriate working temperatures would probably lie between 600 and 700°C, where charcoals with the highest heating value are obtained with satisfactory contents of fixed carbon and volatile matter, and the heating values of the gases is acceptable. Miranda *et al.* (2007) evaluated the combustion behavior of liquid and solid olive mill wastes in a prototype rectangular combustion chamber. They concluded that both the olive kernel and the residual olive cake present a good behavior in the prototype furnace,

with suitable efficiency and a reduced presence of unburned mass. The heating value of the olive cake was determined as 22.4 MJ/kg.

Jauhiainen *et al*. (2004, 2005) dealt with the human and environmental risk involved with the pyrolysis of the residues. They studied the kinetics and evaluated the potential for hazardous gaseous emissions from the pyrolysis and combustion of olive mill solid waste. Their work involved the identification and quantification of the combustion pollutants produced in a laboratory horizontal furnace. The thermal treatment was found to produce low amounts of pollutants, and in fact a small quantity of oxygen was enough to diminish the yields to extremely low levels, showing this way that the combustion efficiency was high. The ashes contained a significant quantity of potassium, however, no toxic or dangerous inorganic compounds were detected.

Gasification

Gasification is a process that converts carbonaceous materials, such as coal, petroleum, biofuel, or biomass, into carbon monoxide and hydrogen (syngas) by reacting the raw material at high temperatures with a controlled amount of oxygen and/or steam. The advantage of gasification is that the use of the syngas is potentially more efficient than direct combustion of the original fuel because it can be combusted at higher temperatures or even in fuel cells, so that the thermodynamic upper limit to the efficiency is higher. Gómez-Barea *et al*. (2005) and Skoulou *et al*. (2008a) used bubbling-fluidized-bed reactors to study the gasification performance of olive cake. The pilot-plant gasification tests were carried out at atmospheric pressure and temperatures within the range of 700-850°C in order to assess the technical viability of gasifying untreated olive stone. Both studies revealed that the gasification process at higher temperatures is better as far as the carbon conversion and gas yield are concerned. The well-known ash-related problems of olive stone, such as sintering and agglomeration deposition, were overcome by using ofite and olivine as an inert bed material, respectively. Both authors reported an optimum air-to-biomass equivalence ratio in the range of 0.2-0.26. Using the same type of gasifier, Fryda *et al*. (2008) studied the agglomeration tendency during the gasification of two energy crops (giant reed and sweet borghum bagasse) and olive cake. Olivine and quartz were used as bedding materials. The defluidisation temperatures of the energy crops were 790 and 810°C respectively, in both bed materials, while the olive cake caused defluidisation of the quartz bed at 830°C and olivine bed at >850°C. Gasification of olive

cake resisted defluidisation up to higher temperatures because of its lower potassium and higher calcium content, especially in the case of olivine bed.

Using a downdraft fixed-bed gasifier, Skoulou *et al*. (2008b) reported that gasification with an equivalence ratio of 0.42 at high temperatures (950°C), favored gas yields and heating values. Syngas production increased with reactor temperature, while CO_2, CH_4, light hydrocarbons and tar followed the opposite trend. These findings agree with those reported by García-Ibañez *et al*. (2004) who studied the gasification of olive cake in a circulating fluidized bed reactor. High temperature steam gasification is another effective technology for production of hydrogen-rich gas from olive kernels (Skoulou *et al*. 2009). Athanasiou *et al*. (2009) proposed a different scheme for the gasification of olive cake. The integration of solid oxide fuel cells (SOFCs) in biomass gasification–turbine processes was studied for the estimation of the overall electrical efficiency. An equivalence ratio of 0.21 was determined as the optimum. The results showed that the overall electrical efficiency of the integrated process for olive kernel can, ideally, reach 62% of the heating value of the biomass feed, whereas conventional technologies, like turbines, can only randomly reach 40% of the heat supplied to their inlet.

Considerable work has been performed on the co-gasification of biomasses with coal. Co-gasification of poor quality coals mixed with wastes has the advantage of diversifying energy resources and decreasing the dependency on fossil fuels. This practice has the potential to reduce both NOx and SOx levels from existing pulverized coal fired power plants. A comprehensive introduction in the co-firing of biomass with coal, the parameters involved and the economics of the process is provided by Demirbas 2003. Rui Neto *et al*. (2005, 2009) studied the effect of experimental conditions on the co-gasification process at a pilot scale fluidized bed reactor, to enhance gas production and improve its composition and energetic content. They pointed out that the olive cake content should not exceed 40% (w/w) to guarantee gasification stabilization and to prevent the formation of high amounts of tars and heavier hydrocarbons. The presence of dolomite in the fluidized bed had the benefit of decreasing tars content and rising gas yield, the gas being richer in hydrogen content. The optimum temperature was determined in the range of 850-900°C.

The economical feasibility of biomass utilization for direct production of electric energy by means of combustion and gasification-conversion processes, has been investigated and evaluated over a capacity range from 5 to 50 MW, taking into account total capital investments, revenues from energy sale and total operating costs, also including a

Table 5 Comparison of char, tar and biogas characteristics.

	Temperature (°C)	Char yield (%)	Char heating value (MJ/kg)	Tar yield (%)	Tar heating value (MJ/kg)	Biogas yield (%)	Biogas heating value (MJ/Nm³)
Uzun *et al*. 2007	550	-	-	38.1	22.6	-	-
Encinar *et al*. 1996	900	-	9.5	-	-	-	1.8
Encinar *et al*. 1998	600	32.1	-	46.3	-	21.6	25
Encinar *et al*. 2009	700	22.3	28.8	31.2	3.1	46.5	15.3
Encinar *et al*. 2008	700	24	29.6	34.2	3.6	41.7	5.2
Skoulou *et al*. 2008a	750	-	-	-	-	-	6.5
Skoulou *et al*. 2008b	950	-	-	-	-	-	8.6
Skoulou *et al*. 2009	1050	20	25.5	-	25.2	-	13.6
Gómez-Barea *et al*. 2005	700	-	-	-	-	1.56 (kg/kg)	5.2
Zabaniotou *et al*. 2000	600	33	-	29	-	33	-
Demirbas 2001a	877	32.8	32.8	13.4	-	54.4	-
Demirbas 2001b, 2002	750	22.8	-	32.6	-	44.6	-
Çağlar and Demirbas 2002	700 (6.7 wt.% ZnCl₂ used as catalyst)	29.8	-	39.6	-	30.6	-
Demirbas 2004	800	32	-	-	-	-	-
Blanco-López *et al*. 2002	600	35	12.2	58	7.3	7	1.9
Taralas *et al*. 2009	700	10	-	15	-	75	5.9
García-Ibañez *et al*. 2004	780	-	-	-	-	-	3.8
Athanasiou *et al*. 2009	950	-	-	-	-	35	10.5

- : data not performed or not reported

detailed evaluation of logistic costs (Caputo *et al*. 2005). The authors evaluated two different experimental cycles: fluid bed combustor and steam turbine cycle (C/ST) and fluid bed gasifier and combined gas–steam cycle (G/CC). It was found that profitability of both C/ST and G/CC plant configurations strongly improved with scale-up of plant size. At the same time logistic constraints on economic performances become less restrictive with increasing sizes. Under current technological and market conditions, the combustion-based solution shows better profitability. The waste-to-energy possibilities of the industrial olive and wine-grape by-products were investigated by Celma *et al*. (2007). The watery husk sludge from two-phase olive mills was found to be the waste product with the greatest specific cost of use 8.09 € G/J. Its integration into the energy conversion schemes that were studied would, however, eliminate the costs of treatment in external plants or the environmental problems involved in drying it onsite in open ponds.

Table 5 summarizes the yields and heating values of chars, tars and oils obtained by the authors.

OTHER VALORIZATION OPTIONS

Natural fibers, used to fill and reinforce both thermoplastics and thermosets, represent one of the fastest-growing types of polymer additives. Wood is the main natural fiber used, followed by other fibers such as kenaf, jute, hemp, flax, and sisal. Siracusa et al. (2001) optimized the technology for the production of new plastic composites containing olive cake. They showed that the thermal behavior of olive cake is the fundamental parameter that affects the whole process. Due to the production of volatiles at temperatures above 200°C, the final composite contains voids which affect the mechanical properties of the product. Finally, the authors concluded that the incorporation of the olive cake to composites is possible only if the biomass is fully dehydrated and the temperature is maintained between 180-200°C.

CONCLUSIONS

The solid waste residues from olive oil mills constitute an environmental threat if disposed of in the natural environment, as it is common practice in many areas. This review summarizes the efforts of the scientific and technical community to develop appropriate technologies for the valorization of these wastes. The majority of the research towards this purpose focuses on the recovery of high-added value compounds, the production of adsorbents, the production of compost or soil amendment products, and applications related to energy generation either through biotechnological processes or through advanced thermal processes. Among the substances which were recovered, phenolic compounds are of interest due to their antioxidant and antimicrobial potential. Energy utilization of olive cake is currently limited as combustion material (mainly after extraction of the pomace oil) in boilers for heating of small installations, such as greenhouses, brick production, etc. More recent efforts have concentrated on either combustion in advanced combustion reactors or in co-combustion with coal. Activated carbons with surface areas equivalent to commercially available ones have been prepared (typical surface areas ranged from 500 to 1500 m^2/g). The adsorptive capacity of these for the removal of heavy metals and organic substances has also been demonstrated. Other thermal processes investigated include pyrolysis (for liquid products) and gasification (for gaseous products). Biogas can also be produced during anaerobic co-digestion of both the solid and liquid wastes of olive mills. Finally, the olive cake can be utilized as soil amendment for land application after appropriate biological treatment (composting). Despite extensive research in these areas, further evaluation is necessary with regards to process scale-up and economic feasibility.

REFERENCES

Abu-El-Shár WY, Gharaibeh SH, Mahmoud S (2000) Removal of dyes from aqueous solutions using low-cost sorbents made of solid residues from olive-mill wastes (JEFT) and solid residues from refined Jordanian oil shale. *Environmental Geology* **39**, 1090-1094

Abu-Zreig M, Al-Widyan M (2002) Influence of olive mills solid waste on soil hydraulic properties. *Communications in Soil Science and Plant Analysis* **33**, 505-517

Akar T, Tosun I, Kaynak Z, Ozkara E, Yeni O, Sahin EN, Akar ST (2009) An attractive agro-industrial by-product in environmental cleanup: Dye biosorption potential of untreated olive pomace. *Journal of Hazardous Materials* **166**, 1217-1225

Albarrán A, Celis R, Hermosín MC, López-Piñeiro A, Cornejo J (2004) Behaviour of simazine in soil amended with the final residue of the olive-oil extraction process. *Chemosphere* **54**, 717-724

Albarrán A, Celis R, Hermosín MC, López-Piñeiro A, Ortega-Calvo JJ, Cornejo J (2003) Effects of solid olive-mill waste addition to soil on sorption, degradation and leaching of the herbicide simazine. *Soil Use and Management* **19**, 150-156

Alburquerque JA, Gonzálvez J, García D, Cegarra J (2004) Agrochemical characterization of "alperujo", a solid by-product of the two-phase centrifugation method for olive oil extraction. *Bioresource Technology* **91**, 195-200

Alburquerque JA, Gonzálvez J, García D, Cegarra J (2006a) Measuring detoxification and maturity in compost made from "alperujo", the solid by-product of extracting olive oil by the two-phase centrifugation system. *Chemosphere* **64**, 470-477

Alburquerque JA, Gonzálvez J, García D, Cegarra J (2006b) Composting of a solid olive-mill by-product ("alperujo") and the potential of the resulting compost for cultivating pepper under commercial conditions. *Waste Management* **26**, 620-626

Alburquerque JA, Gonzálvez J, García D, Cegarra J (2007) Effects of a compost made from the solid by-product ("alperujo") of the two-phase centrifugation system for olive oil extraction and cotton gin waste on growth and nutrient content of ryegrass (*Lolium perenne* L.). *Bioresource Technology* **98**, 940-945

Alfano G, Belli C, Lustrato G, Ranalli G (2008) Pile composting of two-phase centrifuged olive husk residues: Technical solutions and quality of cured compost. *Bioresource Technology* **99**, 4694-4701

Aljundi IH, Jarrah N (2008) A study of characteristics of activated carbon produced from Jordanian olive cake. *Journal of Analytical and Applied Pyrolysis* **81**, 33-36

Al-Khalid TT, Haimour NM, Sayed SA, Akash BA (1998) Activation of olive-seed waste residue using CO$_2$ in a fluidized-bed reactor. *Fuel Processing Technology* **57**, 55-64

Almansa C, Molina-Sabio M, Rodríguez-Reinoso F (2004) Adsorption of methane into ZnCl$_2$-activated carbon derived discs. *Microporous and Mesoporous Materials* **76**, 185-191

Altieri R, Esposito A (2008) Olive orchard amended with two experimental olive mill wastes mixtures: Effects on soil organic carbon, plant growth and yield. *Bioresource Technology* **99**, 8390-8393

Alvim-Ferraz MCM, Gaspar CMTB (2003) Impregnated active carbons to control atmospheric emissions 2. Influence of the raw material on the porous texture. *Journal of Colloid and Interface Science* **266**, 160-167

Alvim-Ferraz MCM, Gaspar CMTB (2005) Impregnated active carbons to control atmospheric emissions: influence of impregnation methodology and raw material on the catalytic activity. *Environmental Science and Technology* **39**, 6231-6236

Al-Widyan MI, Tashtoush G, Hamasha AM (2006) Combustion and emissions of pulverized olive cake in tube furnace. *Energy Conversion and Management* **47**, 1588-1596

André RN, Pinto F, Franco C, Dias M, Gulyurtlu I, Matos MAA, Cabrita I (2005) Fluidised bed co-gasification of coal and olive-oil industry wastes. *Fuel* **85**, 1635-1644

Aqeel AM, Hameed KM (2007a) Implementation of olive mill by products in agriculture. *World Journal of Agricultural Sciences* **3**, 380-385

Aqeel AM, Hameed KM, Alaudatt M (2007b) Effect of olive mill by-products on mineral status, growth and productivity of faba bean. *Journal of Agronomy* **6**, 403-408

Armesto L, Bahillo A, Cabanillas A, Veijonen K, Otero J, Plumed A, Salvador L (2003) Co-combustion of coal and olive oil industry residues in fluidised bed. *Fuel* **82**, 993-1000

Arvanitoyannis IS, Kassaveti A (2007) Current and potential uses of composted olive oil waste. *International Journal of Food Science and Technology* **42**, 281-295

Athanasiou C, Vakouftsi E, Coutelieris FA, Marnellos G, Zabaniotou A (2009) Efficiencies of olive kernel gasification combined cycle with solid oxide fuel cells (SOFCs). *Chemical Engineering Journal* **149**, 183-190

Atimtay AT, Topal H (2004) Co-combustion of olive cake with lignite coal in a circulating fluidized bed. *Fuel* **83**, 859-867

Atimtay AT, Varol M (2009) Investigation of co-combustion of coal and olive cake in a bubbling fluidized bed with secondary air injection. *Fuel* **88**, 1000-1008

Baçaoui A, Dahbi A, Yaacoubi A, Bennouna C, Maldonado-Hódar FJ, Rivera-Utrilla J, Carrasco-Marín F, Moreno-Castilla C (2002) Experimental design to optimize preparation of activated carbons for use in water treatment. *Environmental Science and Technology* **36**, 3844-3849

Baccar R, Bouzid J, Feki M, Montiel A (2009) Preparation of activated carbon from Tunisian olive-waste cakes and its application for adsorption of heavy metal ions. *Journal of Hazardous Materials* **162**, 1522-1529

Baeta-Hall L, Céu-Sàágua, Lourdes Bartolomeu M, Anselmo AM, Fernanda Rosa M (2005) Bio-degradation of olive oil husks in composting aerated piles. *Bioresource Technology* **96**, 69-78

Banat F, Al-Asheh S, Al-Ahmad R, Bni-Khalid F (2007) Bench-scale and packed bed sorption of methylene blue using treated olive pomace and charcoal. *Bioresource Technology* **98**, 3017-3025

Benítez E, Sainz H, Melgar R, Nogales R (2002) Vermicomposting of a lingocellulosic waste from olive oil industry: A pilot scale study. *Waste Management and Research* **20**, 134-142

Blanco-López MC, Blanco CG, Martínez-Alonso A, Tascón JMD (2002) Composition of gases released during olive stone pyrolysis. *Journal of Analytical and Applied Pyrolysis* **65**, 313-322

Blázquez G, Hernáinz F, Calero G, Martín-Lara MA, Tenorio G (2009) The effect of pH on the biosorption of Cr (III) and Cr (VI) with olive stone. *Chemical Engineering Journal* **148**, 473-479

Borja R, Martín A Rincòn B, Raposo F (2003a) Kinetics for substrate utilization and methane production during the mesophilic anaerobic digestion of two phases olive pomace (TPOP). *Journal of Agricultural and Food Chemistry* **51**, 3390-3395

Borja R, Raposo F, Rincòn B (2006) Treatment technologies of liquid and solid wastes from two-phase olive oil mills. *Grasas Y Aceites* **57 (1)**, 32-46

Borja R, Rincòn B, Raposo F, Alba J, Martin A (2003b) Kinetics of mesophilic anaerobic digestion of the two-phase olive mill solid waste. *Biochemical Engineering Journal* **15**, 139-145

Boskou D (2006) *Olive Oil: Chemistry and Technology*, Contributor American Oil Chemists Society, AOCS Press, Champaign (IL), USA, 176 pp

Bouzid J, Elouear Z, Ksibi M, Feki M, Montiel A (2008) A study on removal characteristics of copper from aqueous solution by sewage sludge and pomace ashes. *Journal of Hazardous Materials* **152**, 838-845

Brunetti G, Plaza C, Senesi N (2005) Olive pomace amendment in Mediterranean conditions: effect on soil and humic acid properties and wheat (*Triticum turgidum* L.) yield. *Journal of Agricultural and Food Chemistry* **53**, 6730-6737

Budinova T, Petrov N, Razvigorova M, Parra J, Galiatsatou P (2006) Removal of arsenic(III) from aqueous solution by activated carbons prepared from solvent extracted olive pulp and olive stones. *Industrial and Engineering Chemistry Research* **45**, 1896-1901

Cabrera A, Cox L, Fernández-Hernández A, García-Ortiz Civantos C, Cornejo J (2009) Field appraisement of olive mills solid waste application in olive crops: Effect on herbicide retention. *Agriculture, Ecosystems and Environment* **132**, 260-266

Cabrera A, Cox L, Koskinen WC, Sadowsky MJ (2008a) Availability of triazine herbicides in aged soils amended with olive oil mill waste. *Journal of Agricultural and Food Chemistry* **56**, 4112-4119

Cabrera A, Cox L, Velarde P, Cornejo J (2008b) Terbuthylazine persistence in an organic amended soil. *Journal of Environmental Science and Health Part B* **43**, 713-716

Cabrera A, Cox L, Velarde P, Koskinen WC, Cornejo J (2007) Fate of diuron and terbuthylazine in soils amended with two-phase olive oil mill waste. *Journal of Agricultural and Food Chemistry* **55**, 4828-4834

Çağlar A, Demirbas A (2002) Hydrogen rich gas mixture from olive husk via pyrolysis. *Energy Conversion and Management* **43**, 109-117

Canet R, Pomares F, Cabot B, Chaves C, Ferrer E, Ribó M, Albiach MR (2008) Composting olive mill pomace and other residues from rural southeastern Spain. *Waste Management* **28**, 2585-2592

Caputo AC, Palumbo M, Pelagagge PM, Scacchia F (2005) Economics of biomass energy utilization in combustion and gasification plants: effects of logistic variables. *Biomass and Bioenergy* **28**, 35-51

Caputo AC, Scacchia F, Pelagagge PM (2003) Disposal of by-products in olive-oil industry: waste-to-energy solutions. *Applied Thermal Engineering* **23**, 197-214

Cayuela ML, Sánchez-Monedero MA, Roig A (2006) Evaluation of two different aeration systems for composting two-phase olive mill wastes. *Process Biochemistry* **41**, 616-623

Cegarra J, Alburquerque JA, Gonzálvez J, Tortosa G, Chaw D (2006) Effects of the forced ventilation of a solid olive mill by-product ("alperujo") managed by mechanical turning. *Waste Management* **26**, 1377-1383

Celma AR, Rojas S, López-Rodríguez F (2007) Waste-to-energy possibilities for industrial olive and grape by-products in Extremadura. *Biomass and Bioenergy* **31**, 522-534

Chouchene A, Jeguirim M, Khiari B, Zagrouba F, Trouvé G (2010) Thermal degradation of olive solid waste: influence of particle size and oxygen concentration. *Resources, Conservation and Recycling* **54**, 271-277

Cimino G, Cappello RM, Caristi C, Toscano G (2005) Characterization of carbons from olive cake by sorption of wastewater pollutants. *Chemosphere* **61**, 947-955

Cliffe KR, Patumsawad S (2001) Co-combustion of waste from olive oil production with coal in a fluidised bed. *Waste Management* **21**, 49-53

Daifullah AAM, Girgis BS (2003) Impact of surface characteristics of activated carbon on adsorption of BTEX. *Colloids and Surfaces A: Physicochemical Engineering Aspects* **214**, 181-193

Delgado-Moreno L, Almendros G, Pea A (2007) Raw or incubated olive-mill wastes and its biotransformed products as agricultural soil amendments-Effect on sorption-desorption of triazine herbicides. *Journal of Agricultural and Food Chemistry* **55**, 836-843

Delgado-Moreno L, Peña A (2009) Compost and vermicompost of olive cake to bioremediate triazines-contaminated soil. *Science of the Total Environment* **407**, 1489-1495

Demiral H, Demiral I, Tümsek F, Karabacakoğlu (2008) Adsorption of chromium(VI) from aqueous solution by activated carbon derived from olive cake and applicability of different adsorption models. *Chemical Engineering Journal* **144**, 188-196

Demirbas A (2001a) Carbonization ranking of selected biomass for charcoal, liquid and gaseous products. *Energy Conversion and Management* **42**, 1229-1238

Demirbas A (2001b) Yields of hydrogen-rich gaseous products via pyrolysis from selected biomass. *Fuel* **80**, 1885-1891

Demirbas A (2002) Gaseous products from biomass by pyrolysis and gasification: effects of catalyst on hydrogen yield. *Energy Conversion and Management* **43**, 897-909

Demirbas A (2003) Sustainable co-firing of biomass and coal. *Energy Conversion and Management* **44**, 1465-1479

Demirbas A (2004) Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues. *Journal of Analytical and Applied Pyrolysis* **72**, 243-248

Droussi Z, D'Orazio V, Hafidi M, Ouatmane A (2009) Elemental and spectroscopic characterization of humic-acid-like compounds during composting of olive mill by-products. *Journal of Hazardous Materials* **163**, 1289-1297

El Bakouri H, Usero J, Morillo J, Ouassini A (2009) Adsorptive features of acid-treated olive stones for drin pesticides: Equilibrium, kinetic and thermodynamic modeling studies. *Bioresource Technology* **100**, 4147-4155

El-Hamouz A, Hilal HS, Nassar N, Mardawi Z (2007) Solid olive waste in environmental cleanup: Oil recovery and carbon production for water purification. *Journal of Environmental Management* **84**, 83-92

El-Sheikh AH, Newman AP, Al-Daffaee H, Phull S, Cresswell N, York S (2004a) Deposition of anatase on the surface of activated carbon. *Surface ad Coatings Technology* **187**, 284-292

El-Sheikh AH, Newman AP, Al-Daffaee HK, Phull S, Cresswell N (2004b) Characterization of activated carbon prepared from a single cultivar of Jordanian Olive stones by chemical and physicochemical techniques. *Journal of Analytical and Applied Pyrolysis* **71**, 151-164

Encinar JM, Beltrán FJ, Bernalte A, Ramiro A, González JF (1996) Pyrolysis of two agricultural residues: olive and grape bagasse. Influence of particle size and temperature. *Biomass and Bioenergy* **11**, 397-409

Encinar JM, Beltrán FJ, Ramiro A, González JF (1998) Pyrolysis/gasification of agricultural residues by carbon dioxide in the presence of different additives: influence of variables. *Fuel Processing Technology* **55**, 219-233

Encinar JM, González JF, Martínez G, González JM (2008) Two-stages catalytic pyrolysis of exhausted olive oil waste. *Fuel Processing Technology* **89**, 1448-1455

Encinar JM, González JF, Martínez G, Román S (2009) Catalytic pyrolysis of exhausted olive oil waste. *Journal of Analytical and Applied Pyrolysis* **85**, 197-203

European Union- Directorate General for Agriculture and Rural Development, "The Olive Oil Sector in Europe", 2003. Available online: http://ec.europa.eu/agriculture/publi/fact/oliveoil/2003_en.pdf

European Union- Directorate General for Agriculture and Rural Development, "Agriculture in the European Union – Statistical and Economic information", 2007. Available online: http://ec.europa.eu/agriculture/agrista/2007/table_en/2007enfinal.pdf

European Union, Commission of the European Communities, 2006. Green Paper March A European strategy for sustainable, competitive and secure energy (COM(2006) 105 final). Available online: http://ec.europa.eu/energy/green-paper-energy/doc/2006_03_08_gp_document_en.pdf

European Union, Commission of the European Communities, Communication from the Commission, 2005. Biomass Action Plan (COM(2005)628 final – Official Journal C 9). Available online: http://ec.europa.eu/energy/res/biomass_action_plan/doc/2005_12_07_comm_biomass_action_plan_en.pdf

European Union, Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste

Fernández-Bolaños J, Rodríguez G, Gómez E, Guillén R, Jiménez A, Heredia A, Rodríguez R (2004) Total recovery of the waste of two-phase olive-oil processing: isolation of added-value compounds. *Journal of Agricultural and Food Chemistry* **52**, 5849-5855

Fernández-Bolaños J, Rodríguez G, Rodríguez R, Heredia A, Guillén R, Jiménez A (2002) Total recovery of the waste of two-phase olive-oil processing: isolation of added-value compounds. *Journal of Agricultural and*

Food Chemistry **50**, 6804-6811

Fryda LE, Panopoulos KD, Kakaras E (2008) Agglomeration in fluidized bed gasification of biomass. *Powder Technology* **181**, 307-320

Galiatsatou P, Metaxas M, Kasselouri-Rigopoulou V (2001) Mesoporous activated carbon from agricultural by products. *Mikrochimica Acta* **136**, 147-152

Galiatsatou P, Metaxas M, Kasselouri-Rigopoulou V (2002) Adsorption of zinc by activated carbons prepared from solvent extracted olive pulp. *Journal of Hazardous Materials* **B91**, 187-203

Gañán J, Turegano JP, Calama G, Roman S, Al-Kassir V (2006) Plant for the production of activated carbon and electric power from the gases originated in gasification processes. *Fuel Processing Technology* **87**, 117-122

García-Gómez A, Roig A, Bernal MP (2003) Composting of the solid fraction of olive mill wastewater with olive leaves: organic matter degradation and biological activity. *Bioresource Technology* **86**, 59-64

García-Ibañez P, Cabanillas A, Sánchez JM (2004) Gasification of leached orujillo (olive oil waste) in a pilot plant circulating fluidized bed reactor. Preliminary results. *Biomass and Bioenergy* **27**, 183-194

García-Ibañez P, Sánchez JM, Cabanillas A (2006) Thermogravimetric analysis of olive-oil residue in air atmosphere. *Fuel Processing Technology* **87**, 103-107

Gavala HN, Skiadas IV, Ahring BK, Lyberatos G (2005) Potential for biohydrogen and methane production from olive pulp. *Water Science and Technology* **52**, 209-215

Gayan P, Adanez J, de Diego LF, García-Labiano F, Cabanillas A, Bahillo A, Aho M, Veijonen K (2004) Circulating fluidized bed co-combustion of coal and biomass. *Fuel* **83**, 277-286

Gharaibeh SH, Moore SV, Buck A (1998) Effluent treatment of industrial wastewater using processed solid residue of olive mill products and commercial activated carbon. *Journal of Chemical Technology and Biotechnology* **71**, 291-298

Ghoreishi SM, Shahrestani RG (2009) Subcritical water extraction of mannitol from olive leaves, *Journal of Food Engineering* **93**, 474-481

Girgis BS, Khalil LB, Tawfik TAM (2002) Porosity development in carbons derived from olive oil mill residue under steam pyrolysis. *Journal of Porous Materials* **9**, 105-113

Gómez-Barea A, Arjona R, Ollero P (2005) Pilot-plant gasification of olive stone: a technical assessment. *Energy and Fuels* **19**, 598-605

Gondar D, Bernal MP (2009) Copper binding by olive mill solid waste and its organic matter fractions. *Geoderma* **149**, 272-279

González JF, Román S, Encinar JM, Martínez G (2009) Pyrolysis of various biomass residues and char utilization for the production of activated carbons. *Journal of Analytical and Applied Pyrolysis* **85**, 134-141

González MT, Sepúlveda-Escribano A, Molina-Sabio M, Rodríguez-Reinoso F (1995) Correlation between surface areas and micropore volumes of activated carbons obtained from physical adsorption and immersion calorimetry. *Langmuir* **11**, 2151-2155

Guiza M, Ouederni A, Ratel A (2004) Decomposition of dissolved ozone in the presence of activated carbon: an experimental study. *Ozone: Science an Engineering* **26**, 299-307

Hachicha R, Hachicha S, Trabelsi I, Woodward S, Mechichi T (2009) Evolution of the fatty fraction during co-composting of olive oil industry wastes with animal manure: Maturity assessment of the end product. *Chemosphere* **75**, 1382-1386

Hachicha S, Sallemi F, Medhioub, K, Hachicha R, Ammar E (2008) Quality assessment of composts prepared with olive mill wastewater and agricultural wastes. *Waste Management* **28**, 2593-2603

Haydar S, Ferro-García MA, Rivera-Utrilla J, Joly JP (2003) Adsorption of *p*-nitrophenol on an activated carbon with different oxidations. *Carbon* **41**, 387-395

Jauhiainen J, Conesa JA, Font R, Martin-Gullon I (2004) Kinetics of the pyrolysis and combustion of olive oil. *Journal of Analytical and Applied Pyrolysis* **72**, 9-15

Jauhiainen J, Martin-Gullon I, Conesa JA, Font R (2005) Emissions from pyrolysis and combustion of olive oil solid waste. *Journal of Analytical and Applied Pyrolysis* **74**, 512-517

Juárez-Galán JM, Guiza M, Ouederni A, Ratel A (2004) Decomposition of dissolved ozone in the presence of activated carbon: An Experimental Study. *Ozone: Science and Engineering* **26**, 299-307

Kapellakis IE, Tsagarakis KP, Crowther JC (2008) Olive oil history, production and by-product management. *Reviews of Environmental Science and Biotechnology* **7**, 1-26

Kavdir Y, Killi D (2008) Influence of olive oil solid waste applications on soil pH, electrical conductivity, soil nitrogen transformations, carbon content and aggregate stability. *Bioresource Technology* **99**, 2326-2332

Khalil LB, Girgis BS, Tawfik TAM (2001) Decomposition of H_2O_2 on activated carbon obtained from olive stones. *Journal of Chemical Technology and Biotechnology* **76**, 1132-1140

Kolokassidou K, Szymczak W, Wolf M, Obermeier C, Buckau G, Pashalidis I (2009) Hydrophilic olive cake extracts: Characterization by physicochemical properties and Cu(II) complexation. *Journal of Hazardous Materials* **164**, 442-447

Konstantinou M, Kolokassidou K, Pashalidis I (2009) Studies on the interac-

tion of olive cake and its hydrophylic extracts with polyvalent metal ions (Cu(II), Eu(III)) in aqueous solutions. *Journal of Hazardous Materials* **166**, 1169-1173

Kula I, Uğurlu M, Karaoğlu H, Çelik A (2008) Adsorption of Cd(II) ions from aqueous solutions using activated carbon prepared from olive stone by $ZnCl_2$ activation. *Bioresource Technology* **99**, 492-501

Lafi WK (2001) Production of activated carbon from acorns and olive seeds. *Biomass and Bioenergy* **20**, 57-62

López F, Medina F, Prodanov M, Güell C (2003) Oxidation of activated carbon: application to vinegar decolorization. *Journal of Colloid and Interface Science* **257**, 173-178

Mameri N, Aioueche F, Belhocine D, Grib H, Lounici H, Piron DL, Yahiat Y (2000) Preparation of activated carbon from olive mill solid residue. *Journal of Chemical Technology and Biotechnology* **75**, 625-631

Mantzavinos D, Kalogerakis N (2005) Treatment of olive mill effluents – Part I. Organic matter degradation by chemical and biological processes – an overview. *Environment International* **31**, 289-295

Martínez ML, Torres MM, Guzmán CA, Maestri DM (2006) Preparation and characteristics of activated carbon from olive stones and walnut shells. *Industrial Crops and Products* **23**, 23-28

Martín-Lara MA, Hernáinz F, Calero G, Blázquez G, Tenorio G (2009) Surface chemistry evaluation of some solid wastes from olive-oil industry used for lead removal from aqueous solutions. *Biochemical Engineering Journal* **44**, 151-159

McIlveen-Wright DR, Huang Y, Rezvani S, Wang Y (2007) A technical and environmental analysis of co-combustion of coal and biomass in fluidized bed technologies. *Fuel* **86**, 2032-2042

Mehmeti E, Dogan Ö, Tiris M, Kiran NC, Matuschek G (2008) Thermolysis product distribution of solid waste obtained from olive oil production. *Clean* **36**, 315-319

Michailof C, Stavropoulos GG, Panayiotou C (2008) Enhanced adsorption of phenolic compounds, commonly encountered in olive mill wastewaters, on olive husk derived activated carbons. *Bioresource Technology* **99**, 6400-6408

Miranda MT, Cabanillas A, Rojas S, Montero I, Ruiz A (2007) Combined combustion of various phases of olive wastes in a conventional combustor. *Fuel* **86**, 367-372

Mohan D, Pittman CU, Steele PH (2006) Pyrolysis of wood/biomass for biooil: A critical review. *Energy and Fuels* **20**, 848-889

Molina-Sabio M, Sánchez-Montero MJ, Juarez-Galan JM, Salvador F, Rodríguez-Reinoso F, Salvador A (2006) Development of porosity in a char during reaction with steam or supercritical water. *Journal of Physical Chemistry B* **110**, 12360-12364

Montemurro F, Diacono M, Vitti C, Debiase G (2009) Biodegradation of olive husk mixed with other agricultural wastes. *Bioresource Technology* **100**, 2969-2974

Moreno B, Vivas A, Nogales R, Macci C, Masciandaro G, Benitez E (2009) Restoring biochemical activity and bacterial diversity in a trichloroethylene-contaminated soil: the reclamation effect of vermicomposted olive wastes. *Environmental Science and Pollution Research* **16**, 253-264

Moreno-Castilla C, Carrasco-Marín F, López-Ramón MV, Alvarez-Merino MA (2001) Chemical and physical activation of olive-mill waste water to produce activated carbons. *Carbon* **39**, 1415-1420

Moreno-Castilla C, Pérez-Cadenas AF, Maldonado-Hódar FJ, Carrasco-Marín F, Fierro JLG (2003) Influence of carbon–oxygen surface complexes on the surface acidity of tungsten oxide catalysts supported on activated carbons. *Carbon* **41**, 1157-1167

Mulinacci N, Innocenti M, La Marca G, Mercalli E, Giaccherini C, Romani A, Saracini E, Vincieri FF (2005) Solid olive residues: insight into their phenolic composition. *Journal of Agricultural and Food Chemistry* **53**, 8963-8969

Nakagawa Y, Molina-Sabio M, Rodríguez-Reinoso F (2007) Modification of the porous structure along the preparation of activated carbon monoliths with H_3PO_4 and $ZnCl_2$. *Microporous and Mesoporous Materials* **103**, 29-34

Natarajan EM, Ohman M, Gabra A, Nordin T, Liliedahl A, Rao A (1998) Experimental determination of bed agglomeration tendencies of some common agricultural residues in fluidized bed combustion and gasification. *Biomass and Bioenergy* **15**, 163-169

Nebili F, Bouachir F (2008) Valorisation of the olive cake residue by pyrolysis under water vapour current. *Journal of Engineering and Applied Sciences* **3**, 848-855

Niaounakis M, Halvadakis CP (2006) *Olive-Mill Waste Management: Literature Review and Patent Survey* (2nd Edn), Typothito – George Dardanos Publications, Athens, Greece, 498 pp

Nogales R, Melgar R, Guerrero A, Lozada G, Benítez E, Thompson R, Gómez M (1999) Growth and reproduction of *Eisenia andrei* in dry olive cake mixed with other organic wastes. *Pedobiologia* **43**, 744-752

Obied HK, Allen MS, Bedgood DR, Prenzler PD, Robards K (2005a) Investigation of Australian olive mill waste for recovery of biophenols. *Journal of Agricultural and Food Chemistry* **53**, 9911-9920

Obied HK, Allen MS, Bedgood DR, Prenzler PD, Robards K, Stockmann R (2005b) Bioactivity and analysis of biophenols recovered from olive mill waste. *Journal of Agricultural and Food Chemistry* **53**, 823-837

Obied HK, Bedgood DR, Prenzler PD, Robards K (2007a) Bioscreening of

Australian olive mill waste extracts: Biophenol content, antioxidant, antimicrobial and molluscicidal activities. *Food and Chemical Technology* **45**, 1238-1248

Obied HK, Karuso P, Prenzler PD, Robards K (2007b) Novel secoiridoids with antioxidant activity from Australian olive mill waste. *Journal of Agricultural and Food Chemistry* **57**, 2848-2853

Obied HK, Prenzler PD, Robards K (2008), Potent antioxidant phenols from olive mill waste. *Food Chemistry* **111**, 171-178

Pagnanelli F, Mainelli S, De Angelis S, Toro L (2005) Biosorption of protons and heavy metals onto olive pomace: Modelling of competition effects. *Water Research* **39**, 1639-1651

Pagnanelli F, Toro L, Vegliò F (2002) Olive mill solid residues as heavy metal sorbent material: a preliminary study. *Waste Management* **22**, 901-907

Pala A, Galiatsatou P, Tokat E, Erkaya H, Israilides C, Arapoglou D (2006) The use of activated carbon from olive oil mill residue, for the removal of colour from textile wastewater. *European Water* **13/14**, 29-34

Paraskeva P, Diamadopoulos E (2006) Technologies for olive mill wastewater (OMW) treatment: A review. *Journal of Chemical Technology and Biotechnology* **81**, 1475-1485

Paredes C, Bernal MP, Cegarra J, Roig A (2002) Bio-degradation of olive mill wastewater sludge by its co-composting with agricultural wastes. *Bioresource Technology* **85**, 1-8

Pereira MR, Arroyo PA, Dornellas de Barros MAS, Monteiro Sanches V, da Silva EA, Fonseca IM, Lovera RG (2006) Chromium adsorption in olive stone activated carbon. *Adsorption* **12**, 155-162

Pérez-Cadenas AF, Maldonado-Hódar FJ, Moreno-Castilla C (2003) On the nature of surface acid sites of chlorinated activated carbons. *Carbon* **41**, 473-478

Petrov N, Budinova D, Razvigorova M, Parra J, Galiatsatou P (2008) Conversion of olive wastes to volatiles and carbon adsorbents. *Biomass and Bioenergy* **32**, 1303-1310

Pinto F, André RN, Franco C, Lopes H, Gulyurtlu I, Cabrita I (2009) Co-gasification of coal and wastes in a pilot-scale installation: effects of catalysts in syngas treatment to achieve tar abatement. *Fuel* **88**, 2392-2402

Plaza MG, Pevida C, Arias B, Fermoso J, Casal MD, Martín CF, Rubiera F, Pis JJ (2009) Development of low-cost biomass-based adsorbents for post combustion CO_2 capture. *Fuel* **88**, 2442-2447

Redondo-Gómez S, Cox L, Cornejo J, Figueroa E (2007) Combined effect of diuron and simazine on photosystem II photochemistry in a sandy soil and soil amended with solid olive-mill waste. *Journal of Environmental Science and Health Part B* **42**, 249-254

Rivera-Utrilla J, Ferro-Garcia MA, Mingorance MD, Bautista-Toledo I (1986) Adsorption of lead on activated carbons from olive stones. *Journal of Chemical Technology and Biotechnology* **36**, 47-52

Rodríguez G, Lama A, Rodríguez R, Jiménez A, Guillén R, Fernández-Bolaños J (2008) Olive stone an attractive source of bioactive and valuable compounds. *Bioresource Technology* **99**, 5261-5269

Rodríguez R, Lama A, Trujillo M, Espartero JL, Fernández-Bolaños J (2009) Isolation of powerful antioxidant from *Olea europaea* fruit-mill waste: 3,4-dihydroxyphenylglycol. *LWT-Food Science and Technology* **42**, 483-490

Rodríguez-Reinoso F, Nakagawa Y, Silvestre-Albero J, Juárez-Galán JM, Molina-Sabio M (2008) Correlation of methane uptake with microporosity and surface area of chemically activated carbons. *Microporous and Mesoporous Materials* **115**, 603-608

Rodríguez-Valero MA, Martínez-Escandell M, Molina-Sabio, M, Rodríguez-Reinoso F (2001) CO_2 activation of olive stones carbonized under pressure. *Carbon* **39**, 320-323

Roig A, Cayuela ML, Sánchez-Monedero MA (2004) The use of elemental sulphur as organic alternative to control pH during composting of olive mill wastes. *Chemosphere* **57**, 1099-1105

Román S, González JF, González-García CM, Zamora F (2008) Control of pore development during CO_2 and steam activation of olive stones. *Fuel Processing Technology* **89**, 715-720

Romero E, Benítez E, Nogalez R (2005) Suitability of wastes from olive-oil industry for initial reclamation of a Pb/Zn mine tailing. *Water, Air, and Soil Pollution* **165**, 153-165

Salas-Peregrín MA, Carrasco-Marín F, López-Garzón FJ, Moreno-Castilla C (1994) Adsorption of CO_2 on activated carbons from diluted ambient environments. *Energy and Fuels* **8**, 239-243

Sánchez-Arias V, Fernández FJ, Villaseñor J, Rodríguez L (2008) Enhancing the co-composting of olive mill wastes and sewage sludge by the addition of an industrial waste. *Bioresource Technology* **99**, 6346-6353

Sarika R, Mantzavinos D, Kalogerakis N (2005) Treatment of olive mill effluents – Part II. Complete removal of solids by direct flocculation with polyelectrolytes. *Environment International* **31**, 297-304

Schievano A, D'Imporzano G, Adani F (2009) Substituting energy crops with organic wastes and agro-industrial residues for biogas production. *Journal of Environmental Management* **90**, 2537-2541

Schmidt A, Knobloch M, Olive oil-mill residues: The demonstration of an innovative system to treat wastewater and to make use of generated bioenergy

and solid remainder, in: Proceedings of the First World Conference on Biomass for Energy and industry, Seville, June 5–9, 2000, pp 452-454

Schröder E, Thomauske K, Weber C, Hornung A, Tumiatti V (2007) Experiments on the generation of activated carbon from biomass. *Journal of Analytical and Applied Pyrolysis* **79**, 106-111

Sellami F, Hachicha S, Chtourou M, Medhioub K, Ammar E (2008b) Maturity assessment of composted olive mill wastes using UV spectra and humification parameters. *Bioresource Technology* **99**, 6900-6907

Sellami F, Jarboui R, Hachicha S, Medhioub K, Ammar E (2008a) Co-composting of oil exhausted olive-cake, poultry manure and industrial residues of agro-food activity for soil amendment. *Bioresource Technology* **99**, 1177-1188

Silvestre-Albero A, Silvestre-Albero J, Rodríguez-Reinoso F (2009a) Synthesis of activated carbon with highly developed "mesoporosity". *Microporous and Mesoporous Materials* **117**, 519-521

Silvestre-Albero A, Silvestre-Albero J, Sepúlveda-Escribano A, Rodríguez-Reinoso F (2009b) Ethanol removal using activated carbon: Effect of porous structure and surface chemistry. *Microporous and Mesoporous Materials* **120**, 62-68

Siracusa G, La Rosa AD, Siracusa V, Trovato M (2001) Eco-compatible use of olive husk as filler in thermoplastic composites. *Journal of Polymers and the Environment* **9**, 157-161

Skodras G, Diamantopoulou I, Zabaniotou A, Stavropoulos G, Sakellaropoulos GP (2007) Enhanced mercury adsorption in activated carbons from biomass materials and waste tires. *Fuel Processing Technology* **88**, 749-758

Skoulou V, Koufodimos G, Samaras Z, Zabaniotou A (2008a) Low temperature gasification of olive kernels in a 5-kW fluidized bed reactor for H_2-rich producer gas. *International Journal of Hydrogen Energy* **33**, 6515-6524

Skoulou V, Swiderksi A, Yang W, Zabaniotou A (2009) Process characteristics and products of olive kernel high temperature steam gasification (HTSG). *Bioresource Technology* **100**, 2444-2451

Skoulou V, Zabaniotou A, Stavropoulos G, Sakelaropoulos G (2008b) Syngas production from olive tree cuttings and olive kernels in a downdraft fixed bed gasifier. *International Journal of Hydrogen Energy* **33**, 1185-1194

Spahis N, Addoun A, Mahmoudi H, Ghaffour N (2008) Purification of water by activated carbon prepared from olive stones. *Desalination* **222**, 519-527

Stavropoulos GG, Zabaniotou AA (2005) Production and characterization of activated carbons from olive-seed waste residue. *Microporous and Mesoporous Materials* **82**, 79-85

Suárez M, Romero MP, Ramo T, Maciá A, Motilva MJ (2009) Methods for preparing phenolic extracts from olive cake for potential application as food antioxidants. *Journal of Agricultural and Food Chemistry* **57**, 1463-1472

Taralas G, Kontominas MG (2005) Thermochemical treatment of solid and wastewater effluents originating from the olive oil food industry. *Energy and Fuels* **19**, 1179-1185

Tejada M, Gonzalez JL (2007) Influence of organic amendments on soil structure and soil loss under simulated rain. *Soil and Tillage Research* **93**, 197-205

Topal H, Atimtay AT, Durmaz A (2003) Olive cake combustion in a circulating fluidized bed. *Fuel* **82**, 1049-1056

Ubago-Pérez R, Carrasco-Marín F, Fairén-Jiménez D, Moreno-Castilla C (2006) Granular and monolithic activated carbons from KOH-activation of olive stones. *Microporous and Mesoporous Materials* **92**, 64-70

Uğurlu M, Gürses A, Açıkyıldız M (2008) Comparison of textile dyeing effluent adsorption on commercial activated carbon and activated carbon prepared from olive stone by $ZnCl_2$ activation. *Microporous and Mesoporous Materials* **111**, 228-235

Undabeytia T, Sanchez-Verdejo T, Morillo E, Maqueda C (2004) Effect of organic amendments on the retention and mobility of imazaquin in soils. *Journal of Agricultural and Food Chemistry* **52**, 4493-4500

United Nations Conference on Trade and Development (UNCTAD), Market Information in the Commodities Area – Olive oil, 2005. Available online: http://r0.unctad.org/infocomm/anglais/olive/market.htm

Uzun BB, Pütün AE, Pütün E (2007) Rapid pyrolysis of olive residue. 1. Effect of heat and mass transfer limitations on product yields and bio-oil composition. *Energy and Fuels* **21**, 1768-1776

Varol M, Atimtay AT (2007) Combustion of olive cake and coal in a bubbling fluidized bed with secondary air injection. *Fuel* **86**, 1430-1438

Vlyssides AG, Barampouti EMP, Mai ST (2008) Physical characteristics of olive stone wooden residues: possible bulking material for composting process. *Biodegradation* **19**, 209-214

Vlyssides AG, Loizidou M, Zorpas AA (1999) Characteristics of solid residues from olive oil processing as bulking material for co-composting with industrial wastewaters. *Journal of Environmental Science and Health Part A* **34**, 737-748

Zabaniotou A, Kalogiannis G, Kappas E, Karabelas AJ (2000) Olive residues (cuttings and kernels) rapid pyrolysis product yields and kinetics. *Biomass and Bioenergy* **18**, 411-420

Zabaniotou A, Stavropoulos G, Skoulou V (2008) Activated carbon from olive kernels in a two-stage process: Industrial improvement. *Bioresource Technology* **99**, 320-326