Biodiesel production from olive-pomace oil of steam-treated alperujo

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Abstract

Recently interest has been revived in the use of plant-derived waste oils as renewable replacements for fossil diesel fuel. Olive-pomace oil (OPO) extracted from alperujo (by-product of processed olives for olive oil extraction), and produced it in considerable quantities throughout the Mediterranean countries, can be used for biodiesel production. A steam treatment of alperujo is being implemented in OPO extraction industry. This steam treatment improves the solid-liquid separation by centrifugation and facilitates the drying for further extraction of OPO. It has been verified that the steam treatment of this by-product also increases the concentration of OPO in the resulting treated solid, a key factor from an economic point of view. In the present work, crude OPO from steam-treated alperujo was found to be good source for producing biodiesel. Oil enrichment, acidity, biodiesel yield and fatty acid methyl ester composition were evaluated and compared with the results of the untreated samples. Yields and some general physicochemical properties of the quality of biodiesel were also compared to those obtained with other oils commonly used in biodiesel production. As for biodiesel yield no differences were observed. A transesterification process which included two steps was used (acid esterification followed by alkali transesterification). The maximum biodiesel yield was obtained using molar ratio methanol/triglycerides 6:1 in presence of sodium hydroxide at a concentration of 1% (w/w), reaction temperature 60 °C and reaction time 80 min. Under these conditions the process gave yields of about 95%, of the same order as other feedstock using similar production conditions.
Keywords: Alperujo, Biodiesel, steam treatment, Methyl esters, Olive-pomace oil, Transesterification

1. Introduction

Biofuels are sustainable and renewable energy sources derived from biological materials wastes. The production and consumption of biofuels continues to increase as more attention is paid to the environment protection, the rapid rate of growth in world energy requirements mainly in developing countries and the depletion of conventional fossil-fuel resources. Biodiesel, a fuel produced from natural/virgin edible and non-edible vegetable oils including used cooking oils or animal fats like tallow and fish oil [1], is a good substitute for petroleum-diesel fuel representing an alternative source of energy, which can supplement or totally replace fossil fuels in diesel engines without any major modification. According to the United States Environmental Protection Agency (EPA), biodiesel may be blended with conventional diesel to obtain different blends such as B20 (20% biodiesel) or it can be used as 100% biodiesel (B100). Biodiesel is technically defined as a mixture of long-chain fatty acid methyl esters (typically C_{14}-C_{22}). Biodiesel is non-toxic, biodegradable and significantly reduces pollutant emissions such as carbon monoxide (44%), particulate matter (40%), and sulphur dioxide (100%) [2].

The benefits to using biodiesel have promoted research on a variety of raw materials that can be used to produce it. Exploring other sources of renewable oils is of interest, not only to further increase the economic viability of biodiesel, but also to increase the
potential supply of this fuel. It is observed that there is a close relationship between
the availability of oils and the publication of papers since, depending upon the climate,
soil conditions and geographical location, each country studies mostly those vegetable
oils which has available: for example, soybean oil in the US; rapeseed and sunflower
oils in Europe and palm oil in Asia [3-5]. In the Mediterranean region countries, the
corresponding renewable feedstock and one of the possible sources for biodiesel
production would be olive-pomace oil (OPO) extracted from solid waste called two-
phase pomace or “alperujo”. OPO is a by-product very abundant, in the 2005-06
season, the annual OPO production is estimated at 56,000 tonnes in Spain (Agency for
Olive Oil) [6]. In the last years, only a very few authors have explored the possibility of
using OPO for biodiesel production and have concluded that it can be considered as a
good potential feedstock [7-9] for this purpose. On the other hand the problems
concerning the detection of benzopyrene in OPO discovered in 2001 have drastically
reduced the human consumption. Therefore, biodiesel production is converted into an
important alternative commercial for the OPO. OPO extraction plants would not have
to perform the refining process of crude OPO, increasing biodiesel profit margins.
However, although alperujo is easily available (only Spain generates approximately 4-6
million tonnes every year) and a low-cost raw material, it should be taken into
consideration other important aspects such as its high moisture (50-70%) and low oil
content. The technological changes performed in olive oil mills have introduced more
efficient methods of olive oil extraction such as the two-phase centrifugation system.
Moreover, alperujo is usually treated in a second centrifugation to extract the residual
oil, with which final oil content is left around 1-2.5%. With these data, production costs
from a solid so exhausted increase as a result of drying the alperujo and subjected it to
solvent extraction with hexane in order to obtain OPO. The oil content is of fundamental significance and the price of oil may mean between 60-75% of the total cost [10] of biodiesel production and, in the future, is likely to become the main competitive factor determining on international markets [11].

It is possible to reduce the moisture content and to increase oil yield of alperujo to make of OPO an alternative economically competitive for biodiesel production. From an environmental point of view, alperujo represents a serious trouble in the Mediterranean area countries due to its highly polluting organic load which limit its biodegradation because of their high toxicity. In recent years, many management options have been proposed for the treatment and valorization of alperujo. One of the most interesting is a steam treatment developed and patented by Fernández-Bolaños and co-workers [12] already implemented at industrial scale by one of the most important OPO extraction industries in Spain, so that all processed alperujo will be treated by means of this system in a future. This treatment is conducted in a continuous reactor using steam at high pressures and temperatures (150-170 °C, 5-8 kg/cm²) and allows the separation of alperujo into two phases (liquid and solid), operation that is practically impossible without treatment. Therefore, the solid fraction resulting has a lower moisture content (30-35%). The treatment combines a physicochemical effect that helps break cell wall structure, cellulose depolimerization and autohydrolysis of hemicellulosic material due to the generation of acids such as acetic and formic. As a consequence of this a release of phenolic compounds (hydroxytyrosol, 3,4-dihydroxyphenylglycol), lignans, fermentable simple sugars, oligo- and polysaccharides and other high-added value compounds is produced. The result is
a significant solubilization of the solid fraction in the liquid phase. The solubilization causes a substantial reduction of dry weight of alperujo (20-50%) and together with the efficient solid-liquid separation lead to a final solid material enriched in components such as cellulose and proteins. The oil is also concentrated in it producing an extra yield of OPO [13], making more interesting to recover this non-edible waste oil for biodiesel. The effects of the steam treatment on both fractions separated from the treated alperujo are reported in Table 1 (the data shown on this table correspond to one of the alperujo samples used in this study).

In this work, crude olive-pomace oil (non-refined) from steam-treated alperujo was used for the production of biodiesel by alkali-catalyzed transesterification. The aim of the paper was to study the use of OPO extracted of steam-treated alperujo for biodiesel production and to check whether the steam treatment has some effect on yield of biodiesel production and there are differences between OPO from steam-treated and untreated alperujo samples. The possibility of obtaining valuable products such as biodiesel from OPO not only is a solution environmentally friendly, but also is important because increase the value of alperujo.

2. Methods

2.1. Materials

Two fresh alperujo samples from different olive cultivars and consecutive seasons (2007-2008 and 2008-2009) were supplied by an experimental olive oil mill plant
located at the Instituto de la Grasa (CSIC) in Seville (Spain) and directly collected from a two-phase centrifugal system decanter. In particular the alperujo of the 2007-2008 season was obtained from olive fruit of marteña variety while the alperujo of the 2008-2009 season correspond to picual variety. The reason is that this olive oil mill plant often processes olive fruits from diverse regions. These alperujo samples had moisture content 65% and 60%, and contained 8.5% and 10.2% of oil, respectively, because they were not subjected to a second centrifugation.

2.2. Steam treatment

The steam treatment was performed using a steam treatment reactor prototype designed at the Instituto de la Grasa (Seville, Spain). The reactor has a 100 L capacity stainless steel reservoir that can operate at temperatures up to 190 °C and at a maximum pressure of 1.2 MPa. Alperujo samples (20 kg) were put in the reactor and uniformly distributed. Heating of the alperujo was performed by direct injection of high-pressure and high-temperature steam enhancing the intimate contact between the steam and the alperujo to be heated. The conditions of treatment were fixed at 160 °C for 60 min. These conditions are enough to have a good solid-liquid separation, solid reduction and a lower moisture content and higher oil concentration. After treatment, alperujo samples were centrifuged at 4700 g (Comteifa S. L., Barcelona, Spain) to separate the liquid and solid fractions. After treatment, the wet solid fraction was stove-dried at 50 °C. Dry alperujo samples were refluxed for 6 h with n-hexane using a Soxhlet apparatus for extracting OPO. The solvent was removed in a vacuum
rotary evaporator. Oils obtained were filtered and the oil content and fat enrichment were determined and compared with control values of untreated alperujo samples.

2.3. Acidity and peroxide value

The determinations of free acidity and peroxide value (PV) in OPO were carried out according to the official methods described in European Community Regulation EEC/2568/91 by titration using an ethanolic solution of potassium hydroxide and phenolphthalein as an indicator; and on the other hand by titration of the liberated iodine with sodium thiosulphate solution, respectively. The results were expressed as a percentage of oleic acid and in terms of milliequivalents of active oxygen per kilogram, respectively. The measure of free acidity is important because the alkali-catalyzed process is affected by free fatty acids (FFA) which can react with base catalysts to form soaps, decreasing biodiesel yield and making difficult the separation of glycerol.

2.4. Biodiesel production

A two-step esterification-transesterification process was used to produce biodiesel from OPO. A schematic process flow chart used in this work for biodiesel production from OPO is shown in Fig. 1. Transesterification (reaction of a fat or oil with an alcohol to form fatty acid alkyl esters and glycerol) is one of the best and most common methods for producing biodiesel from vegetable oils [14]. The experimental device was the same in both steps and consisted of a 5-litre cylindrical glass reactor with a cover fitted with three mouths for the connection of the agitator, thermometer and
sampling tube. The reaction temperature was adjusted by introducing the reactor in a thermostatic bath. The batch reactor was equipped with a reflux condenser to avoid alcohol evaporation. The stirring speed was maintained to 600 rpm.

2.4.1. Acid esterification

Transesterification reaction conditions require the removal of free fatty acids from the oil by preesterification. Free fatty acids were first converted to esters with methanol (using a methanol to oil molar ratio of 8:1) in a pre-treatment process, using an acid catalyst (H$_2$SO$_4$ 1% w/w) to reduce the acid value of OPO and inhibit the saponification reaction during alkaline transesterification. It has been reported that transesterification does not occur if free fatty acid content in the oil is above 3% [15]. In acid esterification, 450 g of OPO were poured into the reactor and heated to 60 °C for 1 h. These conditions were found as optima by Marín et al. [16] for biodiesel production from olive oil soapstock, which composition is constituted mainly by free fatty acids. After the reaction mixture was allowed to cool at room temperature and centrifuged to remove acid-methanol phase.

2.4.2. Alkali transesterification

For the transesterification reaction, treated oil from esterification was used. This second stage is used to transesterify the triglycerides. According to the most literature consulted and to our previous investigations on biodiesel production from different vegetable oils [16], the temperature was fixed at 60 °C for all the experiments. Above
60 °C the yield decreases due to release of methanol through evaporation and decomposition of methyl esters [7]. The catalyst concentration, reaction time and molar ratio methanol/oil were tested as variables to determine the best conditions for highest efficiency in biodiesel production with NaOH as a catalyst. After the transesterification reaction was completed, the reactant mixture was allowed to be separated into two layers. The bottom layer containing catalyst, glycerol, soaps and water was drawn off. The methyl esters along with the free fatty acids remained in the upper layer were then separated and washing with an aqueous solution of sodium chloride to remove the impurities. The sterified product was subjected to vacuum distillation to remove the unreacted methanol and was washed with water to remove impurities and to obtain pure biodiesel.

2.5. Analysis of fatty acid methyl esters

The fatty acid methyl esters (FAME) composition of biodiesel was determined by gas chromatography according to European standard test method EN 14103 [17]. A Varian CP-3800 model gas chromatograph equipped with a GC capillary column TeknokromaTRB-50ht (30 m length x 0.25 mm internal diameter x 0.15 µm film thickness) (Teknokroma, Barcelona, Spain) and a flame ionization detector (FID) was used. The temperature of the injector and detector was set at 250 °C. The oven temperature was held at 155 °C for 10 min, then the temperature program ramps from 155 °C to 205 °C at 3 °C/min and maintained at this temperature for 15 minutes. Hydrogen was the carrier gas at constant flow rate (1 mL/min). Approximately 0.25 g of sample was accurately weighed in a 10 mL vial, and then 5 mL of a methyl
heptadecanoate (C17:0) internal standard solution (10 mg/mL in n-hexane) was added. The injection volume was 1 µL in split mode (50:1).

2.6. Statistical analysis

Statistical analysis was performed using Statgraphics Plus Version 5.1. A 5% level of statistical significance (p value <0.05) is chosen to indicate a significant difference in the biodiesel production between two samples of OPO extracted from treated and non-treated alperujo. Experiments were performed in triplicate and values are expressed as mean ± SD. Results were analyzed by using Student’s t–test and one-way analysis of variance (one-way ANOVA).

3. Results and discussion

Table 2 shows some chemical properties of olive-pomace oils and the effect of steam treatment on the OPO content extracted from alperujo, which exhibit an increase by approximately 50% as the alperujo is treated at 160 °C for 60 min. However, the content of free fatty acids in OPO (expressed as acidity and determined by the standard titrimetry method) and peroxide value also increase as a result of the steam treatment. These results are in agreement with other previously reported [13]. Olive-pomace oils extracted from steam-treated alperujos have an initial acidity value corresponding to 15.1% and 9.0%, which are far above the 3% acceptable limit for a satisfactory transesterification reaction using alkaline catalyst. The free fatty acids can affect the process of biodiesel production in terms of yield, so oils were subjected to a
previous acid esterification. For operating conditions used the percentage of FAME obtained is approximately 90%. Thus the acidity was reduced below the mentioned 3%. Other authors have studied the free fatty acid esterification process of olive pomace oil and with sulphuric acid as catalyst (1%) the FFA concentration decreased from 20.1% to 2.1%, after 1 h reaction [8]. Coming up it was investigated whether the steam treatment had any influence on biodiesel yield analyzing some of the most relevant factors involved with biodiesel production. Fig. 2a shows the molar ratio effect on the yield of biodiesel obtained in the second step (alkali transesterification). Alkali transesterification reaction was evaluated for four different molar ratios. The methanol/oil molar ratio was varied within the range 3:1 to 20:1 (including 6:1, 10:1 and 15:1) and all other factors remaining constant (catalyst 1%, 60 °C for 80 min). From a stoichiometric point of view, transesterification only requires a molar ratio 3:1, but in practice this is not enough to drive the equilibrium to a maximum methyl ester conversion [18]. For a molar ratio of 3:1, the biodiesel yield was low and did not exceed 15%. The maximum methyl ester conversions for olive-pomace oils from treated and non-treated alperujo of the first season (2007-2008) were 93.3% and 95.9%, respectively, at a molar ratio methanol/oil of 6:1. Molar ratios between 3:1 and 6:1 were not tested because some investigators proved that for molar ratios less than 6:1 the reaction was incomplete [14, 19]. As molar ratio of methanol to oil increased from 3:1 to 6:1, the biodiesel production yield also increased and reached the maximum at 6:1 in most investigations with the use of an alkali catalyst [18]. However, when the molar ratio exceeded 6:1, the conversion to biodiesel decreased because the extra amount of methanol increased the solubility of glycerine which helps to return the equilibrium, resulting in lower percentages of biodiesel [20] and increasing cost for
alcohol recovery. While there were significant differences among the biodiesel yields for five different molar ratios studied, there were no differences among treated and non-treated alperuco samples.

The effect of catalyst concentration on the biodiesel yield is shown in Fig. 2b. Three levels of catalyst concentration were selected; the reactions were conducted at 1.0%, 1.1% and 1.3%. Selection of the levels was carried out based on results obtained by other investigators who optimized biodiesel production via alkali-catalyzed transesterification from various oils using these concentrations of sodium hydroxide [21-23]. The production of biodiesel was found to be highly dependent on the catalyst concentration. Transesterification of OPO with 1% (w/w) NaOH gave the best conversions. When the concentration of catalyst exceeded 1%, the biodiesel production decreased due to excess of catalyst can also cause hydrolysis, saponification [24] and formation of emulsions block the reaction [25]. Although typical concentrations for transesterification reactions range from 0.5% to 1.5% [23] and results suggest that a lower catalyst concentration should also be tested, however several articles focused on the production of biodiesel and that have studied variables that affect yield of fatty esters from transesterified vegetable oils found that concentrations in the range of 0.5-1.0% (w/w) NaOH are insufficient amounts of catalyst and resulted in an incomplete conversion of the triglycerides into the fatty acid methyl esters [21, 26]. In this sense, Çaynak et al. [7] studied the biodiesel production from pomace oil and obtained only a maximum yield of 80% at 30% (w/w) methanol/oil ratio, 60 °C for 60 min with 0.5% (w/w) NaOH as catalyst. Moreover, other works that have focused on the optimization of biodiesel production from orujo
olive oil found that the optimal amount of catalyst concentration for the transesterification reaction resulted even higher than the reported in this study [27]. Therefore, the methanol/oil molar ratio and the concentration of catalyst were kept at 6:1 and 1%, respectively in the remaining experiments. These experimental conditions are in accordance with data from other authors and are normally used in industrial processes to obtain methyl esters yields higher than 98% from vegetable oils [26, 28]. Dorado et al. [29] on biodiesel production from olive oil with 1% (w/w) KOH as catalyst have reported yields around 90%. Overall, no significant differences in biodiesel yield were observed among olive-pomace oils obtained from non-treated and treated alperujo. The acid esterification pretreatment reduced the effect of FFA high content in reaction with alkali catalyst and ensured a high yield of biodiesel. Various researchers have proven that two-step transesterification is better than the one-step process [30, 31].

In order to study the effect of reaction time transesterification experiments for OPO were carried out for periods of time between 20 min and 120 min taken aliquots of the upper layer which are used to determine the biodiesel percentage produced. The experimental parameters were 1% of NaOH and reaction temperature 60 °C. As shown in Fig. 3, results obtained from the experiments with OPO extracted from alperujo of the 2008-2009 season revealed that the conversion efficiency increased with the reaction time but 80 min for alkali transesterification was sufficient for the completion of the reactions. Longer reaction times lead to a reduction in the biodiesel yield due to the backwards reaction of transesterification [32] or the decomposition of OPO methyl esters. Therefore, for maximum yield the reaction time must be less than 90 min [15].
Again the maximum conversion efficiency was 95.7% under these reaction conditions, which is similar to value for OPO in the former season. High yields are also achieved with higher molar ratios (80.2%, 75.6% and 71.2%), although problems of separation of glycerin occur after the reaction because a great part of it dissolves in the biodiesel phase. Therefore, molar ratio 6:1 seems to be the most appropriate.

Table 3 shows a comparative summary of yields and some general physicochemical properties for the quality of biodiesel produced from OPO of treated alperujo and other different feedstock obtained under similar production conditions. It is observed that OPO biodiesel can be produced with the same high ester yields than other primary sources for biodiesel production such as soybean oil in the USA and rapeseed oil in Europe. In addition, steam treatment did not affect negatively the biodiesel properties tested in this study, as all values are within the limits established in ASTM D6751 specifications. OPO biodiesel has a cetane number of 54, exceeding those of other oils, excepting the palm oil, what it would provide higher combustion efficiency.

The viscosity is also one of the most important properties of biodiesels since it affects the operation of fuel injection equipment. Low viscosity leads to better atomization of the fuel spray and more accurate operation of the fuel injectors [1]. The kinematic viscosity of the OPO biodiesel is 4.0 mm²/s at 40 °C. Compared to all of oils that are listed in Table 3 is lower. OPO biodiesel also complies with EN 14214 specifications as to kinematic viscosity at 40 °C (3.5-5.0 mm²/s) and cetane number (> 51).

The fatty acid methyl ester composition of biodiesel produced is shown in Table 4. As transesterification does not alter the fatty acid composition of the feedstock it can be
concluded that steam treatment scarcely modified the fatty acid composition of OPO from steam-treated alperujo compared with untreated samples because the fatty acid percentages which are commonly found in OPO are within the range specified by International Olive Council [33] and there were no significant differences between biodiesel samples in the same season. The different composition of fatty methyl esters depending on season is due to that alperujo samples used in this work come from different olive cultivars. Some studies show that fatty acids composition of olive oils has a strong varietal component; many authors coincide in attributing to this factor a considerable importance (more than 70%) in variability found, particularly if takes into account percentage changes in the content of palmitic, stearic, oleic and linoleic acid [34]. After alkali-catalyzed transesterification the biodiesel showed the following fatty acid methyl esters composition: methyl palmitate (16:0), methyl stearate (18:0), methyl oleate (18:1), methyl linoleate (18:2) and methyl linolenate (18:3), with small amounts of other methyl esters also present. OPO biodiesel is rich in methyl oleate and the presence of monounsaturated methyl esters gives it a high cetane number (enhances the ignition quality) which is one of its main advantages compared to conventional diesel fuels.

4. Conclusions

In this study, two different samples of OPO extracted from steam-treated alperujo were tested for the biodiesel production. It was observed that the biodiesel yield was not negatively affected by the steam treatment of alperujo. In addition, the OPO percentage of alperujo increases with steam treatment, approximately 50% under
applied conditions (160 °C for 60 min), but in more severe treatments may reach almost 100%. As a result, extraction costs decrease a similar percentage. This is an advantage and an important economic parameter to consider would make this feedstock much more competitive and commercially viable as a biodiesel source. Taking into consideration all of the parameters studied, the highest conversions for the alkali-catalyzed transesterification of OPO were obtained with methanol/oil molar ratio 6:1, 1% (w/w) of NaOH as catalyst at 60 °C for 80 min. Under the best combination, the conversion to biodiesel reached above 95%. The results indicate that OPO from steam-treated alperujo could be used as a good source of renewable energy for biodiesel production by acid esterification followed by alkali-catalyzed transesterification. Some more specific properties of the quality of biodiesel produced should be tested in further studies to verify whether it complies with standard specifications being established by the ASTM or EN for being used as biofuel in diesel engines and the steam treatment has a significant effect or provides a special advantage on the quality of the methyl esters.

Acknowledgement

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1. Introduction

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It is possible to reduce the moisture content and to increase oil yield of alperujo to 
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and polysaccharides and other high-added value compounds is produced. The result is
a significant solubilization of the solid fraction in the liquid phase. The solubilization causes a substantial reduction of dry weight of alperujo (20-50%) and together with the efficient solid-liquid separation lead to a final solid material enriched in components such as cellulose and proteins. The oil is also concentrated in it producing an extra yield of OPO [13], making more interesting to recover this non-edible waste oil for biodiesel. The effects of the hydrothermal treatment on both fractions separated from the treated alperujo are reported in Table 1.

In this work, crude olive-pomace oil (non-refined) from steam-treated alperujo was used for the production of biodiesel by alkali-catalyzed transesterification. The aim of the paper was to study the use of OPO extracted of steam-treated alperujo for biodiesel production and to check whether the hydrothermal treatment has some effect on yield of biodiesel production and there are differences between OPO from steam-treated and untreated alperujo samples. The possibility of obtaining valuable products such as biodiesel from OPO not only is a solution environmentally friendly, but also is important because increase the value of alperujo.

2. Methods

2.1. Materials

Two fresh alperujo samples from different olive cultivars and consecutive seasons (2007-2008 and 2008-2009) were supplied by an experimental olive oil mill plant located at the Instituto de la Grasa (CSIC) in Seville (Spain) and directly collected from
two-phase centrifugal system decanter. These alperujo samples had moisture content 65% and 60%, and contained 8.5% and 10.2% of oil, respectively, because they were not subjected to a second centrifugation.

2.2. Hydrothermal treatment

The hydrothermal treatment was performed using a steam treatment reactor prototype designed at the Instituto de la Grasa (Seville, Spain). The reactor has a 100 L capacity stainless steel reservoir that can operate at temperatures up to 190 °C and at a maximum pressure of 1.2 MPa. Alperujo samples (20 kg) were put in the reactor and uniformly distributed. Heating of the alperujo was performed by direct injection of high-pressure and high-temperature steam enhancing the intimate contact between the steam and the alperujo to be heated. The conditions of treatment were fixed at 160 °C for 60 min. These conditions are enough to get a good solid-liquid separation, solid reduction and a lower moisture content and higher oil concentration. After treatment, alperujo samples were centrifuged at 4700 g (Comteifa, S. L., Barcelona, Spain) to separate the liquid and solid fractions. After treatment, the wet solid fraction was stove-dried at 50 °C. Dry alperujo samples were refluxed for 6 h with n-hexane using a Soxhlet apparatus for extracting OPO. The solvent was removed in a vacuum rotary evaporator. Oils obtained were filtered and the oil content and fat enrichment were determined and compared with control values of untreated alperujo samples.

2.3. Acidity and peroxide value
The determinations of free acidity and peroxide value (PV) in OPO were carried out according to the official methods described in European Community Regulation EEC/2568/91 by titration using an ethanolic solution of potassium hydroxide and phenolphthalein as an indicator; and on the other hand by titration of the liberated iodine with sodium thiosulphate solution, respectively. The results were expressed as a percentage of oleic acid and in terms of milliequivalents of active oxygen per kilogram, respectively. The measure of free acidity is important because the alkali-catalyzed process is affected by free fatty acids (FFA) which can react with base catalysts to form soaps, decreasing biodiesel yield and making difficult the separation of glycerol.

2.4. Biodiesel production

A two-step esterification-transesterification process was used to produce biodiesel from OPO. A schematic process flow chart used in this work for biodiesel production from OPO is shown in Fig. 1. Transesterification (reaction of a fat or oil with an alcohol to form fatty acid alkyl esters and glycerol) is one of the best and most common methods for producing biodiesel from vegetable oils [14]. The experimental device was the same in both steps and consisted of a 5-litre cylindrical glass reactor with a cover fitted with three mouths for the connection of the agitator, thermometer and sampling tube. The reaction temperature was adjusted by introducing the reactor in a thermostatic bath. The batch reactor was equipped with a reflux condenser to avoid alcohol evaporation. The stirring speed was maintained to 600 rpm.

2.4.1. Acid esterification
Transesterification reaction conditions require the removal of free fatty acids from the oil by preesterification. Free fatty acids were first converted to esters with methanol (using a methanol to oil molar ratio of 8:1) in a pre-treatment process, using an acid catalyst ($\text{H}_2\text{SO}_4$ 1% w/w) to reduce the acid value of OPO and inhibit the saponification reaction during alkaline transesterification. It has been reported that transesterification does not occur if free fatty acid content in the oil is above 3% [15]. In acid esterification, 450 g of OPO were poured into the reactor and heated to 60 °C for 1 h. These conditions were found as optima by Marín et al. [16] for biodiesel production from olive oil soapstock, which composition is constituted mainly by free fatty acids. After the reaction mixture was allowed to cool at room temperature and centrifuged to remove acid-methanol phase.

2.4.2. Alkali transesterification

For the transesterification reaction, treated oil from esterification was used. This second stage is used to transesterify the triglycerides. According to the most literature consulted and to our previous investigations on biodiesel production from different vegetable oils [16], the temperature was fixed at 60 °C for all the experiments. Above 60 °C the yield decreases due to release of methanol through evaporation and decomposition of methyl esters [7]. The catalyst concentration, reaction time and molar ratio methanol/oil were tested as variables to determine the best conditions for highest efficiency in biodiesel production with NaOH as a catalyst. After the transesterification reaction was completed, the reactant mixture was allowed to be
separated into two layers. The bottom layer containing catalyst, glycerol, soaps and water was drawn off. The methyl esters along with the free fatty acids remained in the upper layer were then separated and washing with an aqueous solution of sodium chloride to remove the impurities. The sterified product was subjected to vacuum distillation to remove the unreacted methanol and was washed with water to remove impurities and to obtain pure biodiesel.

2.5. Analysis of fatty acid methyl esters

The fatty acid methyl esters (FAME) composition of biodiesel was determined by gas chromatography according to European standard test method EN 14103 [17]. A Varian CP-3800 model gas chromatograph equipped with a GC capillary column Teknokroma TRB-50ht (30 m length x 0.25 mm internal diameter x 0.15 µm film thickness) (Teknokroma, Barcelona, Spain) and a flame ionization detector (FID) was used. The temperature of the injector and detector was set at 250 °C. The oven temperature was held at 155 °C for 10 min, then the temperature program ramps from 155 °C to 205 °C at 3 °C/min and maintained at this temperature for 15 minutes. Hydrogen was the carrier gas at constant flow rate (1 mL/min). Approximately 0.25 g of sample was accurately weighed in a 10 mL vial, and then 5 mL of a methyl heptadecanoate (C17:0) internal standard solution (10 mg/mL in n-hexane) was added. The injection volume was 1 µL in split mode (50:1).

2.6. Statistical analysis
Statistical analysis was performed using Statgraphics Plus Version 5.1. A 5% level of statistical significance (p value < 0.05) is chosen to indicate a significant difference in the biodiesel production between two samples of OPO extracted from treated and non-treated alperujo. Experiments were performed in triplicate and values are expressed as mean ± SD. Results were analyzed by using Student’s t-test and analysis of variance (ANOVA).

3. Results and discussion

Table 2 shows some chemical properties of olive-pomace oils and the effect of hydrothermal treatment on the OPO content extracted from alperujo, which exhibit an increase by approximately 50% as the alperujo is treated at 160 °C for 60 min. However, the content of free fatty acids in OPO (expressed as acidity and determined by the standard titrimetry method) and peroxide value also increase as a result of the hydrothermal treatment. These results are in agreement with other previously reported [13]. Olive-pomace oils extracted from steam-treated alperujos have an initial acidity value corresponding to 15.1% and 9.0%, which are far above the 3% acceptable limit for a satisfactory transesterification reaction using alkaline catalyst. The free fatty acids can affect the process of biodiesel production in terms of yield, so oils were subjected to a previous acid esterification. For operating conditions used the percentage of FAME obtained is approximately 90%. Thus the acidity was reduced below the mentioned 3%. Other authors have studied the free fatty acid esterification process of olive pomace oil and with sulphuric acid as catalyst (1%) the FFA concentration decreased from 20.1% to 2.1%, after 1 h reaction [8]. Coming up it was
investigated whether the hydrothermal treatment had any influence on biodiesel yield analyzing some of the most relevant factors involved with biodiesel production. Fig. 2a shows the molar ratio effect on the yield of biodiesel obtained in the second step (alkali transesterification). Alkali transesterification reaction was evaluated for four different molar ratios. The methanol/oil molar ratio was varied within the range 3:1 to 20:1 (including 6:1, 10:1 and 15:1) and all other factors remaining constant (catalyst 1%, 60 °C for 80 min). From a stoichiometric point of view, transesterification only requires a molar ratio 3:1, but in practice this is not enough to drive the equilibrium to a maximum methyl ester conversion [18]. For a molar ratio of 3:1, the biodiesel yield was low and did not exceed 15%. The maximum methyl ester conversions for olive-pomace oils from treated and non-treated alperujo of the first season 2007-2008 were 93.3% and 95.9%, respectively, at a molar ratio methanol/oil of 6:1. However, when the molar ratio exceeded 6:1, the conversion to biodiesel decreased because the extra amount of methanol increased the solubility of glycerine which helps to return the equilibrium, resulting in lower percentages of biodiesel [19]. While there were significant differences among the biodiesel yields for five different molar ratios studied, there were no differences among treated and non-treated alperujo samples.

The effect of catalyst concentration on the biodiesel yield is shown in Fig. 2b. Three levels of catalyst concentration were selected; the reactions were conducted at 1.0%, 1.1% and 1.3%. The production of biodiesel was found to be highly dependent on the catalyst concentration. Transesterification of OPO with 1% (w/w) NaOH gave the best conversions. When the concentration of catalyst exceeded 1%, the biodiesel production decreased due to excess of catalyst can also cause hydrolysis,
saponification [20] and formation of emulsions block the reaction [21]. Therefore, the
methanol/oil molar ratio and the concentration of catalyst were kept at 6:1 and 1%,
respectively in the remaining experiments. These experimental conditions are in
accordance with data from other authors and are normally used in industrial processes
to obtain methyl esters yields higher than 98% from vegetable oils [22, 23]. Çaynak et
al. [7] studied the biodiesel production from pomace oil and obtained a maximum yield
of 80% at 30% (w/w) methanol/oil ratio, 60 °C for 60 min with NaOH catalyst. Dorado
et al. [24] on biodiesel production from olive oil with KOH as catalyst have reported
yields around 90%. Overall, no significant differences in biodiesel yield were observed
among olive-pomace oils obtained from non-treated and treated alperujo. The acid
esterification pretreatment reduced the effect of FFA high content in reaction with
alkali catalyst and ensured a high yield of biodiesel. Various researchers have proven
that two-step transesterification is better than the one-step process [25, 26].

In order to study the effect of reaction time transesterification experiments for OPO
were carried out for periods of time between 20 min and 120 min taken aliquots of the
upper layer which are used to determine the biodiesel percentage produced. The
experimental parameters were 1% of NaOH and reaction temperature 60 °C. As shown
in Fig. 3, results obtained from the experiments with OPO extracted from alperujo of
season 2008-2009 revealed that the conversion efficiency increased with the reaction
time but 80 min for alkali transesterification was sufficient for the completion of the
reactions. Longer reaction times lead to a reduction in the biodiesel yield due to the
backwards reaction of transesterification [27] or the decomposition of OPO methyl
esters. Therefore, for maximum yield the reaction time must be less than 90 min [15].
Again the maximum conversion efficiency was 95.7% under these reaction conditions, which is similar to value for OPO in the former season. High yields are also achieved with higher molar ratios (80.2%, 75.6% and 71.2%), although problems of separation of glycerin occur after the reaction because a great part of it dissolves in the biodiesel phase. Therefore, molar ratio 6:1 seems to be the most appropriate.

Table 3 shows a comparative summary of yields and some general physicochemical properties for the quality of biodiesel produced from OPO of treated alperujo and other different feedstock obtained under similar production conditions. It is observed that OPO biodiesel can be produced with the same high ester yields than other primary sources for biodiesel production such as soybean oil in the USA and rapeseed oil in Europe. In addition, hydrothermal treatment didn’t affect negatively the biodiesel properties tested in this study, as all values are within the limits established in ASTM D6751 specifications. OPO biodiesel has a cetane number of 54, exceeding those of other oils, excepting the palm oil, what it would provide higher combustion efficiency. The viscosity is also one of the most important properties of biodiesels since it affects the operation of fuel injection equipment. Low viscosity leads to better atomization of the fuel spray and more accurate operation of the fuel injectors [1]. The kinematic viscosity of the OPO biodiesel is 4.0 mm²/s at 40 °C. Compared to all of oils that are listed in Table 3 is lower. OPO biodiesel also complies with EN 14214 specifications as to kinematic viscosity at 40 °C (3.5-5.0 mm²/s) and cetane number (> 51).
The fatty acid methyl ester composition of biodiesel produced is shown in Table 4. As transesterification does not alter the fatty acid composition of the feedstocks it can be concluded that hydrothermal treatment scarcely modified the fatty acid composition of OPO from steam-treated alperujo compared with untreated samples because the fatty acid percentages which are commonly found in OPO are within the range specified by International Olive Council [28] and there were no significant differences between biodiesel samples in the same season. After alkali-catalyzed transtesterification the biodiesel showed the following fatty acid methyl esters composition: methyl palmitate (16:0), methyl stearate (18:0), methyl oleate (18:1), methyl linoleate (18:2) and methyl linolenate (18:3), with small amounts of other methyl esters also present. OPO biodiesel is rich in methyl oleate and the presence of monounsaturated methyl esters gives it a high cetane number (enhances the ignition quality) which is one of its main advantages compared to conventional diesel fuels.

4. Conclusions

In this study, two different samples of OPO extracted from steam-treated alperujo were tested for the biodiesel production. It was observed that the biodiesel yield was not negatively affected by the hydrothermal treatment of alperujo. In addition, the OPO percentage of alperujo increases with hydrothermal treatment, approximately 50% under applied conditions (160 °C for 60 min), but in more severe treatments may reach almost 100%. As a result, extraction costs decrease a similar percentage. This is an important economic parameter to consider would make this feedstock much more competitive and commercially viable as a biodiesel source. Taking into consideration
all of the parameters studied, the highest conversions for the alkali-catalyzed transesterification of OPO were obtained with methanol/oil molar ratio 6:1, 1% (w/w) of NaOH as catalyst at 60 °C for 80 min. Under the best combination, the conversion to biodiesel reached above 95%. The results indicate that OPO from steam-treated alperujo could be used as a good source of renewable energy for biodiesel production by acid esterification followed by alkali-catalyzed transesterification. Some more specific properties of the quality of biodiesel produced should be tested in further studies to verify whether it complies with standard specifications being established by the ASTM or EN for being used as biofuel in diesel engines and the hydrothermal treatment has a significant effect or provides a special advantage on the quality of the methyl esters.

Acknowledgement

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References


Table 1 Comparison of effect of the steam treatment on each fraction separated from treated alperujo (at 160°C for 60 min) with regard to non-treated alperujo from season 2008/2009.

<table>
<thead>
<tr>
<th>Season 2008/2009</th>
<th>Solid fraction</th>
<th>Liquid fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Moisture content (%)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Total phenols (g Gallic Acid Equivalents/kg alperujo)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>59.4</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>39.0</td>
<td>1.74</td>
</tr>
<tr>
<td></td>
<td>Reduction of dry weight (%)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Sugars (%)&lt;sup&gt;b,c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>37.1</td>
<td>4.75</td>
</tr>
<tr>
<td></td>
<td>Oil (%)&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.2</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>14.9</td>
<td>4.75</td>
</tr>
</tbody>
</table>

<sup>a</sup> Percentages referred to raw dry matter.

<sup>b</sup> Data extracted from [35].

<sup>c</sup> Linked sugars in oligomeric and polymeric forms.
Table 2: Effect of steam treatment on oil content in alperujos and properties of olive-pomace oils extracted.

<table>
<thead>
<tr>
<th>Alperujo</th>
<th>Treatment</th>
<th>OPO content (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Δ (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Acidity (%)</th>
<th>PV&lt;sup&gt;c&lt;/sup&gt; (meqO₂/kg oil)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Non-treated</td>
<td>8.5 ± 0.2</td>
<td>-</td>
<td>3.5 ± 0.1</td>
<td>8.8 ± 0.6</td>
</tr>
<tr>
<td>Season 2007/2008</td>
<td>160 °C/60 min</td>
<td>12.7* ± 0.1</td>
<td>49.4</td>
<td>15.1* ± 0.3</td>
<td>10.7* ± 0.4</td>
</tr>
<tr>
<td></td>
<td>Non-treated</td>
<td>10.2 ± 0.5</td>
<td>-</td>
<td>2.0 ± 0.1</td>
<td>7.4 ± 0.3</td>
</tr>
<tr>
<td>Season 2008/2009</td>
<td>160 °C/60 min</td>
<td>14.9* ± 0.3</td>
<td>46.1</td>
<td>9.0* ± 0.2</td>
<td>12.6* ± 0.1</td>
</tr>
</tbody>
</table>

<sup>a</sup> The percentage of OPO in the alperujo is based on dry weight.

<sup>b</sup> Oil enrichment.

<sup>c</sup> Peroxide value.

* Star symbols indicate significant statistical differences in comparison with the mean value for non-treated alperujo samples (p-value < 0.05).
Table 3 Yields and physicochemical properties of biodiesel produced from OPO of steam-treated alperujo in comparison with other feedstock obtained under similar production conditions.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Production conditions</th>
<th>Yield (%)</th>
<th>Boiling point (°C)</th>
<th>Density at 15 °C (kg/m³)</th>
<th>Viscosity at 40 °C (mm²/s)</th>
<th>Cetane number</th>
<th>Iodine value (g I₂/100 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPO&lt;sup&gt;a&lt;/sup&gt;</td>
<td>6:1, 1% NaOH, 60 °C, 80 min</td>
<td>95.7</td>
<td>230.7</td>
<td>912.4</td>
<td>4.0</td>
<td>54</td>
<td>134.5</td>
</tr>
<tr>
<td>Cotton&lt;sup&gt;b&lt;/sup&gt;</td>
<td>6:1, 0.75% NaOH, 65 °C, 90 min</td>
<td>96.9</td>
<td>-</td>
<td>875.0</td>
<td>4.0</td>
<td>54</td>
<td>104.7</td>
</tr>
<tr>
<td>Palm&lt;sup&gt;c&lt;/sup&gt;</td>
<td>6:1, 1% KOH, 65 °C, 60 min</td>
<td>82</td>
<td>-</td>
<td>876.0</td>
<td>5.7</td>
<td>62</td>
<td>-</td>
</tr>
<tr>
<td>Rapessed&lt;sup&gt;b&lt;/sup&gt;</td>
<td>6:1, 1% KOH, 65 °C, 120 min</td>
<td>95-96</td>
<td>-</td>
<td>880.0-888.0</td>
<td>4.3-5.8</td>
<td>49-50</td>
<td>-</td>
</tr>
<tr>
<td>Soybean&lt;sup&gt;b&lt;/sup&gt;</td>
<td>12:1, 8% CaO,65 °C, 90min</td>
<td>&gt;95</td>
<td>-</td>
<td>885</td>
<td>4.1</td>
<td>52</td>
<td>138.7</td>
</tr>
<tr>
<td>Sunflower&lt;sup&gt;b&lt;/sup&gt;</td>
<td>6:1, 1% NaOH, 60 °C, 120 min</td>
<td>97.1</td>
<td>-</td>
<td>880.0</td>
<td>4.9</td>
<td>49</td>
<td>142.7</td>
</tr>
<tr>
<td>Specifications</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td></td>
<td>ASTM D6751</td>
<td></td>
<td></td>
<td></td>
<td>1.9-6.0</td>
<td>≥47</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>EN 14214</td>
<td></td>
<td></td>
<td></td>
<td>860-900</td>
<td>3.5-5.0</td>
<td>≥51 &lt;120</td>
</tr>
</tbody>
</table>

<sup>a</sup> Purified biodiesel (season 2008-2009). These general parameters are basically the same as those of the season 2007-2008 since the properties and quality of biodiesel depend on the type of feedstock.

<sup>b</sup>,<sup>c</sup> Data extracted from [14] and [11], respectively.
Table 4 GC analysis of fatty acid methyl ester composition of biodiesels produced under the best experimental conditions from olive-pomace oils extracted from non-treated and treated alperujo.

<table>
<thead>
<tr>
<th>Alperujo</th>
<th>Olive-pomace oil</th>
<th>Fatty acid methyl esters (%)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Palmitate</td>
<td>Oleate</td>
<td>Linoleate</td>
<td>Linolenate</td>
<td></td>
</tr>
<tr>
<td>Season 2007-2008</td>
<td>Non-treated</td>
<td>16.2 ± 0.4</td>
<td>69.5 ± 0.6</td>
<td>12.7 ± 0.4</td>
<td>0.5 ± 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>160 °C/60 min</td>
<td>15.8 ± 0.8</td>
<td>69.3 ± 2.2</td>
<td>12.5 ± 1.0</td>
<td>0.6 ± 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td></td>
</tr>
<tr>
<td>Season 2008-2009</td>
<td>Non-treated</td>
<td>11.1 ± 0.7</td>
<td>78.4 ± 1.4</td>
<td>9.0 ± 0.5</td>
<td>0.4 ± 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>160 °C/60 min</td>
<td>11.5 ± 0.6</td>
<td>79.0 ± 0.9</td>
<td>8.4 ± 0.7</td>
<td>0.3 ± 0.1</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td></td>
</tr>
</tbody>
</table>

ns, non-significant. No significant statistical differences in fatty acid methyl ester composition were observed among biodiesel samples from OPO of treated and non-treated alperujo within each season (p-value > 0.05). The different composition of fatty methyl esters depending on season is due to that alperujo samples used in this work come from different olive cultivars.
**Table 1** Comparison of effect of the hydrothermal treatment on each fraction separated from treated alperujo (at 160°C for 60 min) with regard to non-treated alperujo.

<table>
<thead>
<tr>
<th></th>
<th>Solid fraction</th>
<th>Liquid fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Non-treated alperujo</td>
<td>Treated alperujo</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>59.4</td>
<td>39.0</td>
</tr>
<tr>
<td>Total phenols (g Gallic Acid Equivalents/kg alperujo)</td>
<td>-</td>
<td>37.1</td>
</tr>
<tr>
<td>Reduction of dry weight (%)</td>
<td>-</td>
<td>10.2</td>
</tr>
<tr>
<td>Sugars (%)</td>
<td>37.1</td>
<td>1.7</td>
</tr>
</tbody>
</table>

* Percentages referred to raw dry matter.

* Data extracted from [29].

* Linked sugars in oligomeric and polymeric forms.
Table 2 Effect of hydrothermal treatment on oil content in alperujos and properties of olive-pomace oils extracted.

<table>
<thead>
<tr>
<th>Alperujo</th>
<th>Treatment</th>
<th>OPO content (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Δ (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Acidity (%)</th>
<th>PV&lt;sup&gt;c&lt;/sup&gt; (meqO₂/kg oil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Season 2007/2008</td>
<td>Non-treated</td>
<td>8.5 ± 0.2</td>
<td>-</td>
<td>3.5 ± 0.1</td>
<td>8.8 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>160 °C/60 min</td>
<td>12.7 ± 0.1</td>
<td>49.4</td>
<td>15.1 ± 0.3</td>
<td>10.7 ± 0.4</td>
</tr>
<tr>
<td>Season 2008/2009</td>
<td>Non-treated</td>
<td>10.2 ± 0.5</td>
<td>-</td>
<td>2.0 ± 0.1</td>
<td>7.4 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>160 °C/60 min</td>
<td>14.9 ± 0.3</td>
<td>46.1</td>
<td>9.0 ± 0.2</td>
<td>12.6 ± 0.1</td>
</tr>
</tbody>
</table>

<sup>a</sup> The percentage of OPO in the alperujo is based on dry weight.

<sup>b</sup> Oil enrichment.

<sup>c</sup> Peroxide value.
Table 3 Yields and physicochemical properties of biodiesel produced from OPO of steam-treated alperujo in comparison with other feedstock obtained under similar production conditions.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Production conditions</th>
<th>Yield (%)</th>
<th>Boiling point (°C)</th>
<th>Density at 15 °C (kg/m³)</th>
<th>Viscosity at 40 °C (mm²/s)</th>
<th>Cetane number</th>
<th>Iodine value (g I₂/100 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPO</td>
<td>6:1, 1% NaOH, 60 °C, 80 min</td>
<td>95.7</td>
<td>230.7</td>
<td>912.4</td>
<td>4.0</td>
<td>54</td>
<td>134.5</td>
</tr>
<tr>
<td>Cotton</td>
<td>6:1, 0.75% NaOH, 65 °C, 90 min</td>
<td>96.9</td>
<td>-</td>
<td>875.0</td>
<td>4.0</td>
<td>54</td>
<td>104.7</td>
</tr>
<tr>
<td>Palm</td>
<td>6:1, 1% KOH, 65 °C, 60 min</td>
<td>82</td>
<td>-</td>
<td>876.0</td>
<td>5.7</td>
<td>62</td>
<td>-</td>
</tr>
<tr>
<td>Rapessed</td>
<td>6:1, 1% KOH, 65 °C, 120 min</td>
<td>95-96</td>
<td>-</td>
<td>880.0-888.0</td>
<td>4.3-5.8</td>
<td>49-50</td>
<td>-</td>
</tr>
<tr>
<td>Soybean</td>
<td>12:1, 8% CaO, 65 °C, 90 min</td>
<td>&gt;95</td>
<td>-</td>
<td>885</td>
<td>4.1</td>
<td>52</td>
<td>138.7</td>
</tr>
<tr>
<td>Sunflower</td>
<td>6:1, 1% NaOH, 60 °C, 120 min</td>
<td>97.1</td>
<td>-</td>
<td>880.0</td>
<td>4.9</td>
<td>49</td>
<td>142.7</td>
</tr>
</tbody>
</table>

Specifications:
- ASTM D6751: 1.9-6.0 ≥47 -
- EN 14214: 860-900 3.5-5.0 ≥51 <120

*a* Purified biodiesel (season 2008-2009). These general parameters are basically the same as those of the season 2007-2008 since the properties and quality of biodiesel depend on the type of feedstock.

*b*, *c* Data extracted from [14] and [11], respectively.
Table 4 GC analysis of fatty acid methyl ester composition of biodiesels produced under the best experimental conditions from olive-pomace oils extracted from non-treated and treated alperujo.

<table>
<thead>
<tr>
<th>Alperujo</th>
<th>Olive-pomace oil</th>
<th>Fatty acid methyl esters (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Palmitate</td>
</tr>
<tr>
<td>Season 2007-2008</td>
<td>Non-treated</td>
<td>16.2 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>160 °C/60 min</td>
<td>15.8 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>Ns</td>
<td>69.5 ± 0.6</td>
</tr>
</tbody>
</table>

| Season 2008-2009 | Non-treated      | 11.1 ± 0.7 | 78.4 ± 1.4 | 9.0 ± 0.5 | 0.4 ± 0.1 |
|                  | 160 °C/60 min    | 11.5 ± 0.6 | 79.0 ± 0.9 | 8.4 ± 0.7 | 0.3 ± 0.1 |
|                  | Ns               | 79.0 ± 0.9 | 8.4 ± 0.7 | 0.3 ± 0.1 |

ns, non-significant. No significant differences in fatty acid methyl ester composition were observed among biodiesel samples from OPO of treated and non-treated alperujo.
Olive pomace oil → **Preesterification** → Catalyst mixing Methanol + H₂SO₄

H₂O + Na₂SO₄ → Neutralization and Separation → Distillation

**Alkaline transesterification** → Phase separation

Crude biodiesel → **Biodiesel**

Glycerol + Soap → Glycerol

Impurities → Purification Washing H₂O + NaCl → Recovery

Fig. 1
Fig. 2

(a) Biodiesel yield (% w/w) vs. molar ratio methanol/oil for OPO of non-treated and treated alperujo.

(b) Biodiesel yield (% w/w) vs. catalyst concentration (% w/w, NaOH/oil) for molar ratios 20:1 and 10:1 (non-treated and treated alperujo)
Fig. 3

The figure shows the biodiesel yield (%) over time for different molar ratios: 6:1, 10:1, 15:1, and 20:1. The data points and error bars indicate the variability in the yield for each ratio. The biodiesel yield increases with time until it reaches a plateau, indicating the optimal reaction time for each molar ratio.
Figure captions

**Fig. 1** Schematic process flow chart used in this work for alkali-catalyzed biodiesel production from OPO.

**Fig. 2** Influence of the methanol/oil molar ratio (a) and effect of catalyst concentration (b) after process of transesterification at 60 °C for 80 min on biodiesel production employing OPO extracted from alperujo of season 2007-2008. The catalyst concentration was fixed at 1% (w/w) (above). The results (mean ± standard deviation from triplicate runs) are expressed as percent of conversion of OPO to biodiesel. Statistical significance is indicated by the use of star symbols (*). These star symbols indicate results that are significantly different (at p-value < 0.05) in comparison with the stoichiometric molar ratio (3:1) (above) and the catalyst concentration at 1% (w/w) (below). While there were significant differences among the molar ratios, there were no differences among treated and non-treated samples within each molar ratio (p-value > 0.05) for biodiesel yield (above).

**Fig. 3** Effect of reaction time on biodiesel yield using OPO extracted from steam-treated alperujo of season 2008-2009 after the second step. The catalyst concentration was fixed at 1% (w/w). The results (mean ± standard deviation from triplicate runs) are expressed as percent of conversion of OPO to biodiesel.
Fig. 1
Fig. 2
Fig. 3
Figure captions

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