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High oleic safflower oil as a feedstock for stable biodiesel and biolubricant production

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ABSTRACT

Biodiesel and other derivative compounds which could act as biolubricants, can be a suitable alternative for petroleum products, which are less sustainable and harmful to the environment. However, especially when vegetable oils are used as raw materials (for instance *Carthamus Tinctorius*), these products can show poor oxidative stabilities, depending on their fatty acid composition. Apart from adding antioxidants as additives, a good alternative might be the use of genetically modified seeds to facilitate high ratios of stable fatty acids like oleic acid. The aim of this work was to produce biodiesel and biolubricant from high oleic safflower through transesterification with methanol and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol, respectively. The efficiency of these processes and the quality characterization of biodiesel and biolubricant were assessed. As a result, the biodiesel obtained (HOSBD) complied with the standard, with a high oxidative stability value (8.2 h) and not requiring any antioxidant addition. The biolubricant obtained (HOSBL) showed higher oxidative stability (6.72 h) compared to their equivalents produced from rapeseed (*Brassica Napus)* or cardoon *(Cynara Cardunculus L.)*. Consequently, two stable bioproducts were obtained and the role of fatty acid composition of raw material was vital (oleic/linoleic ratio had a strong influence on oxidative stability). In that sense, the use of stable raw materials like high oleic safflower might avoid antioxidant addition in biodiesel or biolubricants, which implies a cleaner and more sustainable production.

1. Introduction

It is well known that there is an increasing concern about the environment at national and international levels. Thus, many governments and international agencies are promoting the use of alternatives for polluting processes and products. A clear example of that is the gradual replacement of natural compounds for petroleum products. That is the reason why there has been a considerable increase in biodiesel production in the past few decades (Knothe and Razon, 2017), using innovative techniques such as ultrasonic-assisted cavitation systems (Asif et al., 2017). On the other hand, many researchers have recently focused their works on biolubricant production (Chen et al., 2019; Ho et al., 2019). The use of this kind of products at the expense of others derived from oil might imply many advantages, like the following:

- They are biodegradable, which can be a suitable property in case of accidental spillage.
- Their flash and combustion points are higher compared to their petroleum equivalent, being a great advantage when it comes to storage and shipping.
- The raw materials used to produce biodiesel and biolubricants are usually abundant (mainly different kinds of vegetable oils, among other products), which makes them easily available. Consequently, the production is more sustainable.
- The production of biodiesel and biolubricants can contribute to the implementation of biorefineries, where many intermediate products (like fatty acid methyl esters (Encinar et al., 2020b; Kleinaite et al., 2014)) or by-products (like glycerol (Liberato et al., 2019; Nda-Umar et al., 2019)) can be re-used.
- As a consequence, a sustainable and local economic development could be possible, being an important point for developing countries or regions.

The use of vegetable oils as a starting point for biodiesel or biolubricant production has gained weight, especially for the former. Concerning biodiesel production, catalysed transesterification with

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methanol is usually the most common way to obtain fatty acid methyl esters from vegetable oils (Rizwanul Fattah et al., 2020; Rodionova et al., 2017), whereas in the case of biolubricant production there is a wide range of chemical routes to obtain multiple products, like transesterification or epoxidation, among others (McNutt and He, 2016). The products obtained in these processes usually meet the abovementioned advantages. However, two main disadvantages are normally related to them. First, their low oxidative stability (influenced by vegetable oil composition). And second, their bad flow properties in cold climates (Hazrat et al., 2020). In order to solve these problems, several additives can be used. The addition of antioxidants to increase oxidative stability is common, with tert-butyl hydroquinone, butylated hydroxytoluene, propyl gallate and tertiary butylhydroquinone as the most popular additives due to their effectiveness (Saluja et al., 2016; Souza et al., 2014; Uğuz et al., 2019). These antioxidants inhibit the initiation and propagation of free radicals, minimizing the generation of degradation compounds. However, some antioxidants can be expensive and show poor biodegradability. As a consequence, the replacement of these antioxidants for natural ones, like ascorbic acid (Shuster et al., 2018), tannic acid (Gülçin et al., 2010) or natural extracts, was investigated (De Sousa et al., 2014). The search for natural extracts (for instance, from moringa (Valenga et al., 2019) or rosemary (Delgado et al., 2014)) or the use of genetically modified crops in order to improve some characteristics of biodiesel and biolubricants are gaining in importance and prominence (França et al., 2017; Gülçin et al., 2010).

In the case of safflower (*Carthamus Tinctorius L.*), it is a crop with high resistance to extreme climates like arid conditions, commonly used for the production of edible oil and biofuel in developing areas (Yesilyurt et al., 2020). Its extension includes remote areas like Kazakhstan, India, Ethiopia, the United States, Argentina or Spain. With a high seed yield (24−37 g per plant) and an oil ratio in the seeds ranging from 30 to 50 % (Yesilyurt et al., 2020), its use for biodiesel can be a suitable way to promote the economic and sustainable growth of developing countries or poor areas, showing a potential biodiesel yield of 80–85 gallons per acre (Hoekman et al., 2012).

As previously mentioned, the adaptation of safflower to Spanish regions is proved, as it has been considered as an oilseed crop. Between 2013 and 2016, its yearly production ranged from 3.7 to 5.8 thousands of tons per year. Moreover, its cultivation area increased up to 8.2 thousands of hectares in 2015. Indeed, it is commonly used in crop rotation with other crops like wheat, due to its long tap root compared to the latter (Ministerio de Agricultura, 2019). Its use as an energy crop can be a suitable starting point for economic diversification of agricultural holdings. In fact, it has been studied as a source for biodiesel production by many authors (Çelebi and Aydın, 2018; Mihaela et al., 2013; Nogales-Delgado et al., 2019a). However, as it was mentioned for biodiesel from vegetable oils, its oxidative stability is not high enough, making the use of alternatives necessary.

Another way to improve the oxidative stability of vegetable oils is by selecting and improving genotypes for the good performance of crops. One option for this purpose is the use of genetically modified crops, which is a plant used for agricultural purposes into which one or several genes coding for desirable traits have been inserted through the process of genetic engineering (Qaim, 2018). Although one of the main objectives of selecting the right genotype is the promotion of more resistant crops for developing countries, some of their properties can be used to improve the performance of energy crops (increasing oxidative stability by modifying the fatty acid composition of vegetable oils). The production of high oleic crops can be a suitable way to improve both their adaptation and yield and the performance of many biofuels or bioproducts, increasing the oxidative stability or heating value (Folayan et al., 2019; Hamid et al., 2016). To the best of our knowledge, the use of high oleic oils (especially in the case of safflower) for biodiesel and biolubricant production is not widely researched so far, being a field that should be explored.

The aim of this work was to assess biolubricant production (through transesterification with methanol and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol, respectively) from high oleic safflower oil. The production of stable biofuels and bioproducts as a starting point for a biorefinery is proposed.

Table 1
Main characteristics of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol.

Molecular weight (g mol^{-1})	134.17
Vapor pressure at 50 °C (hPa)	<0.1
Melting point (°C)	58
Flash point (°C)	179
Autoignition temperature (°C)	375
Bulk density (kg m^3)	700

2. Materials and methods

2.1. Raw material

High oleic safflower oil was used for biodiesel and biolubricant production through double transesterification with methanol and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol. The vegetable oil was high-oleic safflower (CW 99-OL), and supplied by the agricultural research institute "Finca La Orden – Valdesequera", belonging to CICYTEX (Centro de Investigaciones Científicas y Tecnológicas de Extremadura). The crop had a seed yield exceeding 2500 kg ha^{-1}. The seeds were collected in the summer of 2019, extracting the oil through mechanical pressing in November 2019. After filtration, the oil was stored in 25-L tanks, in darkness and at room temperature, before the initial characterization of the oil and the subsequent transesterification. The oil had a density of 0.904 g ml^{-1}. As free fatty acid level was low (0.85 %), pretreatments in order to reduce this parameter were no necessary.

2.2. First transesterification (biodiesel production)

For the first transesterification of high oleic safflower oil to produce fatty acid methyl esters (FAMEs or biodiesel), the suitable amounts of oil and methanol (Panreac Applichem, Barcelona, Spain) are introduced in a three neck flask reactor. The reactor was connected to a laboratory condenser in order to avoid methanol loss during the reaction, a temperature probe to check the temperature reaction. Afterwards, and once the reaction temperature was achieved, the catalyst (sodium methylate, Merck KGaA, Darmstadt, Germany) was introduced, carrying out the reaction time up to 90 min under the following conditions, based on previous studies to assure high FAME yields (Nogales-Delgado et al., 2019b): methanol/oil mole ratio, 6:1; reaction temperature, 60 °C; stirring rate, 350 rpm; catalyst concentration (sodium methylate), 1 % w/w;. Sodium methylate was chosen instead of other catalysts like sodium hydroxide in order to avoid saponification. Once the reaction took place, the purification of biodiesel was carried out, separating glycerol by using a separating funnel by decantation (not proceeding to purification of glycerol as it was not the main purpose of this work) and washing the sample with distilled water in successive stages to remove the catalyst. When the washing water removed all the surplus catalysts (showing a neutral pH), the sample was dried by heating at 110 °C.

The abovementioned operating conditions for the first transesterification were previously studied (Nogales-Delgado et al., 2019a) for a similar vegetable oil (safflower biodiesel), obtaining yields and exceeding the lower limit included in UNE-EN 14,214 (that is, 96.5 % w/w) (UNE-EN 14214, 2018).

Once biodiesel (HOSBD) was purified, it was stored in 2.5 L opaque bottles at room temperature, pending further characterizations or the second transesterification.

Table 2
Chemical conditions for the different optimization experiments, including the effect of mole ratio (BL1, BL2 and BL3), temperature (BL1, BL4, BL5 and BL6) and catalyst concentration (BL1, BL7 and BL8).

Experiment[a]	FAME/alcohol ratio	[Catalyst] (%)	Temperature (°C)
BL1	1	1	100
BL2	0.5	1	100
BL3	0.75	1	100
BL4	1	1	120
BL5	1	1	140
BL6	1	1	160
BL7	1	1.5	100
BL8	1	2	100

[a] All the experiments had the same conditions for vacuum (400 mmHg), reaction time (90 min) and stirring rate (400 rpm).

2.3. Second transesterification (biolubricant production)

For the second transesterification, HOSBD obtained in the previous step (see Section 2.2) reacted with 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (Merck KGaA, Darmstadt, Germany). The main properties of this superior alcohol are shown in Table 1.

The facility used for the second transesterification had one main difference with the scheme explained for the first transesterification (to produce methyl esters), that is, the inclusion of a Dean Stark device for the collection of methanol when it was release from the second transesterification reaction. Thus, the chemical conditions, which will be specified in the following sections, were applied, with the following generic steps:

- The suitable amounts of fatty acid methyl esters and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol were added to the reactor, heating the reaction medium at a certain temperature.
- Once it was obtained, a certain amount of catalyst (sodium methylate, Merck KGaA, Darmstadt, Germany) was added and the vacuum was applied at 400 mmHg, considering this **point** as the beginning of the reaction.
- In order to check the progress of the reaction, the methanol collected in the Dean Stark device as well as the FAME content of samples collected at 0, 1, 2, 5, 10, 15, 30 and 90 min.
- At the end of the chemical reaction, there was a first gravity filtration with filter paper (73 g/m^2) and the sample was cooled down at room temperature. Afterwards, a second vacuum filtration with filter paper and using a Buchner funnel was applied, in order to remove the crystallized surplus alcohol (as it is in a solid state at room temperature).
- The purified biolubricant (high oleic safflower biolubricant, HOSBL) was stored at room temperature in opaque glass bottles for further analysis and characterization.

In order to assess the yield and effectiveness of biolubricant production, three main parameters were varied, like FAME/alcohol mole ratio, temperature and catalyst concentration.

2.3.1. The effect of FAME/alcohol mole ratio

Concerning the effect of FAME/2-ethyl-2-(hydroxymethyl)-1,3-propanediol ratio on biolubricant production, different values for this parameters were selected, ranging from 0.5 to 1.5. The rest of conditions were kept constant (Temperature: 100 °C; catalyst concentration: 1.0 % w/w; vacuum: 400 mmHg; reaction time: 90 min; stirring rate: 400 rpm).

2.3.2. The effect of temperature

Different reaction temperatures (100, 120, 140 and 160 °C) were studied, keeping the rest of parameters constant (FAME/alcohol ratio: 1:1; catalyst concentration: 1.0 % w/w; vacuum: 400 mmHg; reaction time: 90 min; stirring rate: 400 rpm).

Table 3
Conditions selected and temperature program for gas chromatography.

Chromatography conditions	Carrier gas	Helium
	Auxiliary gas	Nitrogen
	Combustible gas	Synthetic air
	Flow in column	1.4 cm^3*min^{-1}
	Air flow	300 cm^3*min^{-1}
	Hydrogen flow	30 cm^3*min^{-1}
Temperature program	Time, min	Temperature, °C
	1–15	190
	15–16	100
	16–31	240
	Injector temperature	260
	Detector temperature	300

2.3.3. The effect of catalyst concentration

Regarding the effect of catalyst concentration on the yield of biolubricant production, three concentrations of sodium methylate were selected (1.0, 1.5 and 2.0 % w/w). The rest of parameters were kept constant for these experiments (Temperature: 100 °C; FAME/alcohol ratio: 1:1; vacuum: 400 mmHg; reaction time: 90 min; stirring rate: 400 rpm).

To sum up, the main chemical conditions for each experiment is included in Table 2, as follows:

Once all the experiments were carried out, the optimum conditions were selected for the production of the final biolubricant, under efficiency criteria. The final biolubricant obtained was selected for biolubricant characterization.

2.4. Biodiesel and biolubricant characterization

Once HOSBD and HOSBL were obtained, their main characteristics were measured, according to the UNE-EN 14,214 standard (UNE-EN 14214, 2018). Thus, FAME composition, density, moisture, acid value, iodine number, flash and combustion points, cold filter plugging point (CFPP), viscosity and viscosity index, oxidative stability, TGA analysis, IR analysis and NMR were considered for the samples studied, and compared with the limits established in the standard. The main details of each characterization are explained in the following sections. Unless otherwise stated, the experiments were done in triplicate and the average value was expressed.

2.4.1. FAME composition

Gas chromatography coupled to FID detection (Varian 3900, Agilent, Santa Clara, CA, USA) was used in order to check the fatty acid methyl ester (FAME) composition of biodiesel, as well as the decrease in these components in the reaction medium for biolubricant production. A polyethylene glycol column (Zebron ZB-WAX PLUS, Phenomenex, length: 30 m, film thickness: 0.5 μm and i.d.: 0.32 mm) was used as a chromatographic column. The main FAMEs usually found in vegetable oils (that is, methyl oleate, linoleate, linolenate or palmitate, among others) were analyzed by using their corresponding standards, using methyl heptadecanoate as an internal standard. All these standards were provided by Sigma-Aldrich (San Luis, USA). The chromatography conditions followed for the analysis are included in Table 3.

Each chromatography run takes 31 min, apart from preconditioning tasks. All the gases used in this technique (see Table 3) were provided by Linde (Linde España, Valencia, Spain) and were of analytical quality.

2.4.2. Density and moisture

Density determination was carry out according to the UNE-EN-ISO 3675 standard, by using a pycnometer (Pobel, Madrid, Spain) and a densimeter (Proton 800–900, Gabsystem, Barcelona, Spain) (UNE-EN-ISO 3675, 1999). For moisture, the UNE-EN-ISO-12937,

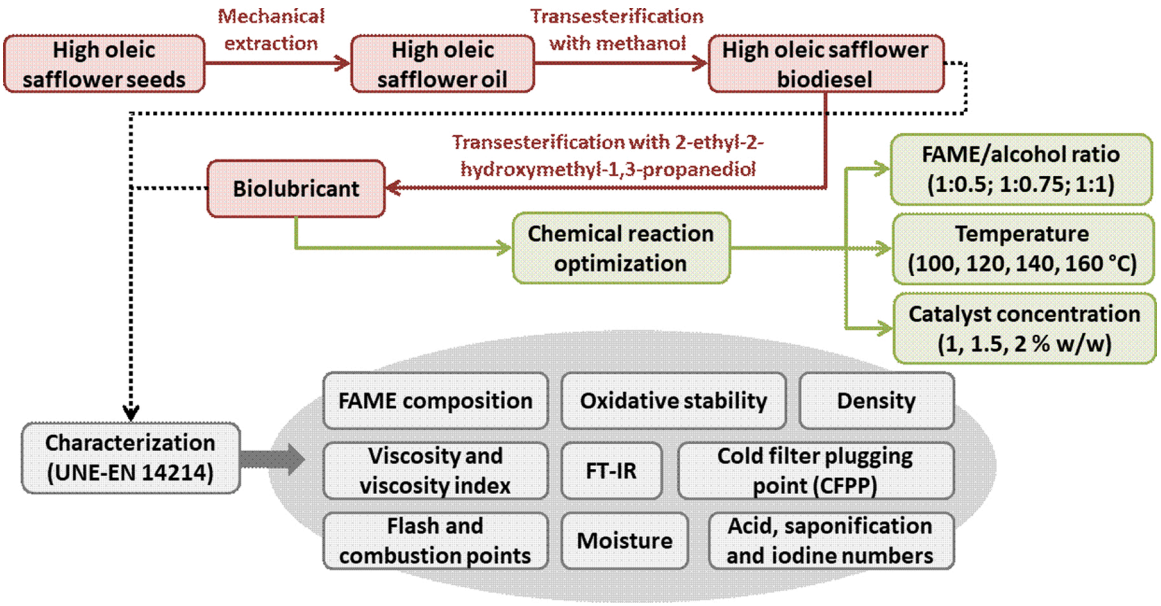

Fig. 1. Experimental design for high oleic safflower biodiesel and biolubricant production.

2000standard was followed, and a Metrohm 870 trinitro plus equipment was used, expressing the results in % w/w (UNE-EN-ISO-12937, 2000) (UNE-EN-ISO-12937, 2000).

2.4.3. Acid value and iodine number

Concerning the acid number was determined according to the UNE-EN, 12634:, 1999 standard (UNE-EN-12634, 1999; UNE-EN ISO 3104/AC, 1999). For iodine number (which can be an estimation of the global presence of unsaturations in the sample), the UNE-EN, 14111:, 2003 standard was followed (UNE-EN 14111, 2003).

2.4.4. Flash and combustion points

Regarding flash and combustion points, the Cleveland open-cup method was followed, included in UNE 51−023-90 standard (UNE-EN 51023, 1990) and using the corresponding equipment (Herzog Cleveland semi automatic, Herzog, Landa-Königshofen, Germany). Flash point is the temperature at which a short ignition is produced when a flame approaches the sample (increasingly heated), whereas in the case of combustion point the ignition in the sample is permanent.

Table 4
Main characteristics of high oleic safflower biodiesel (HOSBD) and comparison with other biodiesel samples found in the literature.

Property	Units	Limit[a]		High oleic safflower biodiesel
		Lower	Upper	
FAME content	% (m/m)	96.5	–	97.9 (±0.3)
Density at 15 °C	kg/m3	860	900	872 (±5)
Viscosity at 40 °C	mm2/s	3.50	5.00	4.58 (±0.19)
Oxidative stability (at 110 °C)	h	8.0	–	8.2 (±0.2)
Acid value	mg KOH/g	–	0.50	0.27 (±0.05)
Flash point	°C	101	–	186 (±4)
Water content	% (w/w)	–	0.05	0.02 (±0.00)
CFPP	°C	−10	0	−3 (±1)
Iodine number	g yodo/100g	–	120	91.7 (±1.3)
Methyl linolenate	% (m/m)	–	12.0	9.3 (±0.3)

[a] According to UNE-EN 14214 standard (14214:2013, 2013).

2.4.5. Cold filter plugging point, viscosity and viscosity index

For cold filter plugging point (CFPP) determination, the EN 116 standard was followed (UNE-EN 116, 2015). For viscosity measurement, the ISO 3104:1994 standard was used, carrying out the tests with an Ostwald viscometer (UNE-EN ISO 3104/AC, 1999,1999). Thus, viscosity values at 40 and 100 °C were obtained for viscosity index calculation, following the ASTM D2270 standard (ASTM-D2270-10, 2016).

2.4.6. Oxidative stability

Oxidative stability was obtained by using the Rancimat method, as explained elsewhere (Focke et al., 2016; Nogales-Delgado et al., 2019b). Thus, 3 g of biodiesel or biolubricant was placed in a test tube, heating the sample at 110 °C and bubbling synthetic air (10 L h^{-1}). The resulting stream of air was bubbled into 50 mL of distilled water, increasing its conductivity (measured by a Mettler Toledo conductivity meter, Mettler Toledo, Columbus, Ohio, USA) due to the dilution of the by-products generated during the oxidation of the sample. The induction point, an indicator of oxidative stability, was the time when conductivity abruptly increased.

2.4.7. TGA analysis

Thermal analysis (thermogravimetric analysis, TGA, and derivative thermogravimetry, DTG) of biodiesel and biolubricant samples was carried out by using a thermobalance (STA449F3, QMS403D, VERTEX70, Netzsch–Bruker, Billerica, MA, USA). Six to seven milligrams of sample was heated from room temperature to 600 °C, with a heating rate of 10 °C min^{-1}. The carrier gas for combustion was synthetic air (100 mL min^{-1}). TGA and DTG curves were obtained by monitoring the weight loss of the sample over temperature.

2.4.8. IR analysis

IR spectrum of the final biodiesel and biolubricant was obtained in order to identify the functional groups of its molecular structure. The FT-IR analysis was carried out by using a device (Perkin-Elmer Spectrum 3F-IR, Waltham, MA, United States) in the range of 4000−650 cm^{-1}. The results were processed with computer software.

2.4.9. NMR (Carbon-13 and Hydrogen-1 NMR)

^{1}H and ^{13}C NMR was determined by using a Bruker spectrometer (Avance, Bruker Biosciences, Madrid, Spain), operating at a frequency of 400.13 and 100.77 MHz, respectively, and using $CDCl_3$ as a solvent.

Table 5
Comparison between high oleic safflower biodiesel and other biodiesel samples from similar vegetable oils (SB, Safflower biodiesel; CB, Cardoon biodiesel), according to FAME composition and oxidative stability.

		HOSBD	SB1 (Nogales-Delgado et al., 2019a)	SB2[a] (Mihaela et al., 2013)	CB(Nogales-delgado and Nuria, 2020)
FAME content (%)	Methyl oleate	82.6	11.2	12.76	24.2
	Methyl linoleate	9.3	75	69.65	58.1
	Methyl stearate	2.9	3	4.37	3.4
	Methyl palmitate	4.4	6	11.07	6.0
	Others	0.8	1	2.15	8.3[2]
Oxidative stability (h)		8.22	1.54	0.57	1.35

[2]Including 7 % of methyl linolenate.
[a] Fatty acid content of the oil was facilitated.

Each spectrum was Fourier-transformed, phase corrected and integrated by using software.

Fig. 1 shows the experimental design carried out in this experience, including biodiesel and biolubricant production and their subsequent characterization.

2.5. Effect of raw material on biolubricant characteristics

The final biolubricant obtained was compared to other biolubricants obtained following the same chemical conditions from different vegetable oils. In this case, *Brassica napus* (rapeseed) and *Cynara Cardunculus L.* (cardoon) oil were selected. A comparison between their main properties, paying attention to oxidative stability and viscosity, was carried out.

3. Results and discussion

3.1. Biodiesel characterization

Table 4 shows the properties of HOSBD. As it can be seen, the sample complied with the standard, especially showing a high flash point value, which implies safe storage and shipping of this product. One of the most common undesired characteristics of biodiesel from vegetable oils is the low oxidative stability. Most biodiesel samples do not comply with the standard, as it was observed in the literature for grape seed, Philippine tung, kesambi and palm biodiesel (Ong et al., 2020). HOSBD showed an oxidative stability exceeding the lower limit, which is an advantage as the addition of antioxidants (in many cases artificial ones), is not required, implying cost reduction and simplification of facilities.

If compared to other biodiesel samples obtained from safflower oil included in Table 4 (according to the literature), the oxidative stability of HOSBD was considerably higher, with the rest of biodiesel samples not exceeding, in any case, an oxidative stability of 6 h. Therefore, the latter can not comply with the standard, needing the addition of antioxidants or the mixture with other more stable biofuels, among other solutions (Varatharajan and Pushparani, 2018; Yang et al., 2014).

The results shown in Table 5 are possibly due to the different FAME composition of HOSBD compared to other safflower and cardoon biodiesel samples. For the former, methyl oleate content, as a consequence of the genetically modified nature of the raw material, is considerably higher (exceeding 80 %) compared to the rest of safflower biodiesel samples considered in this study (ranging from 11 to 13 %), which are in accordance with average composition of safflower found in the literature, where linoleic acid was the majority FAME obtained, exceeding 70 % in di-unsaturated FAMEs, with low mono-unsaturated FAME content (below 15 %) (Hoekman et al., 2012). On the other hand, methyl linoleate in HOSBD was lower (9.3 %) than in the case of common safflower biodiesel (ranging from 69 to 65 %) and cardoon biodiesel (58 %). It is well known that FAME composition plays an important role in many properties of biodiesel, having a special influence on its storage and oxidative stability (Hoekman et al., 2012; Knothe and Razon, 2017). If the molecular structure of these FAMEs is considered, it can be noted the main difference between methyl oleate and methyl linoleate. The former, which is a mono-unsaturated FAME, is less susceptible for oxidation than the latter (a di-unsaturated FAME). Double bonds present in the molecular structure can be a suitable point for reaction with free radicals generated during oxidation. Consequently, higher amounts of methyl oleate (at the expense of di- or poly-unsaturated FAMEs) usually imply better oxidative stabilities. HOSBD could have better oxidative stability values (over 8 h) compared to SB1 and SB2 (1.54 and 0.57 h, respectively) due to the difference in FAME composition. Moreover, CB showed considerable amounts (around 7 %) of methyl linolenate, a poly-unsaturated FAME, explaining its low oxidative stability. As a consequence, the use of antioxidants (combined use of BHA and TBHQ for SB1 and up to 750 ppm of TBHQ, in the case of CB) was required, which is not the ideal scenario for this kind of sustainable and environmental-friendly product, suggesting the use of natural antioxidants (Nogales-Delgado et al., 2020, 2019a).

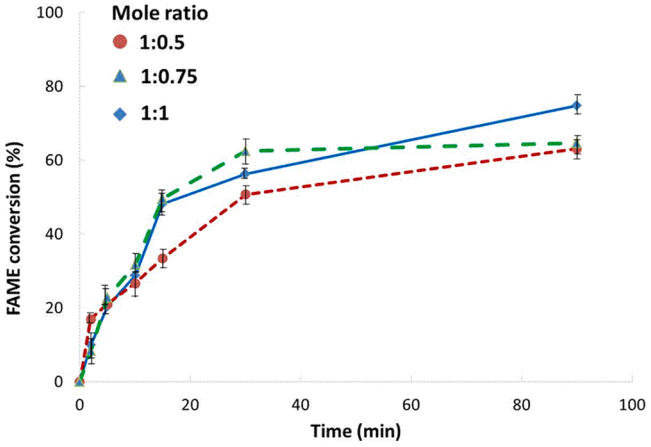

Fig. 2. Effect of mole ratio on biolubricant production.

3.2. Biolubricant production

Concerning the production of high oleic safflower biolubricant (HOSBL), the main findings about the effect of FAME/alcohol ratio, temperature and catalyst (sodium methylate) concentration are explained in the following subsections.

3.2.1. Effect of FAME/alcohol ratio

Fig. 2 shows the effect of FAME/2-ethyl-2-(hydroxymethyl)-1,3-propanediol ratio. It should be noted that experiments at a ratio of 1:2 was also carried out. However, this experiment was not included due to the difficulties presented to remove the surplus alcohol, which adsorbed the resulting biolubricant, not making the chromatographic analysis possible. The best yield was obtained for 1:1 ratio due to the effect of the amount of alcohol, displacing the reaction towards the formation of the

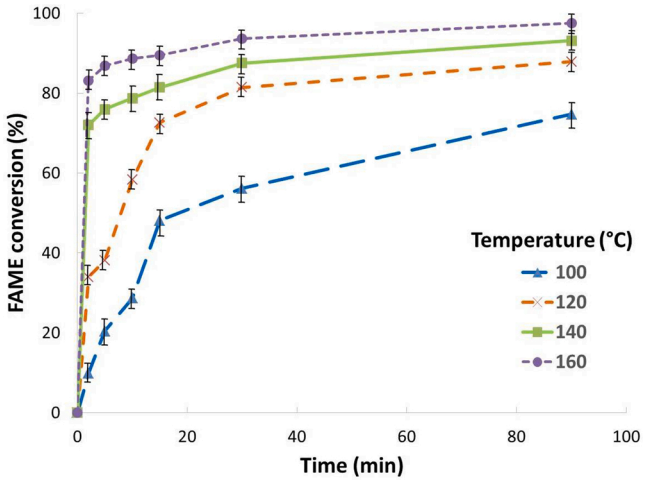

Fig. 3. Effect of temperature on biolubricant production.

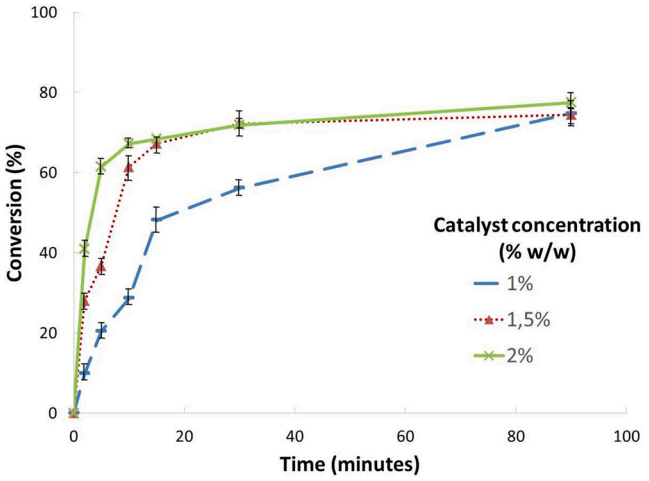

Fig. 4. Effect of catalyst concentration on biolubricant production.

products, as explained in the literature (Encinar et al., 2020a). This was the ratio used for further experiments.

3.2.2. *Effect of temperature*

Concerning the effect of temperature on FAME conversion to biolubricant, Fig. 3 shows the main results for temperatures ranging from 100 to 160 °C. In general, the reaction took place during the first 30 min, especially for temperatures at 140 and 160 °C, where there was an abrupt increase in FAME conversion for the first 5 min, reaching a stable stage at 30 min to obtain high yields (exceeding 92 % at 140 and 160 °C). When temperature decreased, the slope of this first stage was lower, obtaining worse yields (73 and 82 % at 100 and 120 °C, respectively). Changes in yield and reaction rates with temperature were also found in previous studies (Encinar et al., 2020a; Nogales-Delgado et al., 2020).

Consequently, and due to the fact that good yields were obtained for 140 and 160 °C (above 92 %), the optimum temperature selected for the final biolubricant production was 140 °C, according to efficiency and environmental criteria.

3.2.3. *Effect of catalyst concentration*

Concerning the amount of catalyst added to the reaction medium (see Fig. 4), the conversion over time for the three experiments carried out were high after 90 min, reaching similar values in all cases (from 76.2–78.05 % for 1 and 2 % catalyst, respectively). Nevertheless, for catalyst concentration of 1.5 and 2.0 %, FAME conversion was faster, increasing abruptly and exceeding 75 % in 30 min, and then showing a stable trend. This fact was due to the positive effect of catalyst addition on reaction rate (Encinar et al., 2020a).

Consequently, for this experience, a catalyst concentration of 1 % w/w was selected for the final biolubricant production, which was enough to obtain similar yields compared to higher catalyst percentages.

Table 6
Main characteristics of the biolubricant obtained and comparison with commercial products.

Characteristic	HOSBL	Commercial biolubricant	Commercial lubricant
Density at 15 °C, kg m^{-3}	946 (±4)	–	–
Kinematic viscosity at 40 °C, $mm^2 \cdot s^{-1}$	73.39 (± 1.05)	52.40	95
Kinematic viscosity at 100 °C, $mm^2 \cdot s^{-1}$	9.32 (± 0.21)	10.2	10
Viscosity index	103 (± 1)	186	102
Acid value, mg KOH g^{-1}	0.17 (± 0.01)	–	–
Flash point, °C	216 (± 5)	–	–
Combustion point, °C	228 (± 6)	–	–
Oxidative stability, h	6.72 (± 0.36)	–	–
Conversion, %	92.9 (± 0.8)	–	–

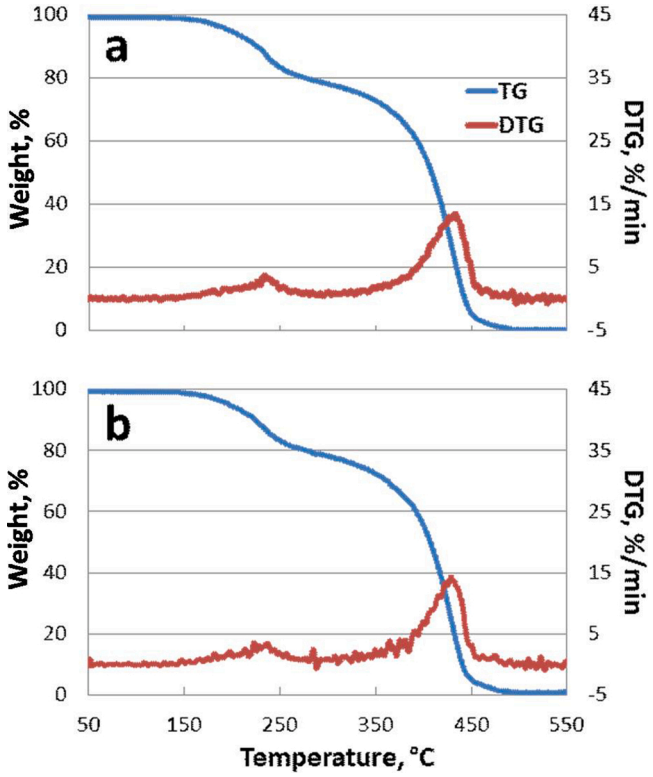

Fig. 5. TG-DTG analysis of HOSBL in air (a) and nitrogen (b).

3.3. *Biolubricant characterization*

As explained during previous subsections, the optimum chemical conditions for biolubricant production were: reaction temperature, 140 °C; catalyst concentration (sodium methoxide), 1 % w/w; vacuum, 400 mmHg; stirring rate, 350 rpm; FAME/alcohol ratio, 1:1. A high conversion of FAMEs to produce the corresponding superior alcohols (biolubricant) was obtained (over 92 %), which assures a high purity of the final product and permanent characteristics of the biolubricant. Table 6

Table 7
Main events in TG-DTG analysis for high oleic safflower biolubricant.

	Air		N_2	
T_{onset}, °C	361		359	
	Stage 1 (HOSBD)	Stage 2 (HOSBL)	Stage 1 (HOSBD)	Stage 2 (HOSBD)
T_{peak}, °C	232	433	231	427

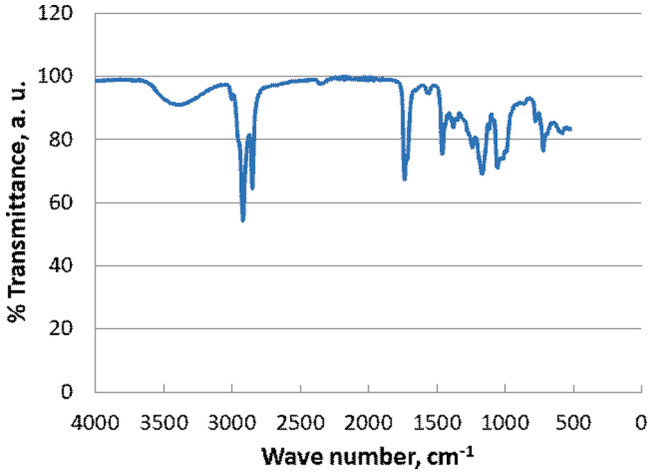

Fig. 6. IR spectra of HOSBL.

shows the main characteristics of HOSBL, comparing its viscosity values to two products: a biolubricant and a lubricant (both commercial).

High flash and combustion points were obtained, being average values according to the literature, where similar biolubricants showed values ranging from around 200 to 240 °C (Salih et al., 2011; Wang et al., 2014). The oxidative stability was high, showing similar results to other tests carried out in similar conditions for trimethylolpropane fatty acid triester (reaching induction points values of around 8 h), although they were slightly higher than equivalent biolubricants obtained from babassu oil (induction point around 6 h) (Bezerra et al., 2020; Wang et al., 2014). The viscosity index, which can be an indicator of the resistance of the biolubricant to changes in viscosity over temperature, was around 100. Compared to other biolubricants or commercial lubricants, this is an average value, similar to those found in the literature for other biolubricants and organic esters (Kania et al., 2015; Saboya et al., 2017; Salih et al., 2011), although it was low compared to other products (Dodos et al., 2015; Gunam Resul et al., 2012; Singh et al., 2020). In addition, high heating value of the biolubricant obtained was 36.92 MJ kg^{-1}.

Concerning the thermal analysis, Fig. 5 shows the TG and DTG curves for HOSBL. Two main degradation steps were observed in both cases (using air or nitrogen as carrier gas), according to these figures, corresponding to DTG peaks. The first one, taking place in the range of 230−235 °C (with a less noticeable peak for N_2), and the second one showing more prominent DTG peaks (and a more pronounced weight loss) at 432 and 430 °C for air and N_2, respectively. The first stage, as observed by other authors, can be due to methyl ester degradation (with temperature peaks at around 220−230 °C (Ferreira et al., 2019; Nogales-Delgado et al., 2019b), which could imply the presence of impurities (mainly HOSBD) in this sample of biolubricant. Through gas chromatography, 6.9 % of FAMEs were found in the final biolubricant, which confirmed these results. Therefore, the second stage could be attributed to HOSBL, showing a weight loss from 370 to 450 °C, both in air and N_2. Different results were obtained for a biolubricant obtained through transesterification with trimetilolpropane, ranging its mail thermal event at around 270 °C (Bezerra et al., 2020).

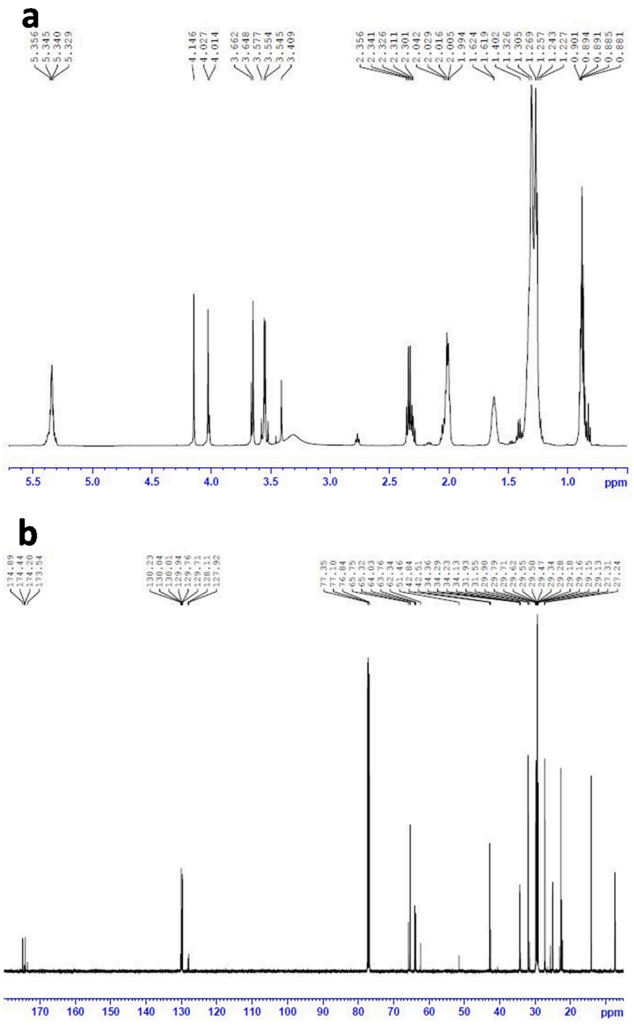

Fig. 7. H NMR of HOSBL a) and C NMR of HOSBL b).

The degradation stage of HOSBL took place at higher temperatures (with DTG peaks at around 430 °C) than in the case of other biolubricants found in the literature (Bezerra et al., 2020; Ferreira et al., 2019), showing similar results to other biolubricants (Nowicki et al., 2019). According to Table 7, where the main events in TG-DTG are described in terms of temperature, the onset temperature (not considering the first stage, which is assigned to HOSBD degradation) was around 360 °C, which is a similar result to other biolubricants obtained by different means (transesterification or epoxidation) (Zhang et al., 2020). As a consequence, it could be said that the biolubricant obtained was thermally stable, in the same order of magnitude compared to the literature.

Fig. 6 shows the IR spectra of HOSBL, where two main absorption bands were observed at 1740 and 1460 cm^{-1}, corresponding to carbonyl C═O. In addition, a peak at around 1100 cm^{-1} was obtained, related to the antisymmetric and asymmetric axial stretching of C—O bond (Nowicki et al., 2019). Finally, a band appeared at 720 cm^{-1}, which could be due to the olefinic carbons (double bonds) in the carbon chain. Similar results were observed for methyl biodiesel and biolubricants derived from it, as the chemical structure of biodiesel and the subsequent biolubricants can present equivalent absorption bands (Ferreira et al., 2019).

With regard to NMR analysis, Fig. 7 shows the main results about this analysis. According to the ^1H NMR spectrum (Fig. 7a), the peak at 4.02 ppm was due to the substitution of the hydroxyl group, in the superior alcohol, by the fatty acid chain, confirming the production of

Table 8
Comparison between different biolubricants obtained with 2-ethyl-2-(hydroxymethyl)-1,3-propanediol from different sources.

Biolubricant	Conversion (%)	Viscosity at 100 °C (mm^2/s)	Induction point (h)
High oleic safflower (HOSBL)	92.90 (± 0.8)	9.32 (± 0.21)	6.72 (± 0.36)
Cardoon (CBL)	94.76 (± 0.91)	9.73 (± 0.22)	2.63 (± 0.17)
Rapeseed (RBL)	97.20 (± 1.02)	10.65 (± 0.19)	5.26 (± 0.32)

biolubricant. However, as it was pointed out in the TG/DTG analysis, the peak at 3.6 ppm indicated the presence of HOSBD impurities (Ferreira et al., 2019).

Concerning ^{13}C NMR (Fig. 7b), the peak due to the ester function was observed at 174 ppm, and the methyl group related to the alcohol and fatty acid chains showed a peak at 7.4 and 14 ppm, respectively. In addition, the peak at 63.76 ppm could be due to oxygenated $-CH_2$ in the alcohol structure once transesterification took place. Similar results were observed by other authors that used the same superior alcohol (Ferreira et al., 2019).

Finally, a comparison between different biolubricants obtained according to the chemical conditions used in this experience, but changing the raw material (using cardoon and rapeseed oil) was carried out (see Table 8). Similar conversion rates and viscosity values were obtained, ranging from 92.3–97.2 % and 9.32 to 10.65 mm^2/s, respectively. There were clear differences in the oxidative stability of the samples. HOSBL showed the highest value, with an induction point of 6.72 h, whereas RBL and especially CBL showed lower induction points, with 5.26 h and 2.63 h, respectively. It should be noted that, compared to HOSBD (8.22 h), the corresponding biolubricant showed a shorter oxidative stability, possibly due to the fact that it is composed of more complex molecules, which could be prone to oxidation.

The difference in oxidative stability among these three biolubricants could be explained by the FAME composition of their corresponding precursors. As it can be seen in Fig. 8, the majority FAMEs were methyl oleate and methyl linoleate for all the samples, exceeding 80 % of total FAME composition. Thus, the most stable FAMEs (saturated or unsaturated) could generate more stable superior esters (biolubricants) compared to di or polyunsaturated FAMEs. HOSBD (the precursor of HOSBL) had the highest percentage of methyl oleate, which was one of the most stable FAMEs, as explained previously (with a methyl oleate/linoleate ratio of 8.88). Rapeseed biodiesel, the precursor of RBL, had lower amounts of this compound, increasing its percentage in methyl linoleate (up to 19 %, with an oleate/linoleate ratio of 3.95). Finally, cardoon biodiesel had the highest amounts of methyl linoleate (exceeding 60 %), which imply a more unstable material (with an oeate/linoleate ratio of 0.42). The corresponding superior esters obtained for rapeseed and cardoon were less stable than in the case of HOSBL, especially for cardoon biolubricant. The influence of the precursor (paying attention to FAME composition) on stability performance was observed in biolubricants obtained through transesterification (with 2-ethyl-1-hexanol, 1-heptanol and 4-methyl-2-pentanol) from similar raw materials (like rapeseed, corn and sunflower, frying and castor oil), and the presence of double bonds or functional groups changed some properties, mainly viscosity (Encinar et al., 2020a) or stability (Encinar et al., 2020b).

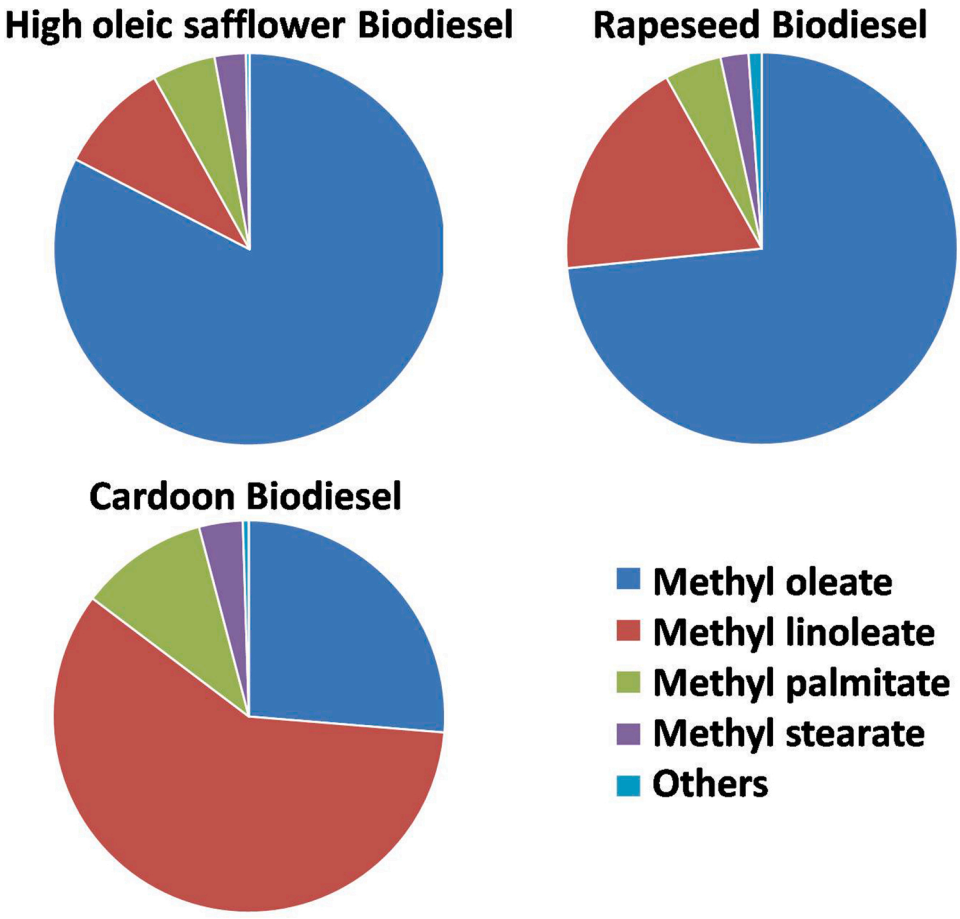

Fig. 8. FAME composition of the biodiesel used for biolubricant production.

4. Conclusions

The main findings of this research work were the following:

- High oleic safflower oil can be a suitable raw material for biodiesel and biolubricant production, with high conversions exceeding 95 % and 92 %, respectively. The most interesting aspect of these products was the high stability compared to other biolubricants found in the literature.
- Regarding the biodiesel obtained, all the requirements of the UNE-EN 14,214 standard, including the oxidative stability (which is hardly fulfilled by any biodiesel without additives), were in accordance with the characteristics of the sample.
- Concerning the biolubricant produced, the optimum chemical conditions were: reaction temperature, 140 °C; catalyst concentration (sodium methoxide), 1 % w/w; vacuum, 400 mmHg; stirring rate, 350 rpm; FAME/alcohol ratio, 1:1. A good yield was obtained (exceeding 92 %) and the final product showed high oxidative and thermal stabilities.
- The characterization of this biolubricant suggests that it can be a polyester, although impurities of its precursor (fatty acid methyl esters) were found.
- The raw material used for biolubricant production played an important role in its final characteristics, especially concerning oxidative stability, where the fatty acid composition of the original oil showed a strong influence on this parameter.
- Taking into account many factors concerning the double transesterification proposed in this study, the production of stable biofuels and bioproducts could be a suitable starting point for the implementation of a biorefinery based on high oleic safflower oil. The generation of intermediate products like fatty acid methyl esters or the generation of by-products such as glycerol or methanol, which can be easily re-used in the process or can contribute to the valorization of the whole process, constitute one of the main characteristics of a biorefinery, including the fact that only one chemical route (with different chemical conditions) is used, which could simplify the design of the facility.

CRediT authorship contribution statement

Sergio Nogales-Delgado: Conceptualization, Methodology, Investigation, Formal analysis, Writing - original draft, Writing - review & editing, Visualization, Supervision. **José María Encinar:** Conceptualization, Methodology, Resources, Writing - review & editing, Visualization, Supervision, Project administration, Funding acquisition. **Álvaro González Cortés:** Investigation, Formal analysis, Writing - original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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