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Valorization of *Cynara Cardunculus* L. Oil as the Basis of a Biorefinery for Biodiesel and Biolubricant Production

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Abstract: The production of sustainable and biodegradable products, for energy or material use, is becoming important for local economies. Thus, biorefineries can play an important role in sustainable development at regional levels and therefore the search for feedstocks with multiple uses is vital. The goal of this research was to assess the implementation of *Cynara Cardunculus* L. oil as the basis of a biorefinery for biodiesel and biolubricant production, proposing the main steps for this purpose. The chemical reaction selected for biodiesel and biolubricant production was transesterification, using methanol and other more complex alcohols. The optimization of each step was carried out, assessing the yield by gas chromatography. Once the optimum conditions were selected, the main characteristics of the biofuel or biolubricant were measured, paying attention to viscosity and oxidative stability. As a result, *Cynara Cardunculus* L. oil could be a suitable feedstock for a biorefinery, as long as some antioxidants are added in final products, especially to increase its oxidative stability in biodiesel (whose value was 1.35 h). Concerning biolubricant production, the yields were acceptable (exceeding 92%) and the products showed variable viscosity values (from 8.6 to 18.85 cSt), implying a desirable diversification of production depending on demand.

Keywords: cardoon; transesterification; 2-ethyl-1-hexanol; 2,2-dimethyl-1,3-propanediol; viscosity; viscosity index; oxidative stability

1. Introduction

In the last years, bio-based lubricants (also known as biolubricants) have received a great attention as substitutes for mineral oil based lubricants. Biolubricants are considered environment friendly products since they are ecofriendly and non-toxic materials, in contrast to petrol-based lubricants which show inherent toxicity and they are non-biodegradable [1]. In general, two different kinds of fluids can be a starting point for the production of environmentally friendly lubricants. These are vegetable oils and synthetic lubricants. Before the development of synthetic lubricants, vegetable oils were used for many years; however, they usually showed poor low temperature behavior or unfavorable oxidation stability. Synthetic biolubricants appeared as a chance to improve vegetable oils lubricant properties and to maintain the environmental friendly nature. These synthetic oils are produced by chemical reaction of low molecular weight components to generate high molecular weight compounds. Nowadays, around 80% of the feedstocks used to produce synthetic lubricants are synthesized hydrocarbons (~50%–55%) and organic esters (~25%) [2]. The synthetic esters acquire most of the properties required for this type of products such as high viscosity index, low volatility, good lubricity and good solubility for fluid additives.

Synthetic esters have been successfully used in lubrication because of their low temperature flow ability and their clean high temperature operation. According to some authors, their nature offers

the possibility that 90% of all lubricants could be produced with biodegradable esters without losing technical performance [3–5]. The industrial exploitation of vegetable oils and fats for biolubricant production is based on the chemical modification of both the carboxyl and unsaturated groups present in fatty acids. One of the most common lubricant conformations is the linkage of an alcohol with the desired structure and the carboxyl group [5]. These alcohols can be either polyhydroxyalcohols such as trimethylolpropane, pentaerythritol or neopentyl glycol or monoalcohols with long carbon chain, such as 2-ethyl-1-hexanol, n-propanol and n-octanol. Biolubricants are usually produced, among other methods, by means of transesterification of fatty acid methyl esters (FAMEs, that is, biodiesel) obtained from vegetable oils with a superior alcohol [5,6].

Synthetic esters are broadly accepted base fluids in lubricants; however its use has been mainly hindered by their high prices [2]. Fatty acids from various sources exhibit many common features; then non-edible crops could be the main way to decrease the price of bio-lubricants.

Cynara Cardunculus L. (commonly known as cardoon) can be an example of this kind of crop (See Figure 1). It is a naturally occurring species, typical of the Mediterranean areas (where Extremadura region is included, for practically all its surface). This plant can be grown on nutrient-deficient land and it does not require irrigation, being a very resistant species, especially to extreme temperatures [7]. Its biological cycle takes place in autumn and winter, whereas it shows an inactive stage in summer. In addition, it is resistant to a wide range of soil pH (from 5 to 8.5) and soil salinity values of 10 dS/m, being a good crop to correct and recover soils used for other agricultural purposes, taking part in crop rotation [7,8].

Figure 1. Cardoon plant (*Cynara Cardunculus* L.). Photo by Capri23auto in Pixabay.

In Mediterranean countries such as Italy, some agronomic studies have been performed to determine the productivity of several species of this plant. The obtained results showed an acceptable cardoon production, ranging from 15 t·ha^{-1} to 30 t·ha^{-1} per year, for wild and domestic species [9,10]. Consequently, good biomass yields were obtained, including seed yields (10% of crop production) which could be another product for energy use through biodiesel production. Indeed, oil production from these seed (exceeding 25% yield) were similar to other closely related species, also proposed for oil production, being compatible with the exploitation of aerial biomass for energy production [11]. In the case of Spain, cardoon growing has been stable for decades, using 1350 hectares and producing 31,000 tons per year, with Andalusia region leading its production [12]. On the other hand, biomass production from *Cynara Cardunculus* L. could be used to obtain valuable compounds for pharmaceutical industry [13].

Thus, this kind of raw material (cardoon oil) and its way of use (transesterification to produce biodiesel and biolubricants) could fit the fundamentals of biorefineries, which are becoming a feasible alternative for energy and product manufacture derived from petrol. In that sense, a biorefinery could be defined as a sustainable processing of biomass into a wide range of bio-based products and bioenergy for the market [14]. It implies a network of facilities that integrates biomass conversion processes and equipment to obtain energy and bioproducts, which can be countless in the case of

biorefineries based on vegetable oils [15,16]. Consequently, the use of vegetable oils (such as cardoon oil) to produce biodiesel and other bioproducts could constitute a perfect example of a biorefinery, obtaining valuable by-products such as glycerol or re-using others like methanol [14]. Generally, a biorefinery should aim the following characteristics:

- Sustainability, using natural products (such as vegetable oils) or even some wastes with a difficult management (for instance, frying oils).
- Reuse of some of the by-products obtained during the process. For instance, in the case of biolubricant production, they can be used in the machineries of the biorefinery.
- Added-value by-products, depending on their degree of purity.
- High yields, in order to be as competitive and effective as other equivalent facilities used in oil industry.
- Contribution to a sustainable economic development of disadvantaged regions.

On the latter issue, Extremadura region could be a suitable area to implement biorefineries, mainly due to the following reasons:

- It is the fourth largest utilized agricultural area in Spain, with $2.5 \cdot 10^6$ hectares, implying almost 11% of the total utilized agricultural area in this country [17]. This way, the use of biomass and agricultural wastes to create value-added products could be extensive in a region with such a great agricultural tradition.
- Due to its variety of agricultural production, different kinds of biorefineries could be feasible in this region, depending on the raw material they are based on. This ensures a great diversification and adaptation to different markets, making the economic development of this region stable.
- However, Extremadura region has the fifteenth (out of seventeen) gross domestic product per capita, with 18,769 € (far below national average, 25,730 €) [18]. Thus, the implementation of biorefineries could be a good way to develop poor areas in a sustainable way.
- Finally, its privileged location in the Iberian Peninsula could make the commercialization of the products manufactured possible; as it is between important industrial areas such as Lisbon, Madrid or Seville (see Figure 2). Consequently, the production of biorefineries could have business goals at a regional, national and international level, which could make the dimensioning of biorefineries variable.

Figure 2. Main connections of cities from Extremadura (Badajoz, B; Cáceres, C; Mérida, M) with other cities in the Iberian Peninsula. Original map obtained on ©d-maps.com, accessed from https://d-maps.com/carte.php?num_car=2199&lang=es.

To sum up, Extremadura region, which is not highly industrialized compared to other areas in Spain, has enough potential to develop a sustainable economic growth based on green technologies, especially focused on the global use of raw materials, as in the case of biorefineries based on agriculture products.

On the basis of the above, the aim of this work was to consider the implementation of *Cynara Cardunculus* L. oil (that is, cardoon oil) as the basis of a biorefinery in order to produce biodiesel and biolubricants, among other products, through transesterification. The biolubricants were synthesized from fatty acid methyl esters obtained from cardoon oil and several alcohols, such as 2-ethyl-1-hexanol and 2,2-dimethyl-1,3-propanediol were used as superior alcohols. The main characteristics of the biodiesel produced, as well as the optimum biolubricant production depending on the kind of alcohol used, were obtained. Thus, the yield of the subsequent chemical reactions was measured by gas chromatography and the main properties of the biodiesel and biolubricants (especially viscosity and oxidative stability) were assessed. Finally, the global chemical route and a biorefinery based on the products that were more suitable were proposed.

2. Materials and Methods

First of all, a brief sum-up of the experimental design is introduced in Figure 3. In this figure, it can be observed the oil production through mechanical pressing, as well as biodiesel and biolubricant production through transesterification with several alcohols. Biolubricant production was optimized in temperature, alcohol/FAME (fatty acid methyl ester) ratio and catalyst concentration. Finally, a characterization of the biodiesel and the final biolubricants obtained was carried out, focusing on viscosity and viscosity index, oxidative stability, Fourier transform infrared (FTIR) or flash and combustion points, among other parameters. In the following sections all these steps will be explained thoroughly.

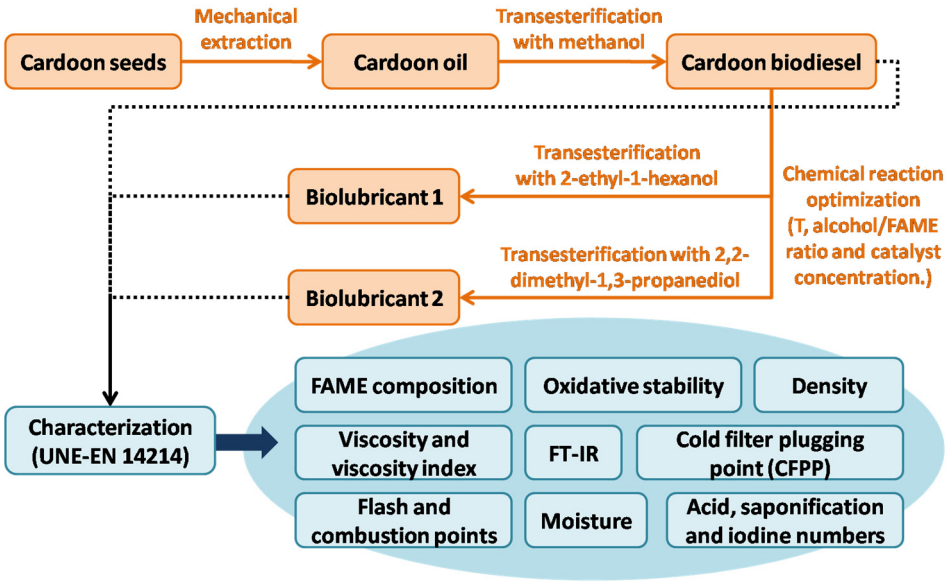


Figure 3. Experimental design.

2.1. Feedstock

Cynara cardunculus L. oil was provided by the Department of Non-Food Crops, from the research center "La Orden" (from Cicytex, Centro de Investigaciones Científicas y Tecnológicas de Extremadura, located in Guadajira, Badajoz, Spain). Cardoon seeds were collected in 2019 season and the oil was obtained by means of a mechanical press. Afterwards, the oil was filtered and stored in opaque containers at room temperature. The acidity index of the oil was checked to ensure a low value

(below 2%) for the subsequent transesterification process, by using an acid-base titration with sodium hydroxide [19]. Thus, the oil was subjected to two successive transesterification reactions, a first one to produce fatty acid methyl esters (FAMEs, biodiesel) and a second one to produce biolubricants.

2.2. Biodiesel Production

In order to prepare the fatty acid methyl esters, optimum conditions previously studied were selected [20,21]. Thus, the methanolysis of this oil with a methanol: oil ratio of 5:1 and a catalyst (CH_3ONa) concentration of 1 wt % at 60 °C during 1 h was carried out. Specifically, 500 mL of *Cynara cardunculus* L. oil and 5 g of sodium methoxide (95%) were dissolved in 81 g of methanol (99.5%) and placed in a 1000 mL glass reactor with a magnetic stirrer (stirring rate: 300 rpm) and a condensation system (to avoid methanol leakage). The reactor temperature was maintained at 60 °C and the reaction was carried out for 60 min. The reaction mixture was cooled to room temperature and the resulting two layers were separated. The upper layer (methyl esters) was washed with acidified distilled water to eliminate the rests of catalyst, methanol and glycerol. Next, once the washing water had a pH around 7 after its mixture with biodiesel, the biodiesel phase was dried at 110 °C, storing it in opaque bottles for further characterization (fatty acid methyl ester profile, density, viscosity, moisture, acid number, iodine value, flash and combustion points, cold filter plugging point and oxidative stability, which will be explained in the following sections) and biolubricant production.

2.3. Biolubricant Production

Then, the methyl esters were transesterified with two different alcohols: 2-ethyl-1-hexanol (98%, Sigma-Aldrich, St. Louis, MO, USA) and 2,2-dimethyl-1,3-propanediol (99%, Sigma-Aldrich). For this process, 150 mL of methyl esters were placed into a spherical glass reactor of 500 mL with the necessary amounts of alcohol and catalyst. The experimental set-up to the production of the bio-lubricant consisted of a spherical glass reactor (500 mL) in a silicone bath, with heating, stirring and temperature control system and a sampling outlet. A condensation system and a Dean-Stark receiver were also used to collect the methanol released during the reaction. After the reaction, the surplus of alcohol was removed by vacuum distillation or filtering, depending on the nature of the alcohol.

Reaction Monitoring

The progress of the reaction was determined by the measurement of the condensed methanol and by chromatographic analysis of the samples taken regularly. Thus, the conversion of FAMEs to produce biolubricants was obtained by the decrease in FAMEs for each reaction (see Equation (1)).

$$Conversion\ (\%) = \frac{FAME_0 - FAME_F}{FAME_0} \times 100, \quad (1)$$

where $FAME_0$ is the FAME content at the beginning of the reaction (biodiesel composition) and $FAME_F$ is the content at the end of the reaction.

The decrease in methyl ester content was determined in a VARIAN 3900 gas chromatograph coupled to a flame ionization detector. 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. Methyl heptadecanoate was selected as the internal standard, with heptane as a solvent. Thus, Figure 4 shows an example of a resulting chromatogram, in this case for cardoon fatty acid methyl esters (FAMEs), where an acceptable peak resolution can be observed.

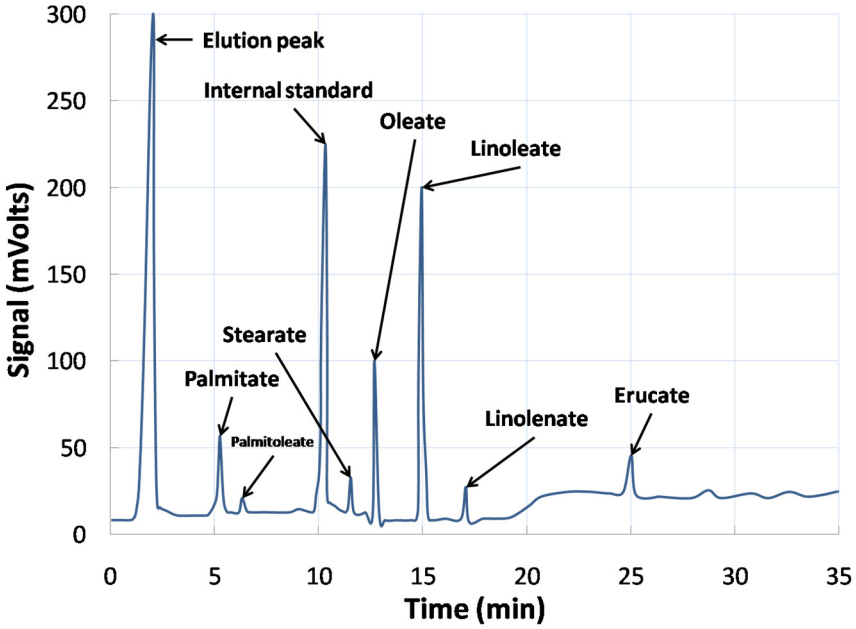


Figure 4. Chromatogram with the main fatty acid methyl esters found in cardoon biodiesel.

Consequently, FAME quantification, expressed in % FAME, can be calculated as follows (Equation (2)):

$$\frac{m_i}{m_{IS}} = g_i \times \frac{A_i}{A_{IS}}, \quad (2)$$

where m_i is the weight of each FAME (in grams), m_{IS} is the weight of the internal standard (in grams), A_i is the analytical area of each FAME standard, A_{IS} is the analytical area of the internal standard and g_i is the slope of the resulting line for each calibration line. Once the mass of each standard is obtained through Equation (2), it can be referred in percentage to the total weight of the biodiesel sample used for chromatography, as follows (Equation (3)):

$$\%FAME_i = \frac{m_i}{m_b} \times 100, \quad (3)$$

where m_i is the weight of each FAME (in grams) and m_b is the total weight of the biodiesel sample used.

2.4. Biolubricant Production Optimization

In order to obtain the better chemical conditions to obtain a biolubricant with a high yield and purity, the main parameters of the chemical reaction (like the kind of catalyst, catalyst concentration, temperature, alcohol/FAME ratio and the kind of alcohol) were assessed, as explained in the following subsections.

2.4.1. Influence of the Kind of Catalyst

Three catalysts were tested in order to check the efficiency of biolubricant production—an organic acid catalyst, p-toluenesulfonic acid (98.5%, Sigma-Aldrich) and two basic catalysts, titanium (IV) isopropoxide (99.8%, Sigma-Aldrich) and potassium methoxide (97%, Merck, Kenilworth, NJ, USA).

2.4.2. Influence of Catalyst Concentration

The concentration of catalyst with the best yield obtained in the previous section was tested. Its concentration was based on the total mass of the reaction mixture, ranging from 0.1 to 2% *w*/*w*, depending on the case.

2.4.3. Influence of Temperature

The reaction temperature ranged between 100 and 160 °C, depending on the kind of alcohol used for the second transesterification, trying not to exceed these temperature values, as the compounds obtained are usually tend to auto-oxidation at high temperatures.

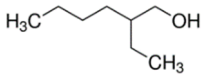
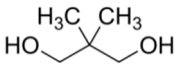
2.4.4. Influence of Alcohol/FAME Ratio

In order to assess the effect of alcohol/FAME ratio, different values were selected, ranging from 0.5:1 to 2:1.

2.4.5. Influence of the Kind of Alcohol

In order to compare the different properties of biolubricants based on cardoon oil, two different alcohols were used in this experience: 2-ethyl-1-hexanol and 2,2-dimethyl-1,3-propanediol. The main characteristics of these reagents are included in Table 1:

Table 1. Main characteristics of the alcohols used for biolubricant production from cardoon fatty acid methyl esters (FAMEs).

Alcohol Used	2-ethyl-1-hexanol	2,2-dimethyl-1,3-propanediol
Molecular structure		
Melting point (°C)	−76	128
Boiling point (°C)	183–186	210
Auto-ignition temperature (°C)	288	399
Density at 25 °C (g·mL^{-1})	0.833	1.042
Vapor pressure (mmHg at 20 °C)	0.2	<0.8

According to these data, there were clear differences between both alcohols, which made the transesterification reaction conditions different for each reagent. Thus, for the transesterification with 2-ethyl-1-hexanol, all the chemical reaction was carried out at atmospheric pressure, removing the surplus alcohol by vacuum, whereas for 2,2-dimethyl-1,3-propanediol, a vacuum at 400 mmHg was applied during the chemical reaction, filtering the surplus alcohol.

2.5. Biolubricant Characterization

2.5.1. General Characterization

Once the biolubricant was obtained under the most suitable conditions and purified, it was characterized according to the standard(UNE-EN 14214) [22]. This way, multiple analyses were done. Density was measured by using a 5-mL pycnometer (Pobel, Madrid, Spain) and a densimeter (Proton 800–900, Gabsystem, Barcelona, Spain) [23]. For cold filter plugging point (CFPP), the EN 116 norm was used [24]. For flash and combustion points, the experiments were done according to the Cleveland open-cup method, included in UNE 51-023-90 standard [25]. Concerning moisture, a moisture meter (Metrohm 870 trinitro plus) was used, following the Karl-Fischer method (UNE-EN ISO 12937:2000) [26]. The saponification number was determined according to the UNE-EN 55012 standard. The Acid number is measured by using the UNE-EN 12634:1999 standard [19]. For Iodine number determination, the UNE-EN 14111:2003 standard was used [27].

2.5.2. Viscosity and Viscosity Index

Viscosity was determined according to the ISO 3104:1994 standard, by using an Ostwald viscometer [28]. Thus, viscosity values at different temperatures (40 and 100 °C) were obtained. The viscosimeter, with the suitable amount of sample, was kept in a silicone gel bath at the corresponding

temperature (by using a heater) for 25 min in order to stabilize the final measurement. In the case of viscosity index, the ASTM D2270 standard was followed, calculating it with the corresponding viscosity values at 40 and 100 °C [29].

2.5.3. Oxidative Stability

For biodiesel and biolubricant samples, oxidative stability was obtained by using the Rancimat method [21,30]. This way, a certain mass of the sample (3 g) was placed in a test tube, heating it at 110 °C and passing an air flow of 10 L·h^{-1}. The evolved stream of air, after oxidizing the biodiesel or biolubricant sample, bubbled 50 mL of distilled water, increasing its conductivity due to the dilution of the by-products generated during oxidation. This value was measured by a conductivity meter. The induction point, an indicator of oxidative stability, was the time when conductivity abruptly increased.

2.5.4. FT-IR Analysis

In the case of the biolubricant produced with 2,2-dimethyl-1,3-propanediol, its IR spectrum was obtained in order to identify the functional groups of its molecular structure. The FT-IR analysis was carried out by using a Perkin-Elmer device, in the range of 4000–650 cm^{-1}. The results were processed with computer software.

3. Results and Discussion

3.1. Biodiesel from Cynara Cardunculus

The main characteristics of the biodiesel obtained from *Cynara Cardunculus* L. oil are shown in Table 2. As it can be inferred from this table, comparing with the UNE-EN 14214 standard [22], the biodiesel synthesized complied with almost all the requirements, which makes this biofuel practically suitable for commercialization. Especially, its flash and combustion points were extremely high, which would imply a safety use during shipping and storage. However, the oxidative stability of cardoon biodiesel was low, not complying with the lower limit (established at 8 h). This result is in accordance with other biodiesel samples from vegetable oils, which usually present very low induction points, not complying with the standard [31].

Table 2. Main characteristics of biodiesel from *Cynara Cardunculus* L. and comparison with the UNE-EN 14214 standard.

Characteristic	Cardoon Biodiesel	UNE-EN 14214
Fatty Acid Methyl Ester, %	96.92	96.5 *
Density at 15 °C, mg·mL^{-1}	879	860–900
Viscosity at 40 °C, cSt	4.179	3.5–5
Moisture, %	0.03	0.05 **
Acid number (mg KOH·g^{-1})	0.2048	0.5 **
Iodine value (gI_2·100 g^{-1})	118.2	120 **
Flash point, °C	178	120 *
Combustion point, °C	198	–
Cold filter plugging point, °C	−1	−20–+5
Oxidative stability [1], h	1.35	8 *

[1] Rancimat method * Lower limit ** Upper limit.

Figure 5 shows the FAME profile of cardoon biodiesel. This way, the influence of the fatty acid methyl ester profile on the characteristics of biodiesel was widely studied by other authors, paying attention to some parameters such as viscosity, iodine value or oxidative stability. For the latter, the presence of high methyl linoleate/methyl oleate ratio plays an important role in the final stability of biofuels [31–33].

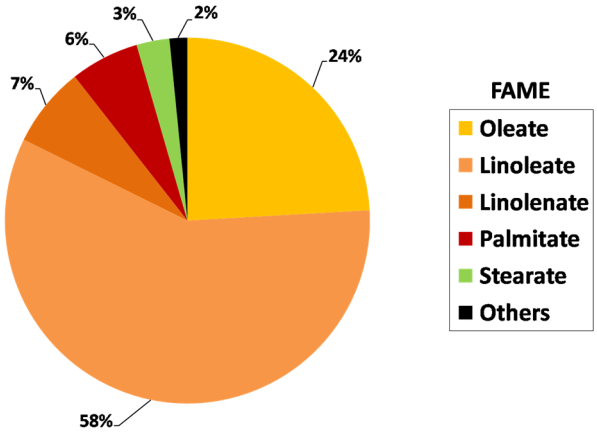


Figure 5. Fatty acid methyl ester of cardoon biodiesel.

This way, higher levels of methyl linoleate, which is a more unstable ester due to the presence of a conjugated double bound in its molecular structure, imply a lower oxidative stability in biodiesel. On the other hand, higher levels of methyl oleate are related to better oxidative stability values, as it is more stable due to the fact that it is a mono-unsaturated ester. As a consequence, in this case, the high proportion of methyl linoleate and the low level of methyl oleate (around 60 and 25%, respectively) could explain the poor oxidative stability of cardoon biodiesel. In order to improve the oxidative stability of biodiesel, antioxidants are usually added to the final product [31,34]. Thus, tert-butylhydroquinone (TBHQ) was proved to be an effective additive for this purpose, improving the oxidative stability at low concentrations of this antioxidant [21,31,35]. Figure 6 shows the effect of TBHQ addition on the oxidative stability of cardoon biodiesel. The adjustment obtained was acceptable, not reaching the saturation effect where higher amounts of antioxidant are less effective or even counterproductive. In this case, a concentration of 750 ppm of TBHQ was required to meet the lower limit of the standard (oxidative stability = 8 h), which is a reasonable amount of antioxidant compared to the concentrations and results obtained in the literature, ranging from 100 to around 1000 ppm of TBHQ in biodiesel to exceed this lower limit [36–38].

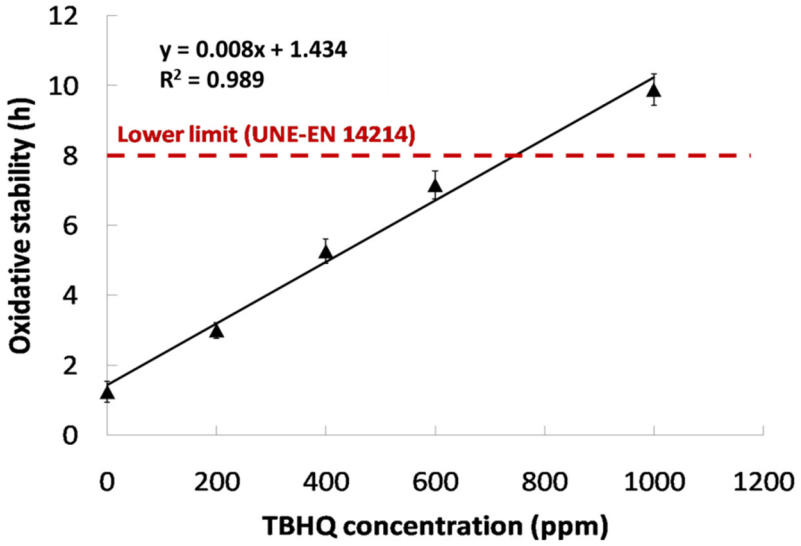


Figure 6. Effect of tert-butylhydroquinone (TBHQ) addition on oxidative stability and concentration optimization.

As a consequence, a high-quality product was obtained, which will imply the starting point for biolubricant production, contributing to the diversification of the biorefinery based on cardoon.

3.2. Biolubricant Production

Once the FAMEs were obtained, the production of biolubricants was carried out, by using two different alcohols as reagents: 2-ethyl-1-hexanol and 2,2-dimethyl-1,3-propanediol. For each kind of alcohol, different parameters were optimized, as explained in the following sections.

3.2.1. Effect of the Kind of Catalyst and Catalyst Concentration

Three catalysts were tested for the transesterification reaction of cardoon FAMEs with 2-ethyl-1-hexanol (HE). All of them showed high activity (Figure 7a) and the maximum reaction rate was achieved with potassium methoxide as a catalyst. However, the product obtained from this reaction showed very high viscosity. It was probably because of the formation of soap or solid particles which can precipitate in the reaction medium leading to a final product with semisolid characteristics and high viscosity. Therefore, Ti(IV) isopropoxide was considered as the most suitable catalyst and the rest of experiments were carried out with this catalyst. This solid is widely used in the industry because it is very energetic. The acid catalysis demonstrated a bit worse capacity to promote the reaction, although it was also effective. This type of catalysts is usually preferred for esterification reactions or when the oil has high free fatty acid content.

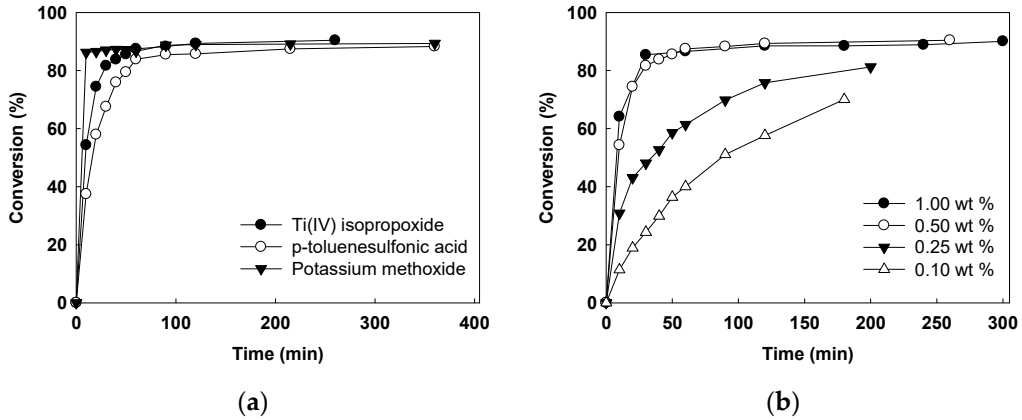


Figure 7. Effect of: (**a**) type of catalyst and (**b**) catalyst concentration. Reaction conditions: HE:ME molar ratio, 2:1; 120 °C, (**a**) 0.5% catalyst and (**b**) Ti(IV) isopropoxide as a catalyst.

The influence of the concentration of Ti(IV) isopropoxide was also studied and the catalyst concentration was varied from 0.1 to 1.0 wt %. The obtained results are shown in Figure 7b. The reaction rate was improved by the increase of catalyst concentration up to 0.5 wt %. The highest tested concentrations were 0.5 and 1.0 wt % and both showed the same results. These behaviors where the results are not enhanced with higher catalyst concentrations are usually observed for the transesterification reaction, even when methanol is used as alcohol. In addition, the conversion profiles for all reactions are typical of an equilibrium reaction such as the transesterification.

Concerning the reaction with 2,2-dimethyl-1,3-propanediol (see Figure 8), a similar behavior was observed, with a catalyst concentration of 1.5 and 2% reaching high yields, close to 80%. Thus, higher amount of Ti(IV) isopropoxide was required to reach high yields at short reaction times, compared to the previous transesterification reaction explained in Figure 5. During the first 30 min, the conversion reached an asymptotic trend, not improving the yield of the reaction once the concentration increased from 1.5 to 2.0%. That was the reason why 1.5% was selected as the optimum concentration for biolubricant production with 2,2-dimethyl-1,3-propanediol.

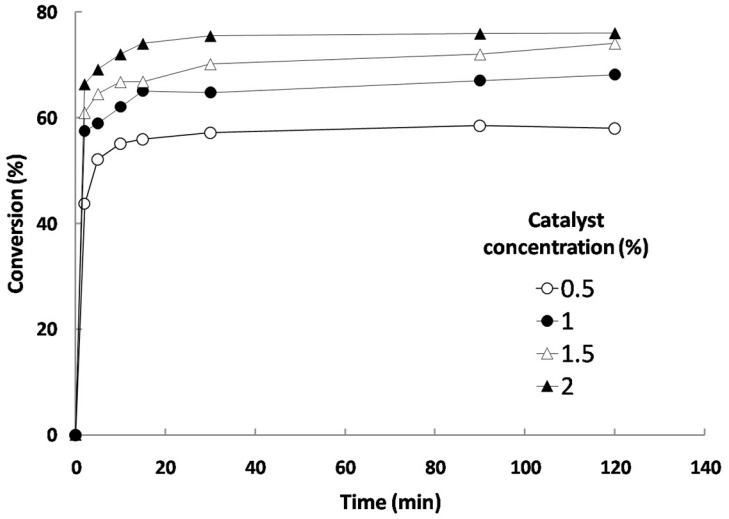


Figure 8. Effect of catalyst concentration on biolubricant production from FAMEs with 2,2-dimethyl-1,3-propanediol. Reaction conditions: Molar ratio, 1:1; 100 °C; Ti(IV) isopropoxide as a catalyst.

3.2.2. Effect of Temperature

The temperature of reaction varied from 120 to 170 °C with HE:ME molar ratio of 2:1 and from 130 to 160 °C with HE:ME molar ratio of 1:1. Catalyst concentration was 1 wt % for both reactions. The results are showed in Figure 9. Temperature had a positive effect on the equilibrium conversion of ME to esters of HE and on the necessary time to achieve this equilibrium. When the highest temperatures were used, the time to reach the final conversion was less than 30 min. The product of the transesterification reaction of ME with HE were the lubricant and methanol. Under the used conditions, the produced methanol was continuously removed by distillation because of all reactions were carried out above the methanol boiling point. In this way, the forward reaction of the equilibrium was promoted to increase the final conversion to the esters of HE. Similar results were seen when ME from rapeseed oil were used to obtain a bio-lubricant via reaction with HE. In this previous work an enzyme was used as catalyst, so the reaction temperatures were lower; nevertheless, the conversion profiles showed the same trend when temperature was increased.

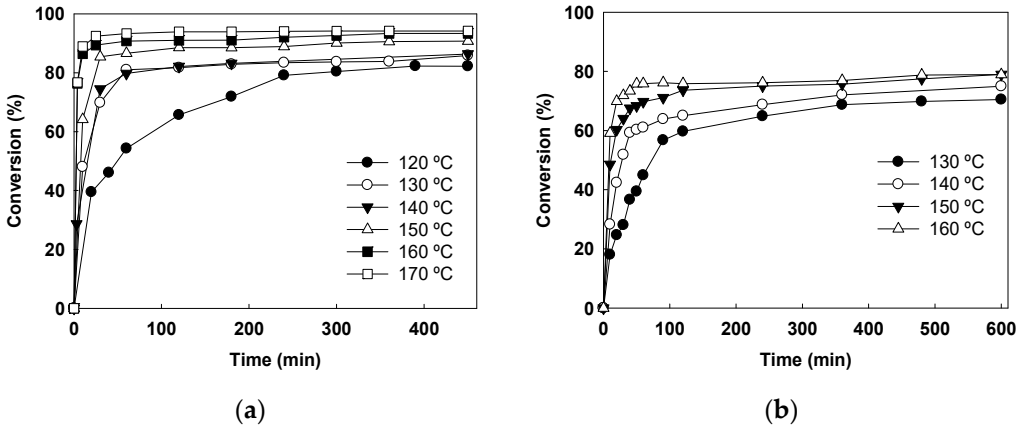


Figure 9. Effect of temperature. Reaction conditions: 1% Ti(IV) isopropoxide and HE:ME molar ratio of (**a**) 2:1 and (**b**) 1:1.

On the other hand, the final conversion was strongly influenced by HE:ME molar ratio. As seen in Figure 9b, when the HE:ME ratio was 1:1, the conversion was always lower than 80%. However,

with higher concentration of alcohol, the conversion reached values close to 95%. The selection of appropriate amount of initial reagents is one of the most important factors for reaction process optimization. Below the effect of molar ratio of HE:ME was analyzed.

In the case of the transesterification with 2,2-dimethyl-1,3-propanediol, as it can be seen in Figure 10, again, a similar behavior compared to Figure 7 was observed. Acceptable yields were obtained for the highest temperatures studied, exceeding 90% for 130 and 140 °C. Thus, a temperature of 130 °C was selected as the optimum value, as a balance between high yield (at high temperature) and an acceptable oxidative stability of the final product (which gets worse at higher temperatures).

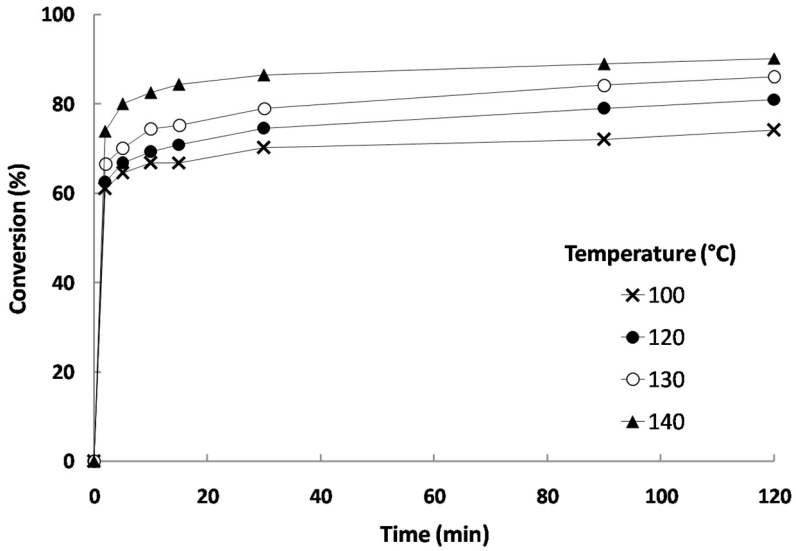


Figure 10. Effect of temperature on biolubricant production from FAMEs and 2,2-dimethyl-1,3-propanediol. Reaction conditions: 1.5% Ti(IV) isopropoxide and molar ratio of 1:1.

3.2.3. Effect of Alcohol/FAME Ratio

The formation of 2-ethyl-1-hexanol esters was followed for the ratios 1:1, 2:1 and 3:1 of HE:ME (Figure 11). The HE:ME molar ratio showed a positive effect in the studied range. When a molar ratio of 1:1 was used, the equilibrium conversion was less than 80%; nevertheless, when the amount of alcohol was increased up to 3:1 molar ratio of HE:ME, the conversion was total, close to 100%. In other cases, large excess of alcohol slightly slowed down the initial reaction rate. The activity of the enzymes used as catalysts could have been inhibited by the presence of large excess of alcohol. The reaction between methyl esters and 2-ethyl-1-hexanol with Ti(IV) isopropoxide as catalyst was not hindered by the presence of excess of alcohol.

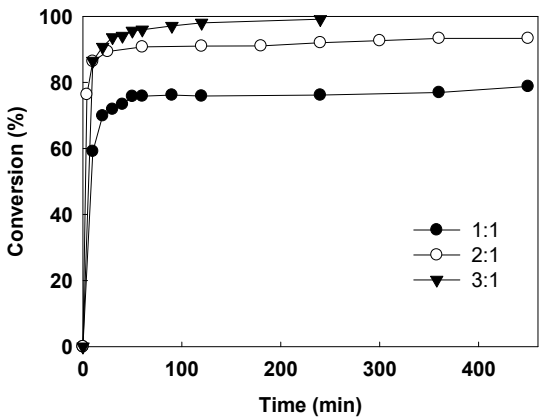


Figure 11. Effect of alcohol molar ratio. Reaction conditions: 1% Ti(IV) isopropoxide and 160 °C.

When HE:ME molar ratio was increased, the final conversion increased too. Then higher viscosity values were observed for greater HE esters content. This property increased with higher concentrations of HE esters because its molecular weight also increased.

Concerning the use of 2,2-dimethyl-1,3-propanediol, the study of the effect of the alcohol/FAME molar ratio was not possible to be carried out, as the addition of alcohol to establish a molar ratio of 2:1 implied the crystallization of the surplus alcohol, which occlude the biolubricant produced, being difficult to separate both compounds. Thus, neither the yield nor the characteristics of the product obtained were possible to be studied.

3.3. Characteristics of the Final Biolubricant and Effect of the Kind of Alcohol Used

After the chemical reaction optimization, the two biolubricants obtained showed the characteristics observed in Table 3. Both biolubricants showed high flash and combustion points, which is a desirable effect, especially for storage [5,39,40]. On the other hand, high yields were obtained in both cases, exceeding 90%, which assures a relatively high purity product, with predictable characteristics. Moreover, the viscosity index obtained was high, which implies lower changes in viscosity with temperature, especially for the biolubricant produced with 2-ethyl-1-hexanol. This is a typical result of biolubricants, which usually offer higher viscosity index values than their equivalent mineral oils [40]. Finally and due to the properties of the raw material used (see previous sections), the oxidative stability of the samples were low, not exceeding 3 h in both cases. As a result, the use of additives or antioxidants is advisable. According to the kind of alcohol used, clear differences were observed between the two samples obtained in this study, especially concerning viscosity. This way, the viscosity value for the biolubricant produced with 2,2-dimethyl-1,3-propanediol doubled the value obtained for the biolubricant produced with 2-ethyl-1-hexanol. This could be possibly due to the more complex molecule structure (as it will be seen in the following section) obtained for the first case, including more functional groups (like methyl) which could contribute to increase the molecular interactions and therefore its viscosity. As a consequence, the kind of alcohol used is vital to obtain a biolubricant for a certain use, which is essentially determined by its viscosity.

Table 3. Chemical conditions and properties of the biolubricants obtained under optimum reaction conditions.

Alcohol Used [1]	**2-ethyl-1-hexanol**	**2,2-dimethyl-1,3-propanediol**
Temperature, °C	160	130
Molar ratio	3:1	1:1
Catalyst concentration, %	1	1.5
Conversion [2], %	99.1	92.76
Viscosity at 40 °C, cSt	8.6	18.85
Viscosity at 100 °C, cSt	3.1	4.29
Viscosity index	276	138
Acid value, mg $_{KOH}$·g^{-1}	0.7	0.3
Flash point, °C	178	193
Combustion point, °C	188	204
Oxidative stability, min	88	163

[1] For the second transesterification. [2] Obtained by FAME decrease.

According to these data, the biolubricants obtained from cardoon biodiesel through transesterification with 2-ethyl-1-hexanol and 2,2-dimethyl-1,3-propanediol can be used as their equivalent ISO VG 10 and ISO VG 22 lubricants, respectively. Consequently and due to the relative low viscosity of both biolubricants, the former can be used in systems with high speed and precision, for lubrication of pneumatic tools in textile industry, whereas the latter can be used as an hydraulic oil. In order to assess the changes in the molecular structure of the biolubricant obtained by using

2,2-dimethyl-1,3-propanediol, the IR spectrum of biodiesel and the corresponding biolubricant was obtained (see Figure 10).

The spectrum of cardoon biodiesel (Figure 12a) was similar to other profiles obtained in the literature with all the characteristic bands observed for fatty acid methyl esters [37]. Thus, the typical absorption bands for the essential ester carbonyl functional at around 1760 cm^{-1}, for CH_3 asymmetric bending at 1425 cm^{-1} and the O-CH_3 stretching band at 1100–1300 cm^{-1}, among others, were found [41]. If this spectrum is compared to the one related to the biolubricant obtained with 2,2-dimethyl-1,3-propanediol (Figure 12b), two main differences can be observed, concerning the C-O band corresponding to esters at 1100–1400 cm^{-1}, where two bands can be observed in both cases. First, in the case of the biolubricant, a more prominent peak was found at 1380 cm^{-1}. Second, the decrease in the peak located at 1060 cm^{-1} which could imply the replacement of the methyl group by a more complex functional group, with the presence of a methylene group. The absence of the characteristic band of alcohols at 3200–3400 cm^{-1} suggest a possible polymerization of the FAMEs with 2,2-dimethyl-1,3-propanediol, reacting the two hydroxyl groups of the superior alcohol (see Table 1, where the molecular structure is shown).

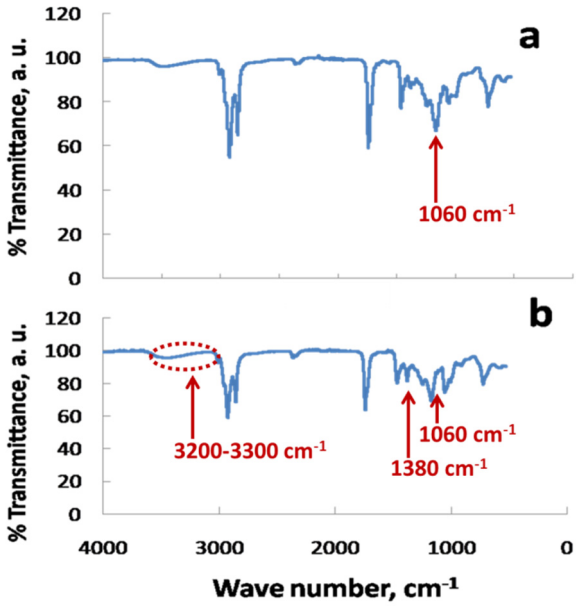


Figure 12. IR spectrum for (**a**) cardoon biodiesel and (**b**) the biolubricant obtained with 2,2-dimethyl-1,3-propanediol.

3.4. Chemical Route and Biorefinery Proposal

To sum up, the chemical route of the global process and a proposal for a biorefinery based on cardoon is shown in Figures 13 and 14, respectively.

From Figure 13, it can be inferred the following:

- Biodiesel and two different biolubricants were obtained by the same chemical reaction, that is, transesterification.
- As it will be explained in Figure 14, many by-products are obtained, which are valuable depending on their degree of purity.
- The main by-product obtained in the second transesterification (that is, methanol) can be reused for the first transesterification.
- The different molecular structure can explain the differences in the properties of these biolubricants, especially in the case of viscosity (see Table 3).

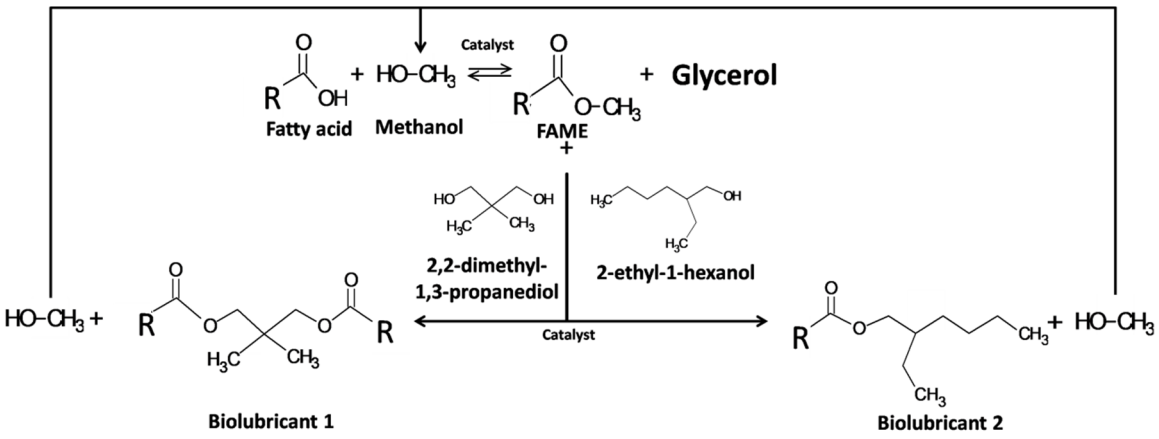


Figure 13. Possible chemical routes carried out in this experience to obtain two different kinds of biolubricants from cardoon through transesterification.

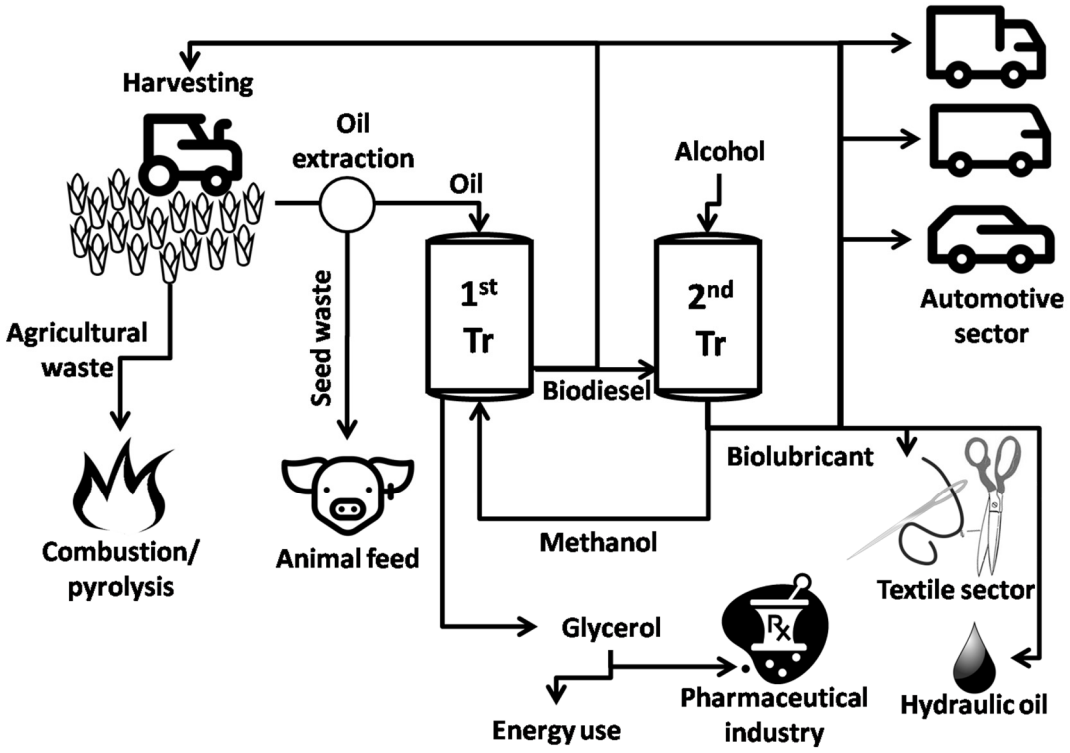


Figure 14. Biorefinery based on cardoon, where 1stTr and 2ndTr are first and second transesterification, respectively. Icons provided by Ilham Albab, Ionescu Georgiana Lavinia and Anthony Ledoux (iconfinder).

According to these figures, the following steps can be found:

- The first step after harvest was oil extraction, where two main products were obtained: On one hand, the oil which is used as the raw material for biodiesel and biolubricant production; on the other hand, an interesting by-product with a great source of vegetable proteins could be used to feed farm animals.
- Afterwards, the first transesterification to obtain fatty acid methyl esters was carried out, by adding methanol and catalyst. This way, biodiesel was produced, which is one of the main products of this biorefinery. In this step, another interesting by-product was obtained, that is, glycerol (which can be more or less valuable depending on its degree of purity, for many uses, such as energy or pharmaceutical purposes [42]).

- Then, the second transesterification of fatty acid methyl esters with superior alcohols was carried out, in order to obtain biolubricants. Thus, depending on the kind of alcohol, two different biolubricants were obtained, devoted to several industrial sectors. In addition, methanol is produced as a by-product, which can be re-used in the first transesterification (which is one of the main characteristics of biorefineries: the possibility of re-using different by-products to make the process more sustainable).
- Thus, multiple value-added products (especially biodiesel and biolubricants) were obtained, which can be directly distributed and commercialized or re-used.
- Consequently, the production of biodiesel and biolubricants can be exploited by the own biorefinery, in order to fuel its machinery (such as tractors for harvesting) or to carry out maintenance tasks (biolubricant use in this kind of facilities).
- However and due to the low oxidative stability of the raw material, it was necessary to add antioxidants to both biodiesel and biolubricants, especially in order to keep their properties during storage.

4. Conclusions

The major findings of this research were:

- Cardoon can be a suitable starting point for the implementation of a biorefinery for biodiesel and biolubricant production. Thus, the biorefinery proposed can be easily implemented, as it requires two similar steps (that is, two successive transesterification reactions of the oil or FAME with different alcohols), which simplifies the facilities required for this purpose.
- Concerning the first transesterification, where biodiesel is produced, the quality of this biofuel was acceptable, requiring the use of antioxidants to improve its oxidative stability due to the high content of methyl linoleate.
- Regarding the second transesterification, where biolubricants are produced, high yields of them were obtained, which makes their production feasible at reasonable conditions (including temperature and catalyst concentration). Also, there was a wide range of properties covered by these biolubricants, especially for viscosity, whose values were clearly different depending on the alcohol used for biolubricant production. Consequently, their use can be diverse. Moreover, the low acid number and the high flash and combustion points make these products suitable for storage and shipping.
- The main reaction conditions were studied and their effect on ester conversion was analyzed. Ti(IV) isopropoxide showed the most appropriated characteristics to be used as catalyst in this process. Catalyst concentration, temperature and HE:ME molar ratio showed positive effects on the conversion of the reaction. In the case of biolubricant production with 2-ethyl-1-hexanol, the total conversion was obtained with 1% wt Ti(IV) isopropoxide, 3:1 molar ratio and 160 °C. For the biolubricant production with 2,2-dimethyl-1,3-propanediol, the optimum chemical conditions were: 1.5% wt Ti(IV) isopropoxide, 1:1 molar ratio and 130 °C.
- The characteristics of the raw material, especially the fatty acid profile of vegetable oils, played an important role on the performance of the final products, including biodiesel and biolubricants, especially concerning oxidative stability.
- The wide variety of products obtained, including some intermediate products such as biodiesel, glycerol and methanol, makes the diversification of this kind of industry easier, varying the production depending on the specific demand. Moreover, most of these products can be re-used in the same biorefinery.
- For further studies, the use of natural antioxidants or genetically modified raw materials, when required, should be taken into account, in order to make the process more sustainable.

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