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Cardoon biolubricant through double transesterification: Assessment of its oxidative, thermal and storage stability

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ABSTRACT

Biolubricants could be a suitable replacement for industrial lubricants, due to their good performance and environmental-friendly quality, showing better flash and combustion points. However, depending on the raw material, the quality of biolubricants can vary, especially concerning oxidative and storage stability. The aim of this research work was to assess the stability of cardoon biolubricant, paying attention to oxidation and thermal and storage stability (by using the Rancimat method, thermogravimetry and viscosity during storage, respectively). The high linoleic acid content in cardoon oil (exceeding 25 %) could influence the low oxidative stability of cardoon biolubricant (3 h), implying changes in quality parameters during storage (viscosity increased above 15 % and viscosity index decreased about 23 %). Thus, the use of antioxidants is advisable to keep its properties over time.

1. Introduction

The use of sustainable products is becoming important. Indeed, many governments and international agencies are promoting the use of biomaterials as alternatives for their equivalent petroleum products. Thus, the implementation of biorefineries could meet with this policy, as it could help developing countries or areas for a sustainable economic growth, by using clean energy through innovation and avoiding water, air and land pollution.

Biorefineries based on vegetable oils could be a feasible way to implement environmentally-friendly industries. The production of biodiesel, biolubricants or glycerol is highly related to this concept [1], mainly through transesterification of fatty acids. Many products and by-products are obtained from local or resistant crops like cardoon (*Cynara Cardunculus*), which could be valorized in the same process depending on the needs. This crop is typical of the Mediterranean areas, growing on nutrient-deficient lands (with pH ranging from 5 to 8.5) and being resistant to extreme temperatures and high soil salinity values (up to 10 $dS \cdot m^{-1}$) [2].

One of the main drawbacks related to biodiesel or biolubricants is their low oxidative stability, which provokes quality changes during storage (because of temperature, exposure to air or light, among others), such as viscosity or acidity increase. The former is due to the formation of long chain saturated compounds and polymers, whereas the latter is due to hydrolysis of fatty esters to free fatty acids, as well as organic acid and aldehyde generation [3,4]. Studies about oxidative, thermal and storage stability are needed for this kind of products, especially for biolubricants, which might present different characteristics depending on the raw material or the chemical reaction employed. To the best of our knowledge, studies about cardoon biolubricant behavior during storage have not been carried out.

2. Materials and methods

2.1. Biolubricant production and characterization

The biolubricant was produced through a double transesterification with cardoon oil, provided by CICYTEX (Centro de Investigaciones Científicas y Tecnológicas de Extremadura). The best chemical conditions to produce the biolubricant were studied elsewhere [5] and included in Table 1.

Two steps were carried out to obtain cardoon biolubricant. First, biodiesel (fatty acid methyl esters, FAMEs) is produced from cardoon oil (fatty acids) through transesterification with methanol. After the purification process (glycerol removal, washing and drying), cardoon biodiesel reacted with 2–2-dimethyl-1,3-propanediol to obtain biolubricant (fatty acid esters). For biodiesel characterization, FAME profile was obtained through gas chromatography, and oxidative stability was

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Table 1
Chemical conditions for cardoon biodiesel and biolubricant production.

1st transesterification (biodiesel production)	Alcohol/oil ratio[1]	5:1
	Catalyst concentration[2], %	1
	Reaction temperature, °C	60
	Reaction time, min	60
2nd transesterification (biolubricant production)	Alcohol/biodiesel ratio[3]	1:1
	Catalyst concentration[4], %	1.5
	Reaction temperature, °C	130
	Reaction time, min	120

The alcohols used were [1]methanol and [3]2,2-dimethyl-1,3-propanediol. The catalysts used were [2]Sodium methylate and [4]Ti(IV)isopropoxide.

carried out by using the Rancimat method. Viscosity index was calculated from the viscosity values of biolubricant at 40 and 100°C, and acid number was obtained as explained elsewhere [6].

Thermal stability tests were carried out through thermogravimetry, by adding 5 mg of biolubricant and heating at 10°C·min^{-1} in air and nitrogen flows of 100 ml·min^{-1}.

2.2. Storage

The biolubricant obtained in previous stages was stored in opaque containers at room temperature (average temperature of 20°C). Thus, acid number, viscosity and viscosity index where determined at the beginning and after 6 and 12 months of storage. These experiments were done in triplicate, showing the average and standard deviation.

Fig. 1 shows the main steps included in this research.

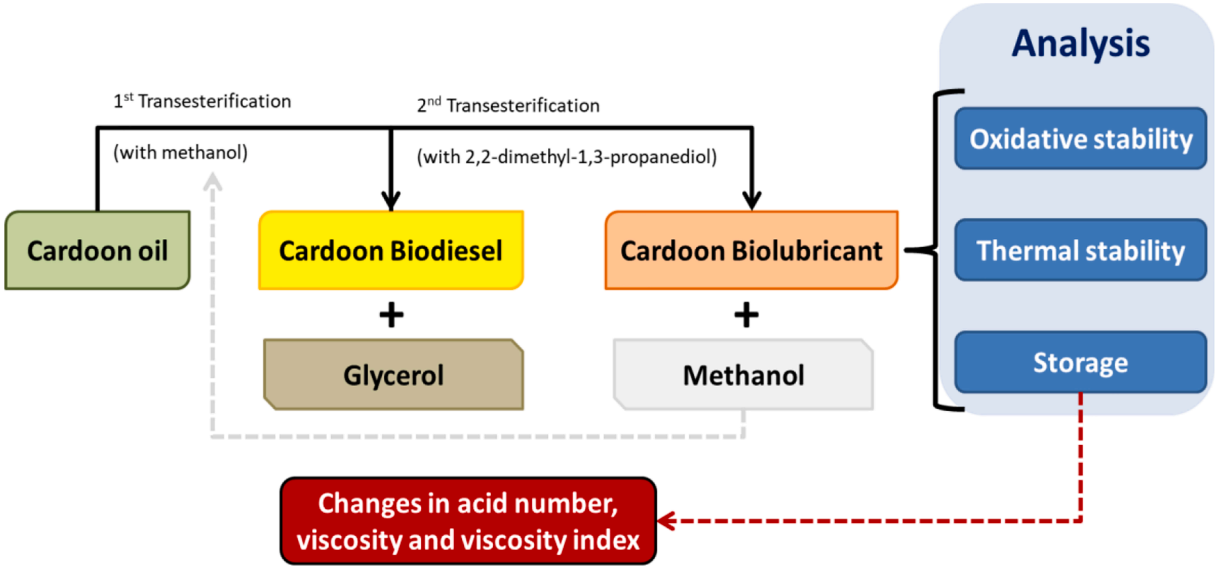

Fig. 1. Experimental design.

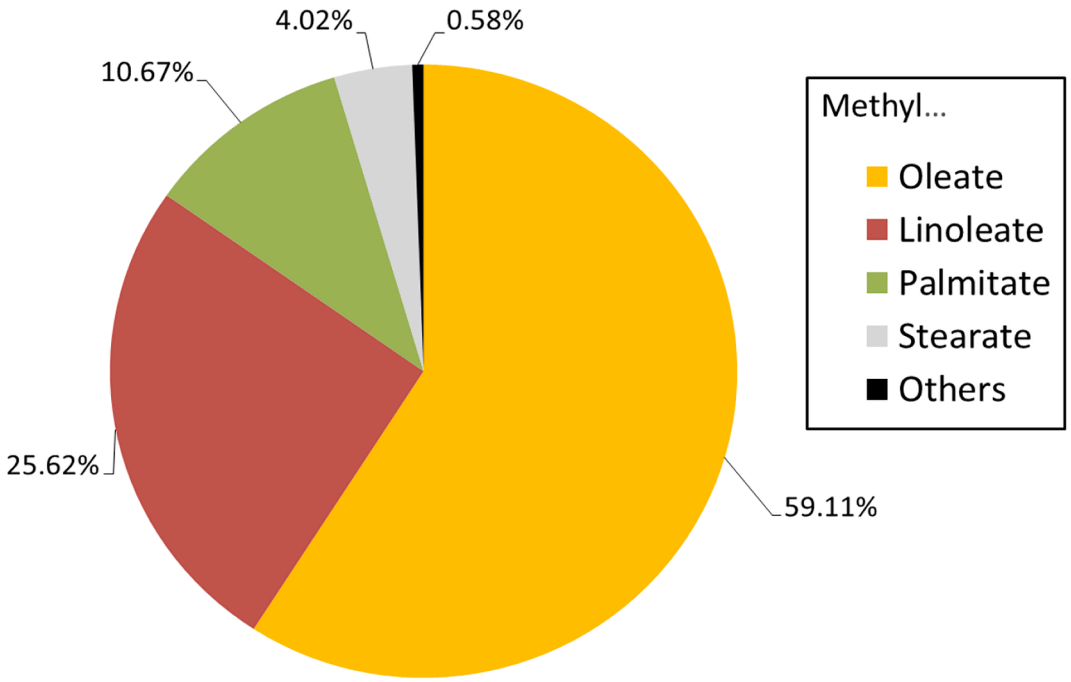

Fig. 2. Main FAMEs found in cardoon biodiesel.

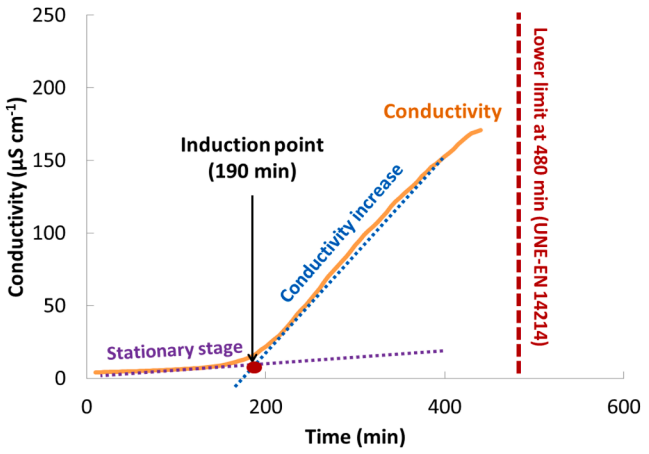

Fig. 3. Induction point determination for cardoon biolubricant.

3. Results and discussion

3.1. Biodiesel and biolubricant properties

Biodiesel and biolubricant yields were high, exceeding 95 %. To monitor the second transesterification, the FAME decrease was measured by gas chromatography, and the total reaction of both hydroxyl groups in the superior alcohol was assessed through infrared spectroscopy, as explained in previous studies [2], assuring the almost total reaction of FAMEs and the superior alcohol to produce the corresponding biolubricant.

One influential factor concerning the oxidative stability of biodiesel and biolubricant is the fatty acid composition of the oil, which will produce equivalent FAME (biodiesel) and ester profiles (biolubricant). Biolubricants usually show shorter oxidative stability values compared to their corresponding raw materials [1,7].

Fig. 2 shows the FAME profile of cardoon biodiesel, with high percentage of methyl linoleate, whereas methyl oleate content was lower. The former presented two double bonds in its molecular structure, which implies a low oxidative stability for this biofuel compared to other biodiesel samples, although most of them do not comply with the standard, needing the addition of antioxidants [4]. The low amount of methyl oleate (with one double bond, which is more stable) did not contribute to increase the oxidative stability. In previous studies, similar FAME profiles (58 % methyl oleate and 24 % methyl linoleate) were observed [2].

Similar esters were obtained in cardoon biolubricant, implying a low oxidative stability (see Fig. 3). This fact could influence the quality of the sample during storage. Similar results were found in previous studies, with induction points from 3 to 6 h for frying oil and rapeseed biolubricant obtained through double transesterification with methanol and 2-ethyl-1-hexanol [6].

3.2. Biolubricant thermal stability

Two stages can be observed in oxidizing and inert atmosphere (Fig. 4). First, the decrease in weight started at around 200°C (207 and 198°C for air and nitrogen), with a peak temperature of 267°C and 265°C for air and nitrogen. The second stage presented the main peak temperature, with the maximum weight loss rate, at 393 and 392°C for air and nitrogen. This might be related to combustion or oxidation of esters, and similar temperature ranges were observed for other biolubricants [8]. Compared to the thermal stability of cardoon oil, it showed higher peak temperatures (at 419 and 426°C for air and nitrogen), implying a lower stability for the biolubricant. These results did not agree with other studies where biolubricants showed higher stabilities than their original vegetable oil due to the absence of β-hydrogen in the corresponding polyol, but in these cases triols were used, whereas in this study a diol was employed [9]. The difference in molecular weight between the oil and the final biolubricant could explain the lower temperature peaks found, as some authors have pointed out that an increase in molecular weight can imply an improvement in thermal stability in cellulose fractions with different molecular weights [10].

3.3. Biolubricant during storage

There was an increase in viscosity, possibly due to the oxidation of esters and the subsequent polymerization, generating long chain saturated compounds or polymers [3,4]. Thus, there was an increase in viscosity, above 15 % at 40°C (Table 2). These differences affected the viscosity index, which decreased over 20 %. The initial viscosity values, which determine the use of a biolubricant, changed during storage, which is an undesirable effect. Moreover, the decrease in viscosity index implies that the viscosity of cardoon biolubricant is more dependent on temperature. Acid value increased from 0.38 at the beginning of storage to 3.81 mg·KOH g^{-1} after 12 months of storage, which pointed out the considerable increase in organic acids (such as free fatty acids) and aldehydes [4]. To avoid these changes, the addition of antioxidants is required [11,12].

Table 2
Viscosity evolution of cardoon biolubricant during storage.

Storage time (months)	0	6	12	Increase at the end of storage, %
Viscosity at 40°C (cSt)	18.85 (±0.02)	19.52 (±0.03)	21.96 (±0.01)	+ 16.49
Viscosity at 100°C (cSt)	4.73 (±0.03)	4.74 (±0.01)	4.76 (±0.02)	+ 0.6
Viscosity index	184 (±1)	174 (±1)	141 (±2)	–23.34

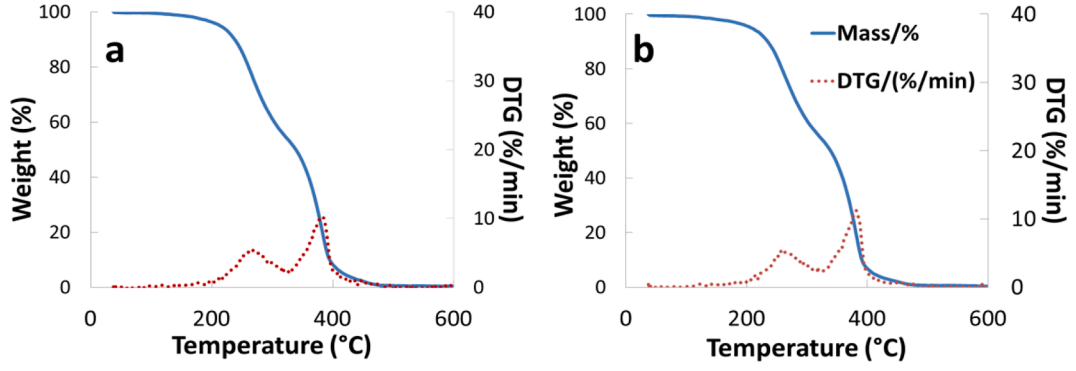

Fig. 4. TG and DTG curves for cardoon biolubricant in: a) air and b) nitrogen.

4. Conclusions

Cardoon biolubricant showed a high thermal stability (temperature peaks exceeding 390°C), among other suitable properties to be a good replacement for lubricants.

The biolubricant obtained showed a short oxidative stability, which was directly related to the composition of its corresponding precursors (oil and biodiesel).

During storage, the viscosity of cardoon biolubricant increased, whereas the viscosity index decreased. This way, its adequacy for certain or specific uses can change over time.

The main properties of this biolubricant were altered during storage, requiring the addition of antioxidants or selecting other raw materials with suitable fatty acid content to avoid this drawback. If the first option is chosen, this biolubricant could be suitable for commercialization.

CRediT authorship contribution statement

Sergio Nogales-Delgado: Conceptualization, Formal analysis, Methodology, Data curation, Investigation. **José María Encinar Martín:** Conceptualization, Supervision, Writing - review & editing, Project administration, Validation.

Declaration of Competing Interest

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

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