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Energy Valorization of Olive Mill Waste Cake – Extraction of Vegetable Oil and Transesterification

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ABSTRACT

The olive mill wastewater, effluents from the trituration of olives, are treated in most Mediterranean countries by natural evaporation. However, this method of treatment is a source of air and soil pollution by the generation of solid waste, called olive mill waste cake. This work focused on extracting of vegetable oil from this by-product for biodiesel production by transesterification. The extraction took place with a Soxhlet extractor, using hexane as solvent. The vegetable oil and biodiesel were characterized by measuring the physicochemical parameters that identify them according to AFNOR standards. The extraction results show that the oil yield is 21.28%. The oil obtained is characterized by density, water and ash content, acidity, saponification, peroxide and ester. The yield of the oil esterification reaction is 86.41% or about 185 Kg of biodiesel/ton of olive mill waste cake, and in terms of energy 2783.7 MJ or 2 GW.t^{-1}. The biodiesel produced is comparable to petroleum diesel according to EN 14214, 2013.

Keywords: olive mill waste cake, extraction, valorization, vegetable oil, transesterification, biodiesel.

INTRODUCTION

Olive oil is an important food in the Mediterranean diet because it has many nutritional benefits for health. Its demand worldwide is increasing from year to year given its virtues. According to a recent report by the International Olive Council (IOC, 2019), the global consumption of olive oil increased by more than 8% during the 2017–18 harvest season, reaching about 2.9,105 tons, most of which are produced in Mediterranean countries (Spain, Morocco, Turkey, Tunisia, Greece, Cyprus, etc.) (Djebari and Meddour, 2020).

In Morocco, the olive tree is the principal cultivation variety that now covers an area of 998,000 ha, with an annual production of 1,143,000 tons of which about 75% of the olives produced are intended for the production of olive oil by crushing (Rahmani, 2017). However, this production is seasonal and takes 4 months each year (from November to February) and has negative effects on the environment, due to pomace and olive mill wastewater that accompany the crushing of 30 to 50% respectively (Ayeda et al., 2019; Atallah et al., 2019).

The olive mill wastewater, very acidic (5.5), contains a moisture content level in the range of 88% by weight. As well as many persistent organic substances, a high content of organic matter assessed by the chemical oxygen demand (COD) between 3,500 and 85,000 mg·L^{-1} (Aktas et al., 2011), phenolic substances between 600 and 25,000 mg·L^{-1}, organic acids, tannins, polysaccharides, etc., which are resistant to biodegradation, color natural waters and modify negatively the quality of the soil. In addition, dissolved phenolic compounds cause high toxicity to exposed aquatic organisms, depending on the exposure time and concentration (Hethnawi et al., 2017).

At present, the only method adopted by most countries for the treatment of olive mill waste is natural evaporation. However, this method only transforms the pollution from a liquid physical

state to other solid and gaseous states. In fact, each ton of evaporated olive mill wastewater gives rise to 120 kg of cakes, i.e., about 51435 t. year^{-1}. The literature review shows that this by-product has been valorized in several fields such as the extraction of phenolic extracts (Suárez et al., 2009), the production of biosorbents (Fernando et al., 2009), the preparation of nanocomposites (Yuney et al., 2020), the extraction of antioxidants and cellulose, hemicellulose and lignin (Bouderbala et al., 2015; Rodriguez-Gutierrez et al., 2014), the feeding of livestock, especially for ruminants (Tzamaloukas et al., 2021; Yagoubi et al., 2021).

Moreover, the production of biodiesel represents an alternative to the production of clean and renewable fuels (Konur, 2021). It is obtained by transforming oils of vegetable, animal or waste origin into alkyl esters (Mathew et al., 2021). The transesterification reaction represents one of the most important methods used to achieve this conversion and obtain an economically reliable and easy-to-implement biofuel. It is a process in which triglycerides are transformed in the presence of an alcohol (methanol or ethanol) and a catalyst into ester and glycerol (Zhang et al., 2021; Nikolić et al., 2021).

In this context, this work aims, on one side, to reduce the pollutant load of the olive mill waste cake and the tonnage produced by the extraction of the oil and its transformation into biodiesel. And, on the other side, contributing to sustainable development, by offering a renewable energy source that meets the energy challenges such as the control of greenhouse gas emissions and the preservation of non-renewable fossil resources, is what makes the novelty of this work.

MATERIALS AND METHODS

Procurement

The olive mill waste cakes (OMWC) are procured from the storage basin of olive mill

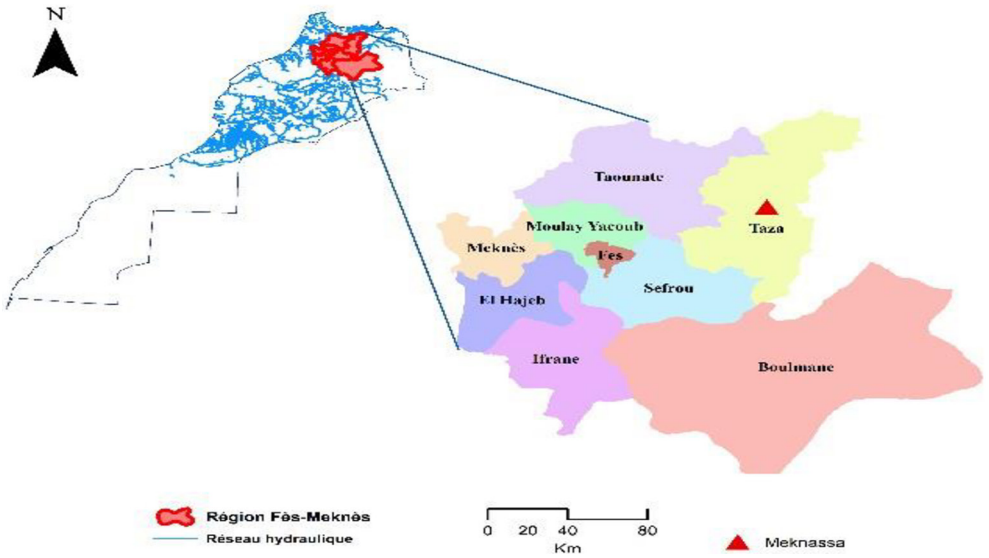

Figure 1. Geographical location of the OMWW evaporation basin of Meknassa-Morocco

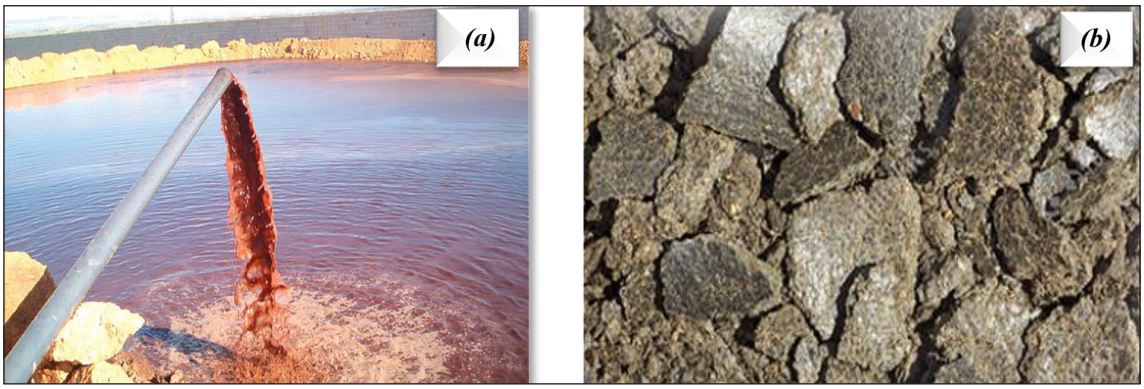

Figure 2. Natural evaporation basin of OMWW (a) and dried OMWC (b)

wastewater (OMWW) for their natural evaporation, located in Meknassa ben Ali 8 km from the city of Taza-Morocco (Figure 1). The sampling took place at the end of August after the total evaporation of the OMWW and cracking of the resulting cake (Figure 2). Sampling was done at different locations in the collection basin in a random fashion. The waste was then collected in plastic bags, transported to the laboratory and stored according to IMANOR standards (IMANOR, 2011).

Physical preparation of the olive mill waste cake

The olive mill waste cake is then broken up with a crusher. The recovered seeds are crushed in a high-power blender. The crushed material is sieved through a 1 mm diameter sieve. The representative sample of the OMWCP was obtained by the method of quartering (Chabbi et al., 2021) and then stored in a plastic box, sealed, and arranged at ambient temperature protected from light until use.

Powder characterization (OMWCP)

The OMWCP was characterized by measuring physicochemical parameters: moisture content (MC%); dry matter (DM%) ISO 6540, 2010; fat matter (FM%) NF EN ISO 734, 2000.

Extraction method

The extraction of the vegetable oil was performed on a laboratory scale using the 150 mL capacity Soxhlet extractor, linked to a 500 mL flask filled with 200 mL of the solvent; which in turn is placed in a heating flask. 70 g of OMWCP sample is introduced into a cartridge covered with a piece of cotton in order to avoid the transfer of the various particles.

The OMWCP sample is then extracted under reflux for 1h30 min, then the vegetable oil is recovered after evaporation of the hexane in a rotary evaporator at 67 °C in a clean flask, weighed and stored for further use.

The yield of vegetable oil is defined as the ratio between the mass of vegetable oil extracted and the mass of the initial plant material. It is expressed in percentage (%) and calculated by the following equation:

$$\%R = \frac{Mass\ of\ vegetable\ oil}{Mass\ of\ dry\ matter\ (g)} * 100 \quad (1)$$

Methods of characterization of vegetable oil (VO)

The physicochemical properties of the produced oil are determined by measuring density (NF EN ISO 3838, 2004), ash content (ISO 21656, 2021), peroxide value (ISO 3960, 2017), acid value (NF EN 14104, 2021), saponification value (NF EN ISO 365, 2020), ester value (NM ISO 7660, 2016). The spectroscopic characteristics were evaluated by ultraviolet-visible and infrared spectroscopy with Fourier transform.

Biodiesel production methods

The production of biodiesel was carried out by the transesterification reaction. This technique consists in transforming the extracted vegetable oil into biodiesel in the presence of methanol and a catalyst (KOH), bringing it under agitation for one hour, at a temperature of 60 °C.

The efficiency of transesterification was evaluated by calculating the yield of biodiesel produced using the following equation:

$$\%R = \frac{Massedebiodiesel}{Mass\ of\ oil\ used} * 100 \quad (2)$$

Methods of characterization of biodiesel

The physicochemical characterization of the produced biodiesel was performed by measuring several parameters such as: density (NF EN ISO 3838, 2022), viscosity, water content (ASTM D95, 2018), ash content (NF ISO 6884, T60-209, 2012) and cloud point (NF T60-153, 1979). The functions characterizing the biodiesel were evaluated by the infrared spectroscopic method.

RESULTS AND DISCUSSION

Physicochemical characterization of the olive mill waste cake

The results of the physicochemical characterization of the olive mill waste cake (Table 1) reveal that the paste is characterized by a very low moisture content due to the natural evaporation of olive mill wastewater, with a very high dryness and fat content.

Table 1. Physicochemical characterization of the olive mill waste cake

Parameters	Moisture content (%)	Dry matter (%)	Fat matter (%)
Values	5.94	94.06	29.92

Physicochemical characterization of the extracted vegetable oil

The results of the characterization of vegetable oil from olive mill waste cakes obtained by Soxhlet extraction with hexane are represented in Table 2.

The density of vegetable oil extracted from olive mill waste cakes (0.88) is relatively lower than the density of olive pomace oil (0.91) (Touati, 2013); most likely due to the increase in density and oxidation state of the oil, followed by the enrichment of polar compounds (primary and secondary oxidation products) in the oil (Touati, 2013). However, several researchers have shown that the high density of oils has adverse effects on diesel engines (Abollé et al., 2009). This is because vegetable oils have a higher inertia than gas oil for the same injection pressure. Thus, that high density will lead to an increase in the length of the fuel jets, dragging them to the bottom of the combustion chamber (Palash et al., 2013).

The viscosity of VO (32.07 $mm^2 \cdot s^{-1}$) is lower than that of olive pomace (63.05 $mm^2 \cdot s^{-1}$) (Touati, 2013) and higher than olive oil (29.4 $mm^2 \cdot s^{-1}$) (Palash et al., 2013). Indeed, the viscosity is directly related to the fluidity of oils; a high value could have a detrimental effect on its use directly as biofuel. the fluidity and the mass-energy of the fuels (viscosity) increase with the H/C ratio: while the carbon dioxide emission factor (g of CO_2 emitted to produce, e.g., 1 kWh) decreases, it is easier and therefore less expensive to transport, and use fluid fuels than solid fuels.

Table 2. Physicochemical characterization of vegetable oil

Parameters	Values
Density at 25 °C ($g.cm^{-3}$)	0,88
Viscosity at 40 °C (mm^2s^{-1})	32.07
Ash content (% by mass)	0.88
Peroxide index (meq d'O_2 kg^{-1})	18
Acid index (mg $KOH.g^{-1}$)	61.77
Saponification index (mg $KOH.g^{-1}$)	193.54
Ester index (mg KOH/g)	78.76
Alteration study by visible UV spectrometer	ʎ = 232 nm (3,0190) ʎ= 270nm (2,4334)

The peroxide index of VO is 18 mg active oxygen equivalent per kilogram of vegetable oil. This value respects the standard set between 0 and 30 mg active oxygen equivalent per kilogram of oil (ISO 3960, 2017) to limit any flammability risk. Indeed, the peroxide value is a parameter for monitoring the progress of the first stage of oxidation of unsaturated fatty acids in vegetable oil; the higher this value, the more oxidized the oil is.

The ash content of VO (0.88%), considered an indicator of purity, is relatively higher than the quality standard of vegetable oil (Kouassi et al., 2015) which is limited to 0.05%. If this value is exceeded, it may cause clogging of the automotive injectors.

The acid index of the VO is very high (61.77 mg $KOH \cdot g^{-1}$) compared to the value set between 0.1 and 0.5 mg $KOH \cdot g^{-1}$ oil by EN 14214, 2019. The results obtained explain that this oil is rich in free fatty acids. This value could be reduced by the saponification of oil before its conversion into biodiesel. Compared to other oils used as biodiesel, the oil of olive mill waste cake is richer in free fatty acid than that of pomace (52 mg $KOH \cdot g^{-1}$) (Touati, 2013), and that of sardine oil (31.4 mg $KOH \cdot g^{-1}$) (ASTDM, 2015).

The saponification index of VO, the amount needed to saponify the free fatty acids in 1 g of oil (NF EN ISO 365, 2020), is in agreement with that of virgin olive oil (184–196). The higher the saponification number of the oil, the lower the yield of the transesterification reaction, signifying the presence of a high level of short-chain fatty acids and a higher glycerol content [23]. This result is justified by the ester value of the vegetable oil in the olive mill waste cake which is 78.76 mg $KOH \cdot g^{-1}$, indicating that one gram of this oil contains a large amount of esterified fatty acids (NM ISO 7660, 2016). This high ester value would contribute to the increase in biodiesel yield (Ahmad et al., 2019).

Spectroscopic characterization of the extracted vegetable oil

Ultraviolet-visible spectroscopy

The UV-visible spectrophotometer alteration study is evaluated by measuring the absorbance of VO at two wavelengths $\lambda 1$ = 232 nm and $\lambda 2$ = 270 nm.

The VO alteration study of OMWCP by UV visible spectrophotometer shows an absorbance value of 3.0190 au at the 232 nm wavelength. This could be explained by the presence of hydroperoxides of linoleic acid and conjugated diene systems.

The absorbance value at wavelength 270 nm is 2.4334 au, revealing the presence of oxidation side products and in particular α-diketones or α-unsaturated ketones (NF T 60-223, 2021).

Analysis of VO by infrared spectroscopy

The infrared spectrum of the vegetable oil of the OMWCP (Figure 3) shows the presence of 4 main bands: 2 bands located respectively at 2850 cm^{-1} and 2900 cm^{-1} relating to the ethyl group $-CH_2-$, a band at a frequency of 1650 cm^{-1} relating to the carbonyl group C=O and the last one at a frequency of 1050 cm^{-1} corresponds to the C-O bond, thus forming a triglyceride molecule.

Physicochemical characterization of biodiesel

Density is one of the important properties of biofuels, because it determines the sizing and technological characteristics of the vehicle's fuel components (pumps, injectors). Furthermore, in an installed system, the use of biofuels with different densities would lead to changes in combustion settings with repercussions on maximum power, efficiency and pollutant emissions (Palash et al., 2013).

In addition, the fuel injection system uses a metered flow device, so if the biodiesel has a higher density, a slightly higher mass of fuel will need to be injected.

The same applies to viscosity, which has an impact on the operation of the injection system. The main objective of using biodiesel instead of vegetable oils directly is to lower their viscosity after transesterification. This reduction is a major advantage since it allows better atomization by the injectors and therefore good combustion (Palash et al.,

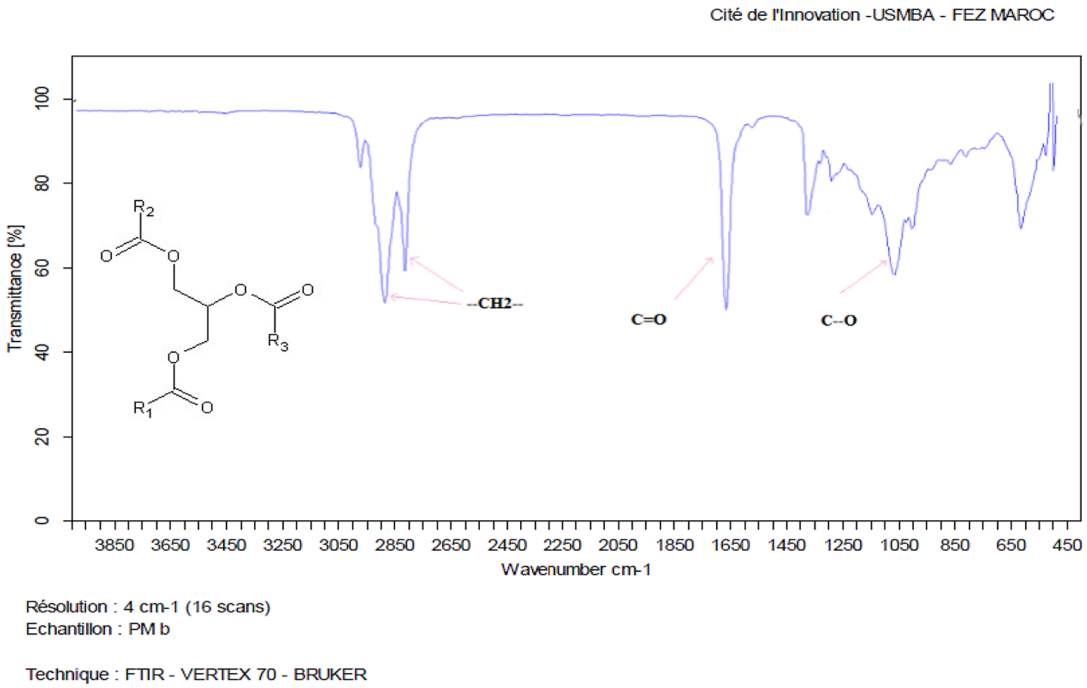

Figure 3. Infrared spectrum of the oil extracted from the olive mill waste cake powder

Table 3. Physicochemical characteristics of biodiesel

Properties	Values	Limit values for biodiesel standard	Standards (International Organization for Standardization)
Density at 25 °C ($g \cdot cm^{-3}$)	0.87	0.86–0.90	EN 14214,2013
Water content ($mg \cdot kg^{-1}$)	150	Max 500	EN 14214,2013
Viscosity ($mm^2 \cdot s^{-1}$)	2.9	3.5-5	EN 14214,2013
Ash (% by mass)	1.41	Max 0,02	EN 14214,2013
Cloud point (°C)	48	+5 °C	EN 116

2013). On the other hand, a high viscosity does not favor atomization during fuel injection. In addition, the pressure required for injection will have to increase, which will lead to incomplete combustion, causing unburnt fuel to clog the injectors, cylinders and pistons. This fact will also lead to the clogging of the motor's feeders (Babaki et al., 2015).

The results of the characterization of biodiesel obtained by transesterification (Table 3) show a density of 0.88 which explains the difficulty of separation between biodiesel and glycerol, but it agrees with the standard of the density of diesel (Palash et al., 2013) and that of biodiesel, (0.86–0.90) (Ballerini et al., 2007). It is comparable to those of previous biodiesels obtained from: Jatropha, Karanja, Canola and Rapeseed which are 0.86–0.88, 0.88–0.89, 0.88–0.90 and 0.87–0.90 respectively (Sakthivel et al., 2018; Kumar et al., 2018).

A viscosity of 2.9 which is slightly lower than the standard (3.5–5), predicts the good combustion of the obtained biodiesel.

A water content is 150 mg/kg, is in accordance with the standard (EN 14214, 2013) which limits this content to 500 $mg \cdot kg^{-1}$. Biofuels are more sensitive to water contamination than other fossil fuels because water hydrolyzes the bonds of fatty acid methyl esters (FAME) and leads to the formation of fatty acids. These acids consume additional KOH and form soaps, which makes the subsequent removal of glycerol more difficult. Biodiesel with a high-water content has significantly lower oxidation stability. The higher the water content, the higher the probability of the formation of oxidation products during storage. These can damage the engine, especially the fuel injection system (Aoun, 2015), as well as water can be a source of corrosion of the injectors, as it can also induce poor engine combustion.

An ash content of 1.41%; an excessive value and far from the European standard which recommends a maximum threshold of 0.02% (Ballerini et al., 2007). This suggests the possibility of coke formation and therefore deposits on the walls of the engine cylinders. In addition, ash can be abrasive and contribute to engine wear (Ismael et al., 2018). Therefore, further purification of the obtained biodiesel will reduce this parameter.

A very high cloud point compared to the standard set at 5 °C (EN 116), this value could have an impact on the filters of the internal system and on the pour point (Syrodoy et al., 2018; Dehaghani et al., 2019). According to the literature, the cloud point of biodiesels from animal and vegetable fats could be reduced by the addition of 5% (V/V) butanal of glycerol/acetal. Similarly, the cold flow properties could be improved by the addition of ethanol (Syrodoy et al., 2018).

Spectroscopic characterization of biodiesel

The Infrared spectrum related to biodiesel, formed by transesterification of the oil extracted

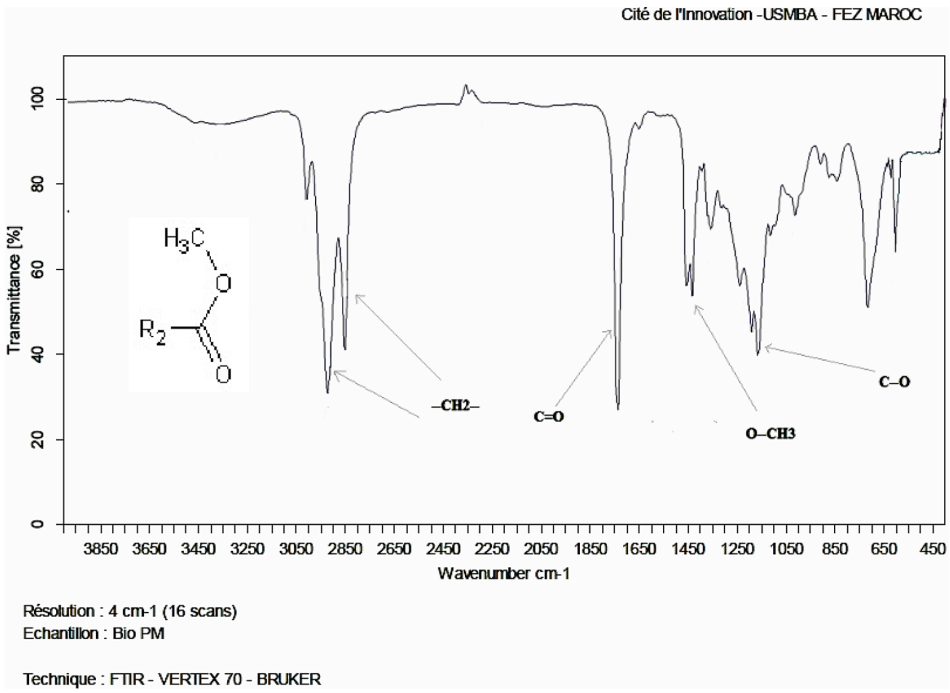

Figure 4. Infrared spectrum of biodiesel produced from vegetable oil of olive mill waste cake

from the olive mill waste cake powder (Figure 4), reflects the presence of the bands already identified for the oil, but more intense and at slightly shifted frequencies, and the appearance of other deformation bands at the frequencies 1425 cm^{-1} and 1450 cm^{-1} related to the methyl ester groups O--CH_3.

The comparison of the bands obtained from the infrared spectra of the vegetable oil extracted from the olive mill waste cake and the biodiesel produced is reported in Table 4.

A comparison of the two spectra shows the presence of a significant difference. The initial triester group is generally described as R1-CO-OR in the residue oil from the olive mill wastewater and by R1-COOCH3 in the biodiesel. R1 represents the hydrocarbon chains. The presence of the saturated hydrocarbons -CH2- (sp^3 hybridized carbon) on the R1 chain is reflected by the presence of their characteristic bands ($\bar{\upsilon}$ =2800 cm^{-1}, $\bar{\upsilon}$ =2900 cm^{-1}) for both oil and biodiesel. The carbonyl group C=O is present in both spectra. Their characteristic bands are found at frequencies 1650 cm^{-1} and 1700 cm^{-1}, respectively. The vibrations towards $\bar{\upsilon}$ =1100 cm^{-1} are characteristic of the C--O ester bond. The greatest influence following transesterification is the appearance of the new signal of two almost confluent bands toward $\bar{\upsilon}$ =1425 cm^{-1} and $\bar{\upsilon}$ =1450 cm^{-1}; this is a deformation vibration that characterizes the O--CH_3 methyl ester group.

Comparative study of biodiesels produced from some agro-food waste

The comparison of physicochemical parameters of biodiesels from some animal and vegetable substances is shown in Table 5. These parameters are the transesterification yield, the acid index which represents the amount of base needed to

Table 4. Infrared vibration frequencies of vegetable oil from olive mill waste cake and biodiesel

Vegetable Oil			Biodiesel		
Group	Vibration	Type	Group	Vibration	Type
--CH_2--	$\bar{\upsilon}$=2850 cm^{-1} $\bar{\upsilon}$=2920 cm^{-1}	Valencia	--CH_2--	$\bar{\upsilon}$=2800 cm^{-1} $\bar{\upsilon}$=2900 cm^{-1}	Valencia
C=O	$\bar{\upsilon}$= 1650cm^{-1}	Valencia	C=O	$\bar{\upsilon}$=1700 cm^{-1}	Valencia
			O--CH_3	$\bar{\upsilon}$=1425 cm^{-1} $\bar{\upsilon}$=1450 cm^{-1}	Deformation
C—O	$\bar{\upsilon}$=1100 cm^{-1}	Valencia	C—O	$\bar{\upsilon}$=1075 cm^{-1}	Valencia

Table 5. Comparison of the quality of biodiesel from different animal and plant sources

Parameter	Biodiesel efficiency (%)	Density at 15 °C	Acid index (mg KOH/g)	Ash (%)	Calorific value (MJ/kg)	Point of trouble (°C)	Water content (mg/kg)	References
Olive mill waste cake	86,41	0.87	-	1.41	-	48	150	This work
Olive pomace	89	0.87	0.36	0.014	40.29	4	960	(Lounis, 2013)
Sardine waste	81	0.89	0.42	-	37.49	-	-	(Bousbaa et al., 2014)
Date seeds	92.5	0.88	-	-	-	-	-	(Benmehdi et al., 2019)
Castor oil	96	0.84	0.12	-	44	-	200	(Keera et al., 2018)
Cotton seed oil	88	0.89	-	-	-	7.30	-	(Boulghiti et al, 2020)
Jatropha oil	78	0.88	-	-	41.63	-	-	(Moussaoui et al., 2020)
Mixing of used oils	86	0.87	0.7	-	41.46	-	-	(Sidohounde, A., et al, 2018)
Used frying oil	82	0.91	0.4	-	40.8	13	-	(Azizi, M et al. 2018)
Biodiesel quality standards	-	(0.86-0.90) EN.ISO 3675	0.5 max EN ISO 14104	0.01 max ASTM D 482	-	+5 °C max EN 116	500 max EN 14214	Boutique des normes ISO/ASTM / AFNOR

neutralize the biodiesel, the mineral content in the form of ash, the water content which gives information on the corrosive character of biodiesel, the temperature at which the biodiesel becomes cloudy which gives information on the flow properties in cold regions, and the viscosity which gives information on the oxidation state of biodiesel.

From this comparison, it is clearly visible that the biodiesel produced from the vegetable oil of the margarine paste has good characteristics in terms of density, water content and viscosity. For ash content and cloud point, the final product requires further processing. And to have a higher yield and an ecological biofuel that perfectly meets the standards of petroleum biodiesel, it is necessary to optimize the parameter of the ash content that could cause clogging of the vehicle engines.

CONCLUSION

Biodiesel is one of the most important renewable energy sources. It is renewable, its use reduces the emission of greenhouse gases.

The objective of this work was to highlight the transformation of an olive co-product previously treated by natural evaporation into biodiesel by extraction of vegetable oil and its conversion into biodiesel by transesterification. The obtained products were characterized by analysis of physicochemical parameters and by Infrared spectrometry.

The extraction led to a good yield of oil (21.28%). That of transesterification is 86.41%; that is 10339.97 tons·year^{-1} of biodiesel if we consider an annual production of olive mill waste cake of 56232 tons, from 440000 tons of olive mill wastewater. Taking into account the density of the biodiesel produced and the conversion of one lease of diesel into kWh (159 L = 1700 kWh), the annual volume of biodiesel that will be produced will be about 11885 m^3, that is to say nearly 112 GWh/year or 403,64 106 MJ in terms of energy.

The vegetable oil extracted from the olive mill waste cakes is characterized by a density of 0.88, a viscosity at 40 °C of 32.07, an ash content of 0.88%, a peroxide value of 10 meq of $O_2 \cdot kg^{-1}$, an acid and ester value of 193.54 and 78.76 mg $KOH \cdot g^{-1}$ respectively.

The biodiesel produced by transesterification has similar characteristics to that obtained from waste oils. It is characterized by a density of 0.87, water content of 150 mg.kg^{-1}, an ash content of 1.41% and a cloud point of 48 °C. Further processing of this biodiesel is recommended to improve its ash content and cloud point, and to purify it.

The analysis of oil and biodiesel by infrared spectrometry proved the presence of triglyceride in the oil and methyl ester in the biodiesel.

In conclusion, the valorization of olive mill waste cake for the production of biodiesel will be a very promising technique since the primary material is available in very large quantities. In fact, it will allow on the one hand to mitigate the degradation of landscape, the occupation of soils, the visual and olfactory pollution, the pollution of soils and of the air; and on the other hand, to have an alternative source of energy.

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