



# Use of mild reaction conditions to improve quality parameters and sustainability during biolubricant production

Sergio Nogales-Delgado<sup>\*</sup>, José María Encinar Martín, Mercedes Sánchez Ocaña

Department of Chemical Engineering and Physical-Chemistry, University of Extremadura, Avda. de Elvas s/n, 06006, Badajoz, Spain

## ARTICLE INFO

### Keywords:

Safflower oil  
Fatty acid methyl esters  
Oxidative stability  
Viscosity  
Viscosity index  
Vacuum atmosphere

## ABSTRACT

The use of alternative sources to produce less pollutant biofuels and biomaterials, replacing petroleum-derived products, is becoming an important issue for international organizations, governments, and society. Thus, biodiesel and biolubricant production has been increasingly researched, offering promising results. These products present some advantages such as sustainability or biodegradability, among others. However, some of their quality parameters can be altered during storage, mainly due to their low oxidative stability. Consequently, auto-oxidation processes can take place, increasing viscosity or acid number, which can compromise their marketability. To avoid these inconveniences, some alternatives have been presented, such as the use of antioxidants, vegetable oil selection or the promotion of mild chemical conditions during production. The aim of this work was to assess the use of vacuum during biolubricant production from high-oleic safflower oil through double transesterification with methanol and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol to obtain mild chemical conditions. Under these circumstances (working pressure at 210 mmHg) and compared to previous studies, temperature and catalyst addition could be reduced from 140 to 100 °C and from 0.5 to 0.3%, respectively, increasing the reaction yield from 92.9 to 94.69% and improving the quality of the biolubricant, with 30% increase in viscosity index.

## 1. Introduction

The use of alternatives for petroleum derivatives has gained prominence in the past decades. Indeed, many signs can be noticed about this fact, such as the successive environmental policies carried out by governments and institutions, reflected in the increasing interest and concern in these subjects by society [1]. In that sense, among other interesting actions, the implementation of new biofuels and biomaterials obtained from natural sources (such as vegetable oils, whose oil can be extracted mechanically, chemically or through other interesting methods such as ultrasound-assisted oil extraction [2]) could be an interesting way to reduce oil consumption [3]. Specifically, biodiesel production has been proved as an efficient and cleaner way to obtain biofuels for their use in Diesel engines [4,5], requiring purification stages such as washing or other innovative ones such as dry washing biodiesel purification through sorbents such as fumed silica [6]. Biodiesel composition is mainly related to fatty acid methyl esters, which are usually obtained from vegetable oils, among other natural sources [7]. Other alternatives, such as waste animal fat,

could be equally interesting for this purpose [8]. Equally, these vegetable oils (or their corresponding fatty acids) can be used as alternative sources for biolubricant production, through different methods such as epoxidation or transesterification, among others [9–14]. If transesterification is used, the concept of biorefinery could play an important role, as a wide range of bioproducts can be obtained from different stages. Thus, a biorefinery based on vegetable oils through double transesterification (see Fig. 1) could produce interesting products such as fatty acid methyl esters (reacting with methanol) with high conversions (up to 96.5%) and fatty acid esters (reacting with more complex alcohols) in successive stages. In addition, some by-products such as methanol (obtained in the second transesterification) can be re-used in the first transesterification. Other by-products such as glycerol (1 kg of glycerol is obtained for 10 kg of oil) can be interesting from many points of view, such as energy or pharmaceutical industries, depending on its purity [15]. Therefore, this biorefinery could be a clear example of sustainability, green chemistry and circular economy.

Some of the main advantages of these kinds of bioproducts

<sup>\*</sup> Corresponding author.

E-mail address: [senogalesd@unex.es](mailto:senogalesd@unex.es) (S. Nogales-Delgado).

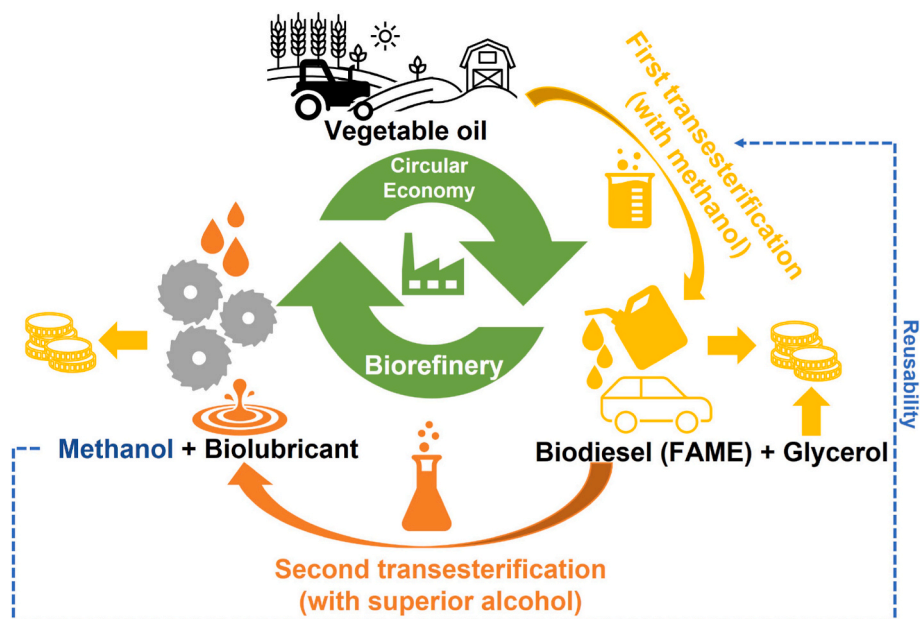


Fig. 1. Main steps related to a biorefinery based on vegetable oils to produce biodiesel and biolubricant through double transesterification.

(biodiesel and biolubricant) have already been mentioned above, concerning clean production. Apart from that, they present higher biodegradability (which is positive in the case of leakages into natural environments), imply cleaner processes and have some characteristics which are better compared to their petroleum equivalents (such as higher flash and combustion points, implying safety during storage or shipping), among others. In addition, the possibility of sustainable economic growth for developing areas is possible, as oil plants can be grown in extreme climate conditions, being a useful starting point for the implementation of biorefineries.

However, and apart from other disadvantages such as their availability, economic feasibility or bad behavior at low temperatures when it comes to cold flow properties [16], one of the main disadvantages of biodiesel and biolubricants is, in general, their low oxidative stability, not exceeding 8 h in most cases [17–20]. Depending on their chemical composition, the oxidative stability might vary, with double bonds or unsaturations playing an important role, as they act as starting points for auto-oxidation processes, with the subsequent polymerization and quality loss [21]. In that sense, an increase in viscosity and acid number was found during storage or oxidation processes, both in the case of biodiesel and biolubricants, which is an undesirable effect for commercialization [22–24].

Nevertheless, there are different methods to avoid these undesirable effects, such as the following:

- Use of antioxidants. The selection of both natural and artificial antioxidants seems to be effective in increasing oxidative stability. Thus, the use of different antioxidants considerably increased this value at low concentrations (1000–2000 ppm), especially in the case of TBHQ or BHA [19,25,26].
- Raw material selection. As fatty acid composition plays an important role in oxidative stability (as the presence of more unstable compounds such as linolenic acid, with three unsaturations, could decrease oxidative stability), the selection of different crops can improve the quality of final products such as biodiesel or biolubricant. This way, the utilization of genetically modified products could be important, as in previous studies has been reported for high-oleic safflower oil to produce biodiesel and biolubricant with 2-ethyl-2-hydroxymethyl-1,3-propanediol [7,27].

- Use of mild reaction conditions. In that sense, low catalyst concentrations (if homogeneous) or low reaction temperatures could be an interesting way to improve the quality of biodiesel and biolubricants, as oxidative stability is influenced by temperature and the presence of some elements such as Na or K, which can promote auto-oxidation processes [28].

Considering the latter, and turning to green chemistry and circular economy, chemical conditions (apart from the design of the main components of a biorefinery) are vital to make these processes more competitive compared to typical fuel processing [28–30]. Thus, the decrease in temperature or catalyst concentration, apart from improving some quality parameters in biodiesel and biolubricants, could be interesting in economic terms, but in these cases the production yield could be compromised. Depending on the process, some alternatives can be presented to increase the reaction yield, such as the use of vacuum to promote the generation of products by shifting the chemical balance if some of the products are volatile. This way, vacuum could be perfectly applied to the second transesterification to produce biolubricants, as methanol is evolved and can be easily removed from the reaction medium by this method. In addition, the use of vacuum does not affect oxidative stability of biolubricant, which could allow to optimize both temperature and catalyst addition.

Considering the above, the aim of this work was to assess the effect of vacuum on biolubricant production from high-oleic safflower oil through double transesterification with methanol and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol, assessing both the yield of the reaction and quality parameters of the final product, comparing with previous works where vacuum did not play an important role.

## 2. Materials and methods

### 2.1. Biodiesel production

The raw material for biodiesel production was high-oleic safflower oil (HSO), which was obtained from the “Agrarian Research Institute Finca La Orden-Valdesequera”, belonging to CICYTEX (Centro de Investigaciones Científicas y Tecnológicas de Extremadura). It was a genetically modified crop (CW-99 OL), with high oleic acid content. Thus, the seeds were collected in 2020 season and the oil was

**Table 1**

Main chemical conditions for each experiment (for all of them, alcohol/HSBD ratio = 1:1; stirring rate = 400 rpm; reaction time = 120 min).

Experience (effect of)	Experiment	Temperature, °C	Catalyst concentration, % w/w	Working pressure, mm Hg
Temperature	1	80	0.3	510
	2	100		
	3	120		
	4	140		
Catalyst concentration	1	80	0.3	510
	5		0.5	
	6		0.7	
	7		0.9	
Working pressure	1	80	0.3	510
	8			760
	9			360
	10			210

mechanically extracted and filtered, showing good properties such as low free fatty acid content in all cases (below 1%), **density (916 kg m<sup>3</sup>) and viscosity (46.7 cSt), not requiring additional pre-treatments and showing similar results compared to other vegetable oils such as sunflower oil [31]**. Afterwards, the oil was stored in 25-L opaque containers at room temperature for further analysis and treatments.

Regarding biodiesel production, a transesterification process was carried out, based on the chemical conditions explained in previous works [21]. In short, the suitable amount of oil was heated up to 60–65 °C, adding methanol to achieve a methanol/oil ratio of 6/1. Afterwards, 1.5% catalyst (sodium methylate, MeONa, Merck KGaA, Darmstadt, Germany) was added, stirring the reaction medium at 450 rpm. Once the reaction took place (after 150 min), different purification stages were followed: glycerol removal by using a separating funnel, washing with ultrapure water, and drying at 110 °C. Finally, the samples (high-oleic safflower biodiesel or fatty acid methyl esters, HSBD) were stored in 5-L opaque bottles for further characterization (according to UNE-EN 14214 standard [32]) and treatment.

## 2.2. Biolubricant production

For the second transesterification, HSBD obtained in the previous step reacted with 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (Merck KGaA, Darmstadt, Germany) to produce high-oleic safflower biolubricant (HSBL) and release methanol.

The facility used for the second transesterification included a Dean Stark device for the collection of methanol when it was released from the second transesterification reaction. The chemical conditions were applied (which will be specified in detail in the corresponding sections), with the following generic steps, based on previous studies [27]:

- The required amounts of HSBD and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol were added to the reactor to obtain an alcohol/HSDB mole ratio of 1:1, heating the reaction medium at a certain temperature. This ratio was selected to avoid surplus alcohol, which would be difficult to filter once the reaction took place [27,33].
- Afterwards, a certain amount of catalyst (sodium methylate, MeONa, Merck KGaA, Darmstadt, Germany) was added and the vacuum was applied at different working pressures, considering this point as the beginning of the reaction.
- In order to check the progress of the reaction, the FAME content of samples collected at 0, 1, 2, 5, 10, 30, 90 and 120 min was obtained through gas chromatography, as explained in following sections.
- At the end of the chemical reaction, there was an initial gravity filtration with filter paper (Dorsan Spain, Barcelona, Spain, 73 g/m<sup>2</sup>) and the sample was cooled down at room temperature. Afterwards, a vacuum filtration with filter paper and using a Buchner funnel was applied, to remove the crystallized surplus alcohol (as it is in a solid state at room temperature). This second step was repeated until a translucent sample (not turbid) was obtained.

- The final product (HSBL) 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 temperature, catalyst concentration and vacuum (or working pressure).

### 2.3. The effect of temperature

Different reaction temperatures (80, 100, 120 and 140 °C) were studied, keeping the rest of parameters constant (FAME/alcohol ratio: 1:1; catalyst concentration: 0.3% w/w; working pressure: 510 mmHg; reaction time: 120 min; stirring rate: 400 rpm).

### 2.4. The effect of catalyst concentration

In this case, three concentrations of sodium methylate were selected (0.3, 0.5, 0.7 and 0.9% w/w). The rest of parameters were kept constant for these experiments (Temperature: 80 °C; FAME/alcohol ratio: 1:1; working pressure: 510 mmHg; reaction time: 120 min; stirring rate: 400 rpm).

### 2.5. The effect of working pressure

Regarding the working pressure, different values were tested (760, 510, 360 and 210 mmHg), keeping the rest of parameters constant (Temperature: 80 °C; FAME/alcohol ratio: 1:1; catalyst concentration, 0.3%; reaction time: 120 min; stirring rate: 400 rpm).

The main chemical conditions for each experiment are included in Table 1, as follows:

### 2.6. Biodiesel and biolubricant characterization

The main characteristics of high-oleic biodiesel and biolubricant were determined, and a comparison with the UNE-EN 14214 standard was carried out [34]. As explained in previous articles [35], the following parameters were assessed:

- Methyl ester content by using gas chromatography [36].
- Moisture, density, viscosity, viscosity index and cold filter plugging point (CFPP) [37].
- Acid and iodine numbers [38].
- Flash and combustion points [39].
- Oxidative stability through the Rancimat Method [40].

Each determination was done in triplicate, showing the average value for each parameter and the corresponding standard deviation when necessary. Conversion (expressed in %) of the process was obtained through the decrease in FAME content during transesterification, as follows (Equation (1)):

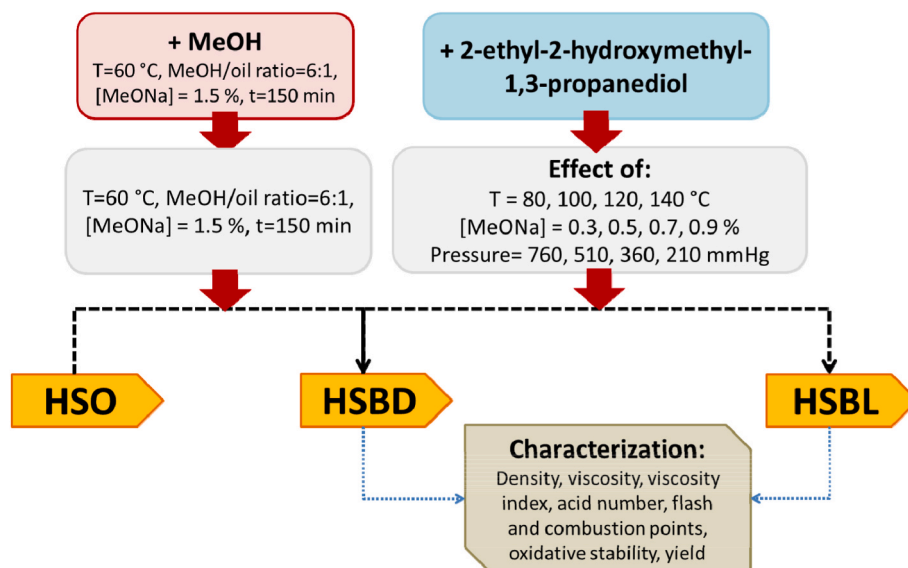


Fig. 2. Experimental design. HSO = High-oleic safflower oil; HSB = High-oleic safflower biodiesel; HSL = High-oleic safflower biolubricant.

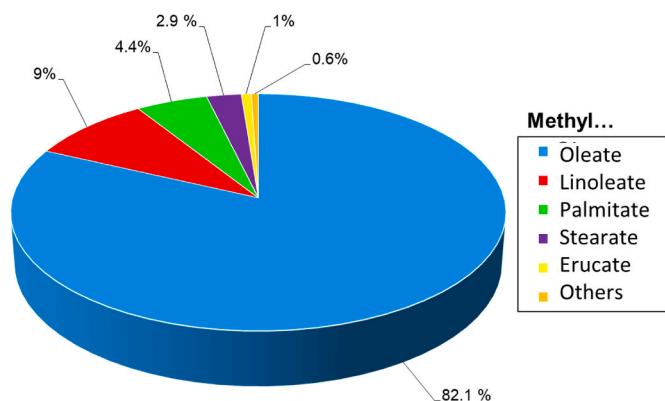


Fig. 3. Fatty acid methyl ester profile of HSB.

Table 2  
Main characteristics of HSB.

Property	Value
FAMES, %	97.1
Density at 15 °C, kg·m <sup>-3</sup>	874
Viscosity at 40 °C, cSt.	4.54
Oxidative stability, h	8.3
Acid number, mg <sub>KOH</sub> ·g <sup>-1</sup>	0.24
Flash point, °C	188
Combustion point, °C	202
Water content, %	0.023
Cold filter plugging point, °C	-3
Iodine number, g I <sub>2</sub> ·(100 g) <sup>-1</sup>	90.9
Methyl linoleate, %	9.15

$$\text{Conversion} = (F_0 - F_t)/F_0 \cdot 100 \quad (1)$$

Where  $F_0$  is FAME content in biodiesel and  $F_t$  is FAME content at a certain reaction time  $t$  (both expressed in %).

To sum up, the main steps carried out in this experience are included in Fig. 2.

### 3. Results and discussion

Regarding HSO, it had low acidity (<1%) and high quality (not showing impurities after filtration), which made it suitable for basic homogeneous catalysis to produce fatty acid methyl esters (that is, high-oleic safflower biodiesel, HSB). Once HSB was produced, its composition was obtained, included in Fig. 3:

As observed, the majority FAME was methyl oleate, clearly exceeding 80%, followed by methyl linoleate, not reaching 10%. This basic composition is similar to previous studies (whose raw material was obtained in crops from previous seasons), which suggested that pre-harvest conditions did not considerably affect FAME composition [27]. It should be noted that FAME profile in this case is different from typical safflower biodiesel, as pointed out in the literature, where the profile seems to be the opposite, with 70–80% methyl linoleate and around 10% methyl oleate [41–43]. In this case, it should be considered that the raw material was obtained from a genetically modified crop,

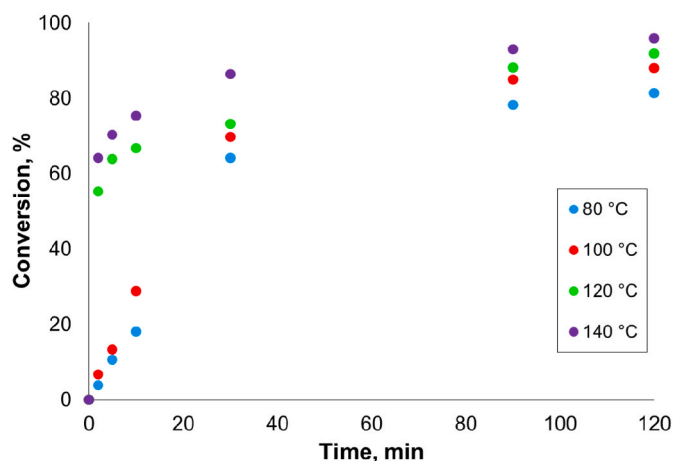


Fig. 4. Effect of temperature on HSB production. Chemical conditions: [MeONa] = 0.3%; working pressure = 510 mmHg; alcohol/HSB ratio = 1:1; stirring rate = 400 rpm; reaction time = 120 min.

and the nature of this oil is completely different, showing different properties as explained in Table 2.

All the characteristics included in this table complied with UNE-EN 14214 standard, even oxidative stability (which clearly exceeded the lower limit of the standard, established at 8 h). This is a very important aspect, as explained in previous studies, since most vegetable oils

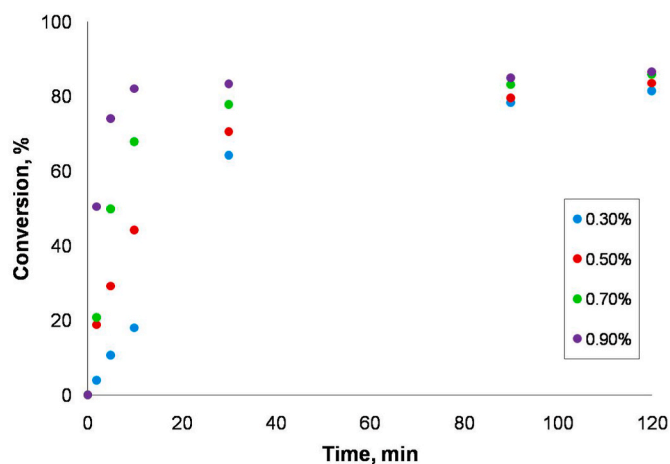


Fig. 5. Effect of catalyst concentration on HSBL production. Chemical conditions: T = 80 °C; working pressure = 510 mmHg; alcohol/HSBD ratio = 1:1; stirring rate = 400 rpm; reaction time = 120 min.

present low oxidative stabilities, requiring conservative techniques (such as antioxidant addition, among others) to comply with the standard [44–46]. In this case, this step is not required, increasing the sustainability of this stage [27]. Consequently, a high-quality product is obtained, which can be a suitable precursor of the final biolubricant. The high oxidative stability of this sample, compared to other similar fuels obtained from safflower is due to the FAME composition. Thus, high methyl oleate contents, at the expense of methyl linoleate, could increase stability during storage, as it presents one single double bond in its molecular structure (whereas methyl linoleate presents two double bonds), which is usually reactive to oxygen to start the initiation stage of auto-oxidation, generating free radicals that react in propagation and termination stages. Consequently, polymerization can take place, compromising the quality of biodiesel during storage (with viscosity increase, for instance).

Regarding the effect of chemical conditions in HSBL production, Fig. 4 shows different experiments carried out at increasing temperatures, from 80 to 140 °C. As observed, conversion increased with temperature, especially during the first 30 min, and afterwards the conversion followed an asymptotic trend, reaching the conversion value corresponding to the chemical balance, especially at high temperatures (from 81.4% at 80 °C to 95.9% at 140 °C). Although the conversion value corresponding to the chemical balance is not completely reached at 120 min, the trend of the curves suggests that this value increased with temperature. Therefore, temperature had a positive effect on conversion and reaction rate. On the other hand, as conversion increased, the oxidative stability gradually decreased (from 6.85 h at 80 °C to 6.21 h at 140 °C). This behavior can be explained by two factors, as explained in previous works [35]: first, the higher complexity of the molecular structure of HSBL can show lower oxidative stabilities; and second, the use of higher temperatures could contribute to the deterioration of the final product. According to these opposite effects, an intermediate temperature value (100 °C) was selected to the final production of HSBL.

Concerning catalyst addition (Fig. 5), it had a clear and positive effect on reaction rate, with a considerable increase at initial stages, reaching the chemical balance in all cases, more rapidly as catalyst concentration increased. Also, the final conversion value was similar regardless the catalyst concentration used. As expected, catalyst concentration affected the initial reaction rate, whereas the final conversion (when balance was achieved) was similar. Accordingly, the lowest catalyst concentration was selected for final HSBL production, as it implied cost savings and lower catalyst amount to be removed at industrial scale [27].

Regarding the effect of vacuum, different working pressures were

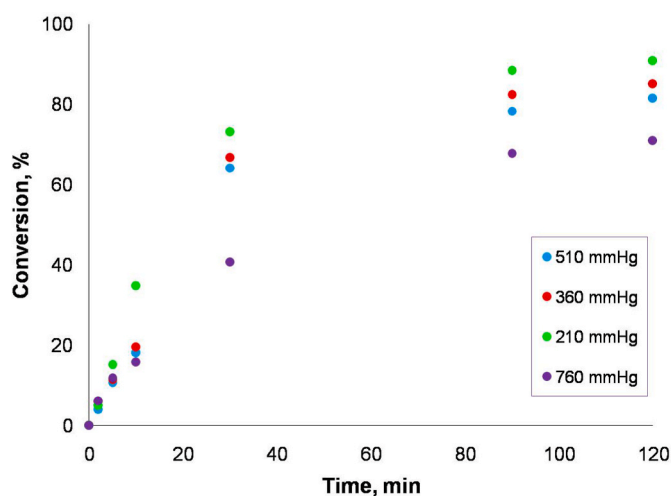


Fig. 6. Effect of vacuum (working pressure) on HSBL production. Chemical conditions: [MeONa] = 0.3%; T = 80 °C; alcohol/HSBD ratio = 1:1; stirring rate = 400 rpm; reaction time = 120 min.

Table 3  
Chemical conditions to produce HSBL.

Alcohol/FAME ratio	1:1
Temperature, °C	100
Catalyst concentration (MeONa), %	0.3
Working pressure, mmHg	210
Stirring rate, rpm	400
Reaction time, min	120

Table 4  
Main properties of HSBL.

Property	Value
Yield, %	94.69
Density at 15 °C, kg·m <sup>-3</sup>	949
Viscosity at 40 °C, cSt	89.11
Viscosity at 100 °C, cSt	12.2
Viscosity index	131
Oxidative stability, h	6.93
Acid number, mg <sub>KOH</sub> ·g <sup>-1</sup>	0.26
Flash point, °C	220
Combustion point, °C	229
Water content, %	0.02

studied in this experience, showing the evolution of conversion in Fig. 6. In this case, when HSBL is obtained, a by-product is obtained (that is, methanol), which can be removed from the reaction medium through vacuum due to its volatility. In light of the results obtained, an increase in vacuum (that is, at lower working pressures), implied a higher conversion, with clear differences between 760 mmHg (70.93%) and 210 mmHg (90.84%). Thus, as one of the by-products (methanol) was removed thanks to vacuum, the chemical balance shifted towards the generation of products at the expense of reagents, increasing the chemical conversion. Due to these marked differences, the lowest working pressure was selected to produce the final biolubricant.

To sum up, the chemical conditions used to produce the final high-oleic safflower biolubricant (HSBL) according to previous experiences were the included ones in Table 3:

It should be noted that, for the first and second transesterification, and taking as a reference the initial weight of oil, yields of 97.8 and 80.1% in weight were obtained for pure biodiesel and biolubricant (which underwent different purification stages such as filtration, where some product could not be recovered).

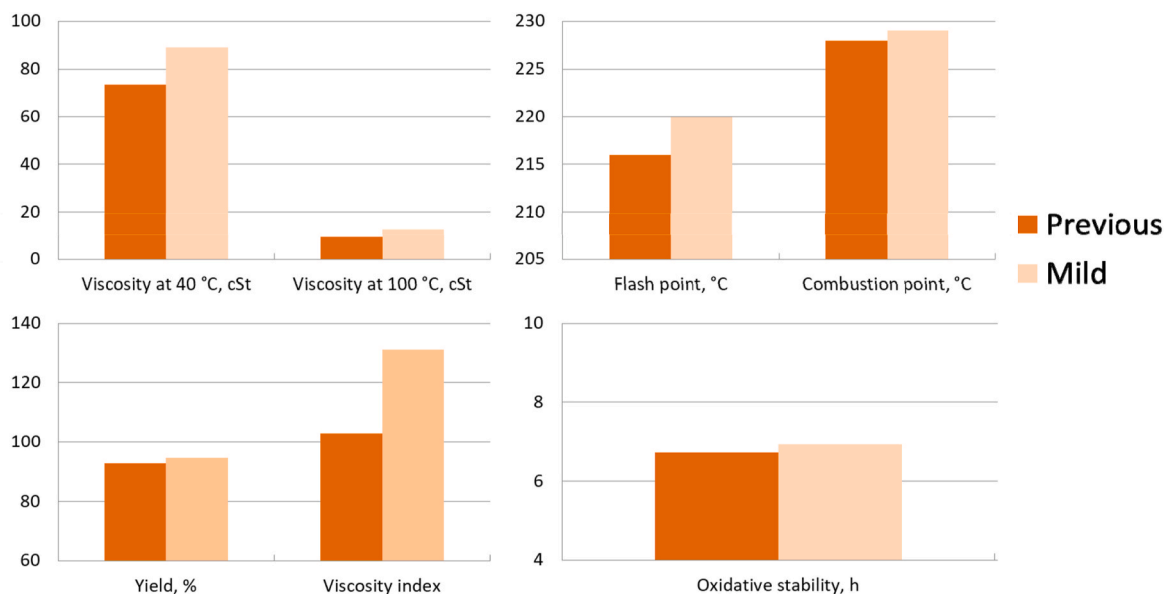


Fig. 7. Comparison of HSBL obtained with previous and mild (current) chemical conditions. Previous conditions were:  $T = 140\text{ }^{\circ}\text{C}$ ;  $[\text{MeONa}] = 0.5\%$  w/w;  $P = 400$  mmHg. Mild conditions were:  $T = 100\text{ }^{\circ}\text{C}$ ;  $[\text{MeONa}] = 0.3\%$  w/w;  $P = 210$  mmHg. The rest of chemical conditions were common: alcohol/HSBD ratio = 1:1; stirring rate = 400 rpm; reaction time = 120 min.

Under these circumstances, the main properties of HSBL were shown in Table 4:

It should be noted that, compared to previous studies and considering the viscosity values at 40 and 100 °C, this biolubricant could be similar to a SAE10W30 lubricant, that is, it could be used as an engine oil [33]. This final product stands out for its high oxidative stability, around 7 h, which is superior to other similar biolubricants found in the literature. Thus, some biolubricants obtained with less complex alcohols (such as 2-ethyl-1-hexanol) had shorter oxidative stabilities, as in the case of rapeseed (about 6 h), waste cooking or corn and sunflower biodiesel (about 3 h) [47]. Other esters obtained from cardoon and 2,2-dimethyl-1,3-propanediol equally offered low oxidative stability values, hardly exceeding 3 h [48]. On the other hand, other biolubricants obtained in a similar way had longer oxidative stabilities around 8 h [49]. In any case, the biolubricant obtained in this study had a high oxidative stability value, above the average esters obtained through transesterification [9], not requiring the use of high amounts of additives to improve this characteristic [50]. Also, its flash and combustion points were high, clearly exceeding 200 °C, which implies safety during shipping and storage. The yield obtained exceeded 90%, which proved the suitability of the chemical conditions selected for this experience. Finally, acid number was below  $1\text{ mg}_{\text{KOH}}\cdot\text{g}^{-1}$ . Consequently, corrosion risks are reduced. The main use of a biolubricant is related to its viscosity and viscosity index. In this case, viscosity index was high, similar to those found for commercial samples, and concerning viscosities at 40 and 100 °C, this biolubricant can be classified as SAE10W30, as viscosity at 100 °C was within the range of 9.3–12.5 cSt and viscosity at 40 °C was between 79.5 and 113 cSt [51]. In that sense and considering that the viscosity index is near 140 (within the range of similar biolubricants found in the literature [52]), these products can be considered a multigrade biolubricant, with diesel and gasoline engine application in any climate.

Comparing the most decisive properties of HSBL to previous studies, where the same raw material, alcohol and procedure were followed under different chemical conditions, some differences were observed (as shown in Fig. 7). Thus, the previous experience had higher temperature reaction (140 °C) and catalyst concentration (0.5%), with higher working pressure (400 mmHg). The use of lower working pressures (210 mmHg) in this experience allowed to reduce the temperature

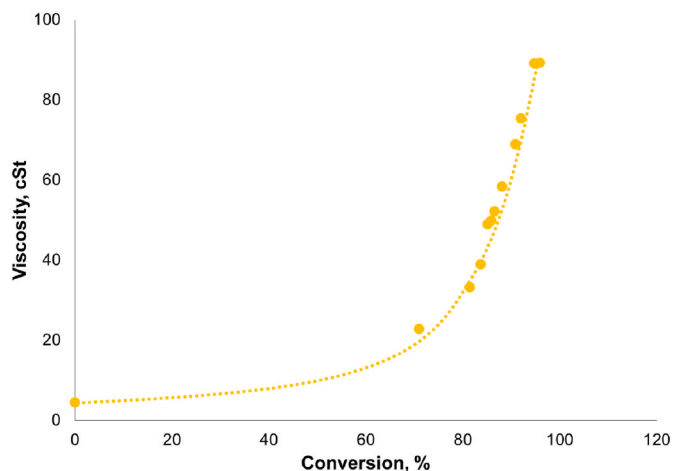
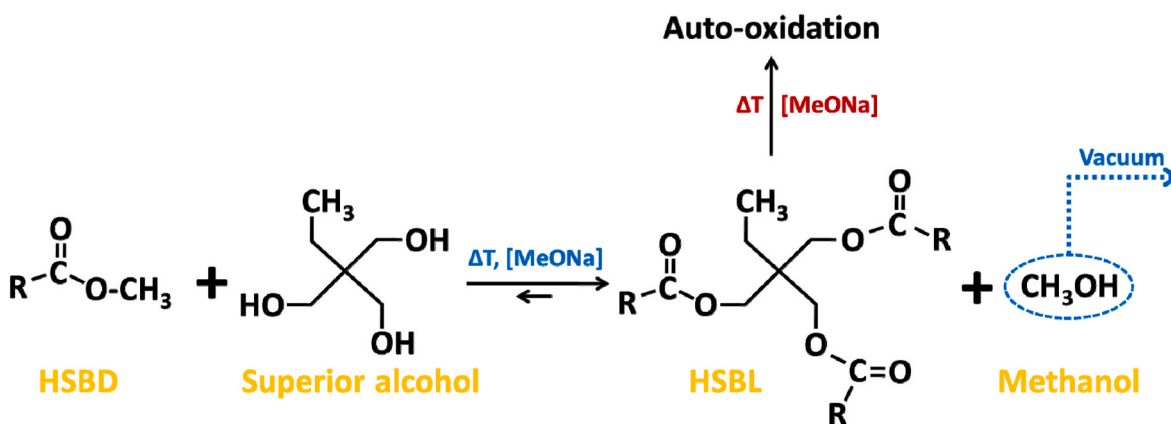


Fig. 8. Influence of conversion on viscosity in final products.

reaction (100 °C) and catalyst addition (0.3%) reaching similar yields.

As inferred from this figure, although mild conditions thanks to the increase in vacuum (that is, lower working pressures) were used, better yields were obtained compared to previous conditions included in the literature [27]. Therefore, a pure biolubricant was obtained, whose impurities were not considerable and their influence was not significant in some final properties. In that sense, higher flash and combustion points were obtained with mild conditions, as it is a characteristic property which can be altered by small amounts of impurities (such as methanol or superior alcohols). Equally, the increase in viscosity in the case of mild conditions could be due to the higher yield obtained, as conversion and viscosity in the reaction medium are highly connected, as shown in Fig. 8:

Thus, there was an increase in viscosity with conversion, and this trend was more marked as the conversion was around 90–100%. This could be due to the lower amount of impurities (mainly biodiesel) whose viscosity is much lower. Consequently, the purer the sample was (with high conversion values), the higher viscosity was found. Additionally, viscosity index (whose high values are desirable, as it implies lower



**Fig. 9.** Main chemical conditions affecting to high HSBL conversions (in blue) and poor HSBL oxidative stability (in red). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

changes in viscosity with temperature) increased 30% and oxidative stability increased above 20 min by using mild conditions, which proved the high quality of the final biolubricant compared to previous experiences where temperature or catalyst addition were relatively excessive. This could be due to the use of lower temperatures and catalyst concentrations (with trace metals), which can avoid auto-oxidation processes as explained in the literature. Thus, during biolubricant production, these high temperatures can partially deteriorate the final product up to its cooling to room temperature, and surplus catalysts remaining after the purification process can trigger auto-oxidation processes of fatty acid esters during storage due to the presence of some metals such as sodium or potassium [24,40]. In that sense, there are offsetting effects, as it can be seen in Fig. 9.

On one hand, as inferred from this figure, temperature and catalyst addition promoted biolubricant production (by shifting the chemical balance towards products), but on the other hand they can contribute to the subsequent degradation step of the final product during storage. Concerning vacuum, its effect was positive in two ways: first, the removal of methanol promoted biolubricant generation (shifting the chemical balance towards products), whereas lower temperatures and catalyst additions could be used to achieve better yields during the process, delaying auto-oxidation of the final product during storage and making the process more sustainable and competitive compared to other equivalent petrol-based processes.

Finally, a short cost analysis for the production of this biolubricant was considered for the best reaction conditions. Thus, considering a biolubricant production of 2300 tonnes per year, and taking into account the costs of raw materials (including oil, methanol, catalyst and superior alcohol, implying around 1.5 million euros), workforce, energy and depreciation periods, the final yearly costs would be around 2 million euros. It should be noted that 75% of the costs depend on the raw materials, and therefore the use of mild conditions (decreasing catalyst, for instance) could contribute to a considerable cost reduction.

#### 4. Conclusions

The main findings of this research work were the following:

- HSBD complied with the UNE-EN 14214 standard, which proved the high quality of the raw material used for biolubricant production. Its high oxidative stability was especially interesting, mainly due to the high amount of methyl oleate at the expense of other unstable FAMES such as methyl linoleate.
- The best chemical conditions for HSBL production were: Temperature, 100 °C; alcohol/HSBD ratio, 1:1; sodium methoxide concentration, 0.3%; working pressure, 210 mmHg; reaction time, 120 min; stirring rate, 400 rpm.

- The final product obtained had a high conversion (94.69%), with higher oxidative stability (6.93 h), flash and combustion points (220 and 229 °C) and viscosity index (130) compared to previous studies where higher temperatures and catalyst concentrations were used. This was due to the use of lower working pressures, which removed more efficiently methanol, and consequently the reaction shifted towards HSBL production, allowing lower reaction temperatures and catalyst concentration and **subsequently improving** the stability of biolubricants.
- Under these circumstances and characteristics, HSBL was suitable for its use in Diesel engines, and vacuum promoted the use of milder chemical conditions which made the final product more stable and the process more sustainable.

#### Authors' contributions

S. Nogales-Delgado performed the experimental work and sample preparation and characterization, original draft preparation, paper writing and final editing of the manuscript. J. M. Encinar Martín took care of the conceptualization, supervision, funding acquisition. M. Sánchez Ocaña performed the experimental work and carried out the sample characterization.

#### Declaration of competing interest

The authors declare no conflict of interest.

#### Acknowledgements

Prof. Dr. José María Encinar would like to state the following: “Now that my professional career comes to an end, I would like to acknowledge the support and love received by my wife Ana, for more than 50 years together. Also, I would like to thank my children Jose, Ana (†) and Lara, my daughter-in-law María Jesús and my son-in-law Víctor. For work reasons, I probably have not spent with them as many hours as they deserved. Finally, I am grateful to my grandchildren Raúl, Ana, Alex, Alba and Eva for the joy and encouragement that your existence has given to my life.

The authors would like to thank the “Junta de Extremadura” (Ayudas para la realización de actividades de investigación y desarrollo tecnológico, de divulgación de transferencia de conocimiento por los Grupos de Investigación de Extremadura) and the FEDER “Fondos Europeos de Desarrollo Regional (Una manera de hacer Europa)” for the financial support received (GR 21139 and IB18028).

## References

- [1] UN, Sustainable Development Goals, 2019. <https://www.un.org/sustainabledevelopment/>.
- [2] F. Ideris, A.H. Shamsuddin, S. Nomanbhay, F. Kusumo, A.S. Silitonga, M.Y. Ong, H. C. Ong, T.M.I. Mahlia, Optimization of ultrasound-assisted oil extraction from *Canarium odontophyllum* kernel as a novel biodiesel feedstock, *J. Clean. Prod.* 288 (2021), 125563, <https://doi.org/10.1016/j.jclepro.2020.125563>.
- [3] J. Moncada B, V. Aristizábal M, C.A. Cardona A, Design strategies for sustainable biorefineries, *Biochem. Eng. J.* 116 (2016) 122–134, <https://doi.org/10.1016/j.bej.2016.06.009>.
- [4] V. Rathore, B.L. Newalkar, R.P. Badoni, Processing of vegetable oil for biofuel production through conventional and non-conventional routes, *Energy Sustain. Dev.* (2016), <https://doi.org/10.1016/j.esd.2015.11.003>.
- [5] S.M.A. Rahman, H.H. Masjuki, M.A. Kalam, M.J. Abedin, A. Sanjid, S. Imtenan, Effect of idling on fuel consumption and emissions of a diesel engine fueled by *Jatropha* biodiesel blends, *J. Clean. Prod.* 69 (2014) 208–215, <https://doi.org/10.1016/j.jclepro.2014.01.048>.
- [6] M. Catarino, E. Ferreira, A.P. Soares Dias, J. Gomes, Dry washing biodiesel purification using fumed silica sorbent, *Chem. Eng. J.* 386 (2020), 123930, <https://doi.org/10.1016/j.cej.2019.123930>.
- [7] G. Martínez, N. Sánchez, J.M. Encinar, J.F. González, Fuel Properties of Biodiesel from Vegetable Oils and Oil Mixtures. Influence of Methyl Esters Distribution, *Biomass and Bioenergy*, 2014, <https://doi.org/10.1016/j.biombioe.2014.01.034>.
- [8] J. Hancsók, D. Sági, J. Valyon, Diesel fuel blending components from mixture of waste animal fat and light cycle oil from fluid catalytic cracking, *J. Environ. Manag.* 223 (2018) 92–100, <https://doi.org/10.1016/j.jenvman.2018.06.011>.
- [9] J. McNutt, Q.S. He, Development of biolubricants from vegetable oils via chemical modification, *J. Ind. Eng. Chem.* 36 (2016) 1–12, <https://doi.org/10.1016/j.jiec.2016.02.008>.
- [10] L.A. García-Zapateiro, J.M. Franco, C. Valencia, M.A. Delgado, C. Gallegos, Viscous, thermal and tribological characterization of oleic and ricinoleic acids-derived estolides and their blends with vegetable oils, *J. Ind. Eng. Chem.* 19 (2013) 1289–1298, <https://doi.org/10.1016/j.jiec.2012.12.030>.
- [11] G. Karmakar, P. Ghosh, B.K. Sharma, Chemically modifying vegetable oils to prepare green lubricants, *Lubricants* 5 (2017) 1–17, <https://doi.org/10.3390/lubricants5040044>.
- [12] F.J. Owuna, M.U. Dabai, M.A. Sokoto, S.M. Dangoggo, B.U. Bagudo, U.A. Birnin-Yauri, L.G. Hassan, I. Sada, A.L. Abubakar, M.S. Jibrin, Chemical modification of vegetable oils for the production of biolubricants using trimethylolpropane: a review, *Egypt. J. Petrol.* 29 (2020) 75–82, <https://doi.org/10.1016/j.ejpe.2019.11.004>.
- [13] A.A. Cerón, R.N. Vilas Boas, F.C. Biaggio, H.F. de Castro, Synthesis of biolubricant by transesterification of palm kernel oil with simulated fusel oil: batch and continuous processes, *Biomass Bioenergy* 119 (2018) 166–172, <https://doi.org/10.1016/j.biombioe.2018.09.013>.
- [14] R.Z.K. Hussein, N.K. Attia, M.K. Fouad, S.T. ElSheltawy, Experimental investigation and process simulation of biolubricant production from waste cooking oil, *Biomass Bioenergy* 144 (2021), 105850, <https://doi.org/10.1016/j.biombioe.2020.105850>.
- [15] M. Checa, S. Nogales-Delgado, V. Montes, J.M. Encinar, Recent advances in glycerol catalytic valorization: a review, *Catalysts* 10 (2020) 1–41, <https://doi.org/10.3390/catal10111279>.
- [16] A. Anwar, A. Garforth, Challenges and opportunities of enhancing cold flow properties of biodiesel via heterogeneous catalysis, *Fuel* 173 (2016) 189–208, <https://doi.org/10.1016/j.fuel.2016.01.050>.
- [17] J. Salimon, N. Salih, E. Yousif, Biolubricants: raw materials, chemical modifications and environmental benefits, *Eur. J. Lipid Sci. Technol.* 112 (2010) 519–530, <https://doi.org/10.1002/ejlt.200900205>.
- [18] M. Dehghani Soufi, B. Ghobadian, M. Atashgaran, S.M. Mousavi, G. Najafi, Biolubricant production from edible and novel indigenous vegetable oils: mainstream methodology, and prospects and challenges in Iran, *Biofuels, Bioprod. Biorefining.* (2018) 1–12, <https://doi.org/10.1002/bbb.1953>.
- [19] R.O. Dunn, Antioxidants for improving storage stability of biodiesel, *Biofuels, Bioprod. Biorefining.* (2008), <https://doi.org/10.1002/bbb.83>.
- [20] M. Ramos, A.P.S. Dias, J.F. Puna, J. Gomes, J.C. Bordado, Biodiesel production processes and sustainable raw materials, *Energies* 12 (2019), <https://doi.org/10.3390/en12234408>.
- [21] S. Nogales-Delgado, J.M. Encinar, A. Guiberteau, S. Márquez, The effect of antioxidants on corn and sunflower biodiesel properties under extreme oxidation conditions, *JAACS, J. Am. Oil Chem. Soc.* (2019), <https://doi.org/10.1002/aocs.12288>.
- [22] Z. Yang, B.P. Hollebone, Z. Wang, C. Yang, C. Brown, M. Landriault, Storage stability of commercially available biodiesels and their blends under different storage conditions, *Fuel* (2014), <https://doi.org/10.1016/j.fuel.2013.07.039>.
- [23] S. Nogales-Delgado, A. Guiberteau, J.M. Encinar, Effect of tert-butylhydroquinone on biodiesel properties during extreme oxidation conditions, *Fuel* 310 (2022), 122339, <https://doi.org/10.1016/j.fuel.2021.122339>.
- [24] P. Verma, M.P. Sharma, G. Dwivedi, Investigation of metals and antioxidants on stability characteristics of biodiesel, *Mater. Today Proc.* 2 (2015) 3196–3202, <https://doi.org/10.1016/j.matpr.2015.07.114>.
- [25] S. Nogales-Delgado, J.M. Encinar, J.F. González, Safflower biodiesel: improvement of its oxidative stability by using BHA and TBHQ, *Energies* 12 (2019), <https://doi.org/10.3390/en12101940>.
- [26] K. Varatharajan, D.S. Pushparani, Screening of antioxidant additives for biodiesel fuels, *Renew. Sustain. Energy Rev.* 82 (2018) 2017–2028, <https://doi.org/10.1016/j.rser.2017.07.020>.
- [27] S. Nogales-Delgado, J.M. Encinar, Á. González Cortés, High oleic safflower oil as a feedstock for stable biodiesel and biolubricant production, *Ind. Crop. Prod.* 170 (2021), 113701, <https://doi.org/10.1016/j.indcrop.2021.113701>.
- [28] I. Raheem, M.N. Bin Mohiddin, Y.H. Tan, J. Kansedo, N.M. Mubarak, M. O. Abdullah, M.L. Ibrahim, A review on influence of reactor technologies and kinetic studies for biodiesel application, *J. Ind. Eng. Chem.* 91 (2020) 54–68, <https://doi.org/10.1016/j.jiec.2020.08.024>.
- [29] M.N. Bin Mohiddin, Y.H. Tan, Y.X. Seow, J. Kansedo, N.M. Mubarak, M. O. Abdullah, Y.S. Chan, M. Khalid, Evaluation on feedstock, technologies, catalyst and reactor for sustainable biodiesel production: a review, *J. Ind. Eng. Chem.* 98 (2021) 60–81, <https://doi.org/10.1016/j.jiec.2021.03.036>.
- [30] J. Gupta, M. Agarwal, A.K. Dalai, An overview on the recent advancements of sustainable heterogeneous catalysts and prominent continuous reactor for biodiesel production, *J. Ind. Eng. Chem.* 88 (2020) 58–77, <https://doi.org/10.1016/j.jiec.2020.05.012>.
- [31] T. Saba, J. Estephane, B. El Khoury, M. El Khoury, M. Khazma, H. El Zakhem, S. Aouad, Biodiesel production from refined sunflower vegetable oil over KOH/ZSM5 catalysts, *Renew. Energy* (2016), <https://doi.org/10.1016/j.renene.2016.01.009>.
- [32] UNE-EN 14214:2013 V2+A1:2018, Liquid Petroleum Products - Fatty Acid Methyl Esters (FAME) for Use in Diesel Engines and Heating Applications - Requirements and Test Methods, 2018.
- [33] J.M. Encinar, S. Nogales-Delgado, A. Pinilla, Biolubricant production through double transesterification: reactor design for the implementation of a biorefinery based on rapeseed, *Processes* 9 (2021) 1224, <https://doi.org/10.3390/pr9071224>.
- [34] U.-E. 14214, Liquid Petroleum Products – Fatty Acid Methyl Esters (FAME) for Use in Biodiesel Engines and Heating Applications – Requirements and Test Methods, 2013.
- [35] J.M. Encinar, S. Nogales, J.F. González, Biodiesel and biolubricant production from different vegetable oils through transesterification, *Eng. Rep.* (2020) 1–10, <https://doi.org/10.1002/eng.2.12190>.
- [36] UNE-EN ISO 12966-2:2011, Animal and Vegetable Fats and Oils – Gas Chromatography of Fatty Acid Methyl Esters – Part 2: Preparation of Methyl Esters of Fatty Acids, 2011.
- [37] UNE-EN 116, Diesel and Domestic Heating Fuels – Determination of Cold Filter Plugging Point- Stepwise Cooling Bath Method, 2015, 2015.
- [38] UNE-EN 14111, Fat and Oil Derivatives. Fatty Acid Methyl Esters (FAME). Determination of Iodine Value, 2003, 2003.
- [39] UNE-EN 51023, Petroleum Products. Determination of Flash and Fire Points, Cleveland open cup method, 1990, 1990.
- [40] W.W. Focke, I. Van Der Westhuizen, X. Oosthuysen, Biodiesel oxidative stability from Rancimat data, *Thermochim. Acta* (2016), <https://doi.org/10.1016/j.tca.2016.03.023>.
- [41] P. Mihaela, R. Josef, N. Monica, Z. Rudolf, Perspectives of safflower oil as biodiesel source for South Eastern Europe (comparative study: safflower, soybean and rapeseed), *Fuel* 111 (2013) 114–119, <https://doi.org/10.1016/j.fuel.2013.04.012>.
- [42] S. Nogales-Delgado, J.M. Encinar, J.F. González, Safflower biodiesel: improvement of its oxidative stability by using BHA and TBHQ, *Energies* (2019) 19–22.
- [43] C. Ilkiliç, S. Aydin, R. Behçet, H. Aydin, Biodiesel from safflower oil and its application in a diesel engine, *Fuel Process. Technol.* 92 (2011) 356–362, <https://doi.org/10.1016/j.fuproc.2010.09.028>.
- [44] L.S. De Sousa, C.V.R. De Moura, J.E. De Oliveira, E.M. De Moura, Use of natural antioxidants in soybean biodiesel, *Fuel* 134 (2014) 420–428, <https://doi.org/10.1016/j.fuel.2014.06.007>.
- [45] E.H.S. De Cavalcanti, A. Zimmer, M.F. Ferrão, F.M. Bento, Storage stability studies and shelf life determinations of commercial brazilian biodiesels stocked in suboptimal conditions in carbon steel containers, in: IASH 2017 - 15th Int. Conf. Stability, Handl. Use Liq. Fuels. 236, 2017, pp. 993–1007, <https://doi.org/10.1016/j.fuel.2018.09.043>.
- [46] I. van der Westhuizen, W.W. Focke, Stabilizing sunflower biodiesel with synthetic antioxidant blends, *Fuel* 219 (2018) 126–131, <https://doi.org/10.1016/j.fuel.2018.01.086>.
- [47] J.M. Encinar, S. Nogales, J.F. González, Biodiesel and biolubricant production from different vegetable oils through transesterification, *Eng. Rep.* (2020) 1–10, <https://doi.org/10.1002/eng.2.12190>.
- [48] S. Nogales-Delgado, J.M. Encinar Martín, Cardoon biolubricant through double transesterification: assessment of its oxidative, thermal and storage stability, *Mater. Lett.* 302 (2021), <https://doi.org/10.1016/j.matlet.2021.130454>.
- [49] E. Wang, X. Ma, S. Tang, R. Yan, Y. Wang, W.W. Riley, M.J.T. Reaney, Synthesis and Oxidative Stability of Trimethylolpropane Fatty Acid Triester as a Biolubricant Base Oil from Waste Cooking Oil, *Biomass and Bioenergy*, 2014, <https://doi.org/10.1016/j.biombioe.2014.03.022>.
- [50] L.A. Quinchia, M.A. Delgado, C. Valencia, J.M. Franco, C. Gallegos, Viscosity modification of high-oleic sunflower oil with polymeric additives for the design of new biolubricant formulations, *Environ. Sci. Technol.* 43 (2009) 2060–2065, <https://doi.org/10.1021/es803047m>.
- [51] SAE, Biolubricant Classification, 2021. [www.sae.org](http://www.sae.org). (Accessed 29 September 2021).
- [52] W.C.A. Carvalho, J.H.H. Luiz, R. Fernandez-Lafuente, D.B. Hirata, A.A. Mendes, Eco-friendly production of trimethylolpropane triesters from refined and used soybean cooking oils using an immobilized low-cost lipase (Eversa® Transform 2.0) as heterogeneous catalyst, *Biomass Bioenergy* 155 (2021), 106302, <https://doi.org/10.1016/j.biombioe.2021.106302>.