catalysts

Review

A Review on Biolubricants Based on Vegetable Oils through Transesterification and the Role of Catalysts: Current Status and Future Trends

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Abstract: The use of biolubricants as an alternative to petroleum-based products has played an important role in the last decade. Due to the encouragement of global policies, which mainly support green chemistry and circular economy, there has been an increasing interest in bio-based products, including biolubricants, from scientific and industrial points of view. Their raw materials, production, and characteristics might vary, as biolubricants present different applications for a wide range of practical uses, making this field a continuously changing subject of study by researchers. The aim of this work was to study biolubricant production from vegetable oil crops from a bio-refinery perspective, paying attention to the main raw materials used, the corresponding production methods (with a special focus on double transesterification), the role of catalysts and some techno-economic studies. Thus, the main factors affecting quality parameters such as viscosity or oxidative stability have been covered, including catalyst addition, reaction temperature, or the use of raw materials, reagents, or additives were also analyzed. In conclusion, the search for suitable raw materials, the use of heterogeneous catalysts to improve the effectiveness and efficiency of the process, and the optimization of chemical conditions seem to be the most interesting research lines according to the literature.

Keywords: fatty acids; fatty acid methyl esters; transesterification; epoxidation; catalyst; viscosity; oxidation stability; acidity; biorefinery; sustainability; circular economy

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1. Introduction

1.1. Global Energy and Materials Scenario: The Role of Biolubricants

Due to the global concern about environmental and sustainable subjects, the promotion of new concepts such as circular economy, green chemistry, or sustainability has become popular in recent years. Indeed, global agencies and organizations, as well as national or local governments (along with society's environmental awareness), have encouraged these kinds of practices, as in the case of Europe, has established a long-term goal to develop a competitive, resource-efficient, and low carbon economy by 2050, pointing out the important role of biomass in future bioeconomy policies [1].

On the other hand, the 2030 Horizon and Sustainable Development Goals (SDG) established by the United Nations (UN) are a reference for the launch of specific national or regional guidelines regarding sustainability, green practices, and circular economy, among others [2].

In this context, the role of bioproducts as a replacement for petroleum products can be strategic, fostering economic and sustainable growth of developing countries or regions (as well as developed countries whose green policies have changed their strategies in the medium and long term). For instance, the implementation of technologies devoted to biofuel production has been widely studied in the literature, including biodiesel or bioethanol, among others.

Regarding bioproducts, the specific case included in this review, that is, biolubricants, has been considered an interesting research field, as explained later. Biolubricants could act as the replacement for mineral lubricants, implying many advantages and challenges. This way, biolubricants are more biodegradable, presenting higher flash and combustion points compared to traditional lubricants. Also, biolubricant production usually presents a high atom efficiency. These properties imply a product with a reduced environmental impact, as well as increased safety during storage or transport. On the other hand, these biolubricants may also have disadvantages, like short oxidative stability values, which could worsen viscosity or acidity during storage, with subsequent problems for its direct use in machines, engines, or gears.

In general, apart from the abovementioned advantages, and depending on the raw material used and the kind of production, biolubricants could comply with some Sustainable Development Goals, like the ones included in Figure 1:

Figure 1. Main Sustainable Development Goals related to biolubricant production [2,3].

Therefore, as can be seen in this figure, biolubricant production, which can be considered in a biorefinery context, could comply directly with many of the Sustainable Development Goals (SDGs) established by the UN. For instance, as explained in the following sections, biolubricant production can present intermediate products, such as fatty acid methyl esters, which could contribute to affordable and clean energy.

Regarding decent work and economic growth, the use of bio-based products obtained from typical raw materials in a certain area can contribute to the energy and material independence of this region, developing sustainable economic growth. Indeed, local crops and the subsequent vegetable oils could be an interesting starting point for a biorefinery based on biodiesel and biolubricant production (usually through double transesterification), promoting sustainable industries, innovation, and responsible production of many components such as biodiesel, glycerol, biolubricants, methanol recovery, etc.

Finally, and since natural raw materials are used in a sustainable way, obtaining a biodegradable product, biolubricant production could help to improve climate action, protecting life on land and below water (as, for instance, a biolubricant spill would not be as harmful as its petrol-based equivalent). Furthermore, other SDGs could be positively influenced (such as "No poverty", "Good health and well-being", or "Reduced inequalities"), but in an indirect way.

These SDGs point out another interesting point that supports sustainable strategies, possibly being the real and definitive starting point for the implementation of these policies all over the world. Unfortunately (or not, if green policies are finally taken by national and international agencies at this point, after learning the hard way), the energy and material dependence of most countries (especially concerning natural gas or oil), along with the subsequent and unstable changes on many raw material prices (including oil and, as observed after the war between Russia and Ukraine, vegetable oils such as corn oil) has implied an unstable period where economic crisis (pressed by this energy instability) became the general tone, affecting almost every corner of the globe in a direct or indirect manner.

However, this is just a simple example of how international relations and wars in recent history influenced aspects such as energy, food, or transport [4,5]. This way, concepts such as renewable energy, circular economy, or green chemistry are nowadays as linked to geopolitics as ever (although this issue is not new), apart from the obvious economic and industrial concepts, in order to reduce the negative effect of international stress [6–9].

As observed in Figure 2, two significant trends are observed that point out the negative effects of energy and material dependency. First, according to Figure 2a, it is clear that oil price evolution has been a roller coaster since 2005, with increases of 100% in a few years, followed by abrupt decreases of over 50%. With this uncertainty related to oil prices, it is difficult for countries (especially developing ones) to carry out a correct industrial development plan, among other economic issues, with negative consequences for industries and, accordingly, citizens.

Another paradigmatic example is the Russo-Ukrainian war, whose consequences regarding fuel prices are included in Figure 2b. Considering that the Russian invasion of Ukraine took place in February 2022, its consequences were noticeable almost instantaneously, with a considerable increase in FAME (120%), gasoline (90%), and diesel (92%) prices compared to average prices in 2018–2019. As expected, these unstable prices (including some metals like gold or nickel) implied a global economic crisis, affecting developing countries to a greater extent [10]. Consequently, this event could be the "last straw" to definitively change the public and institutional support towards a green transition [11].

Another event to take into consideration was the COVID-19 pandemic, whose effect was also noticeable (apart from the obvious impact on health and economic issues) in energy consumption all over the world, especially in cities (where the different stringency responses taken by governments to mitigate the spread of COVID-19 had an influence on the reduction in urban energy consumption) [12], energy market (whose effect was persistent for an extended period) [13–15] or renewable energy, with an increasing interest in subjects such as green policies or clean energy investments (to revitalize the economy after the pandemic) in such a stable stage like the post-pandemic era.

Equally, energy efficiency research related to renewable energy has gained importance in recent years in order to compete with previous energy sources and promote the sustainable development of green processes [16,17]. As a result, many countries, such as those included in G20, have encouraged green policies through fiscal stimulus as a consequence of the coronavirus crisis [18]. Considering that similar events could take place in the medium to long term, it is no wonder that this trend can be enhanced in the future.

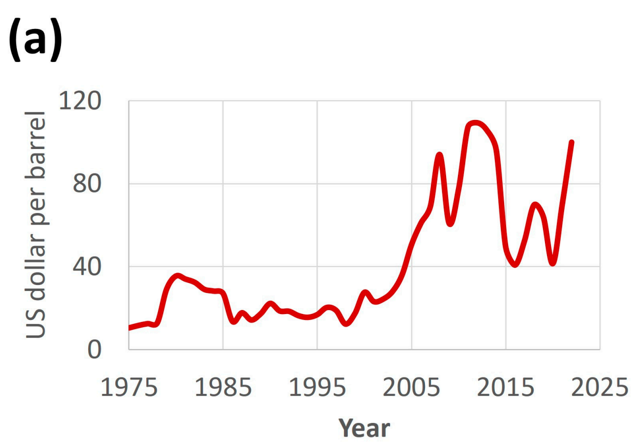

Figure 2. *Cont.*

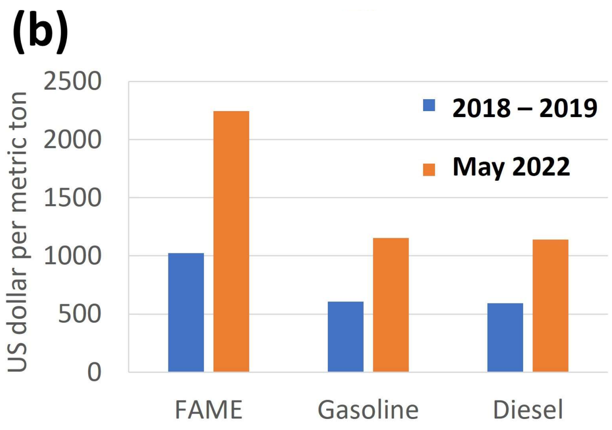

Figure 2. Different trends pointing out the negative effect of energy dependency: (**a**) Average annual OPEC crude oil price from 1975 to 2022; (**b**) Comparison of average wholesale motor fuel prices (FAME, gasoline, and diesel) in Europe in 2018/19 and May 2022 as a result of the Russia-Ukraine war, expressed in U.S. dollars per metric ton of oil equivalent. Sources: [19,20].

Consequently, green policies have become as important as ever, influencing or even changing the current international status when it comes to geopolitics during the energy transition [7,21,22].

Thus, energy and material independence (especially in developing countries, but also at a global level) is necessary, and the use of concepts such as green chemistry or circular economy could contribute to the sustainable development of industrial activities. In this case, as explained in further sections in this review work, the role of some raw materials such as vegetable oils (along with some wastes) could be vital, as they can contribute to the production of very interesting goods, serving as an energy source (for instance, through biodiesel production) or providing important products such as biolubricants (the perfect replacement for lubricants obtained from petroleum industry). But is the use of biolubricants really a great opportunity to contribute to the abovementioned purposes? It will depend on market opportunities and production efficiency, as will be discussed in the following sections.

1.2. Industrial Activity, Lubricant Demand, and the Subsequent Opportunity for Biolubricants

There is no doubt that industrial activity has been constantly increasing since the industrial revolution took place. Indeed, there are plenty of indicators that support this trend, not only in world powers such as China or the United States but also in other developing countries, especially in Africa. Africa's economic awakening is interesting in many ways, but as far as this work is concerned, there are three key points that should be considered, like the following:

- Its economic growth and industrial development are becoming more and more noticeable, with the subsequent risks if environmental measures are not suitably taken.
- There is a great opportunity for sustainable development according to the SDGs, with the subsequent decrease in economic dependence on traditional trade relations with some countries, especially in the case of former colonial powers.
- For this purpose, many sustainable processes can contribute to the industrial network of developing countries.

The role of vegetable oils could be crucial, as there are many oilseed crops (especially safflower, cardoon, or rapeseed) that can be easily adapted to extreme climate conditions and poor soils worldwide, which could encourage developing countries to implement or foster oilseed crops in non-arable areas, with the subsequent benefits related to the production of fuels and other bio-based products such as biolubricants. Indeed, the real implementation of biolubricant production will depend on the real demand for these products.

In that sense, there is a steady industrial development, which usually implies the use of industrial machinery and the subsequent demand for lubricants. Thus, considering the above, the role of biolubricants could be an interesting starting point for the implementation of sustainable processes, green chemistry, or circular economy. This fact can be supported by the demand for biolubricants, as shown in Figure 3. As observed, there was a steady increase in the global demand for biolubricants, forecasting for 2023 a demand of 37.4 million metric tons, that is, over an 8% increase compared to 2010. Consequently, biolubricant production presents a promising future, although it is still in an emerging stage.

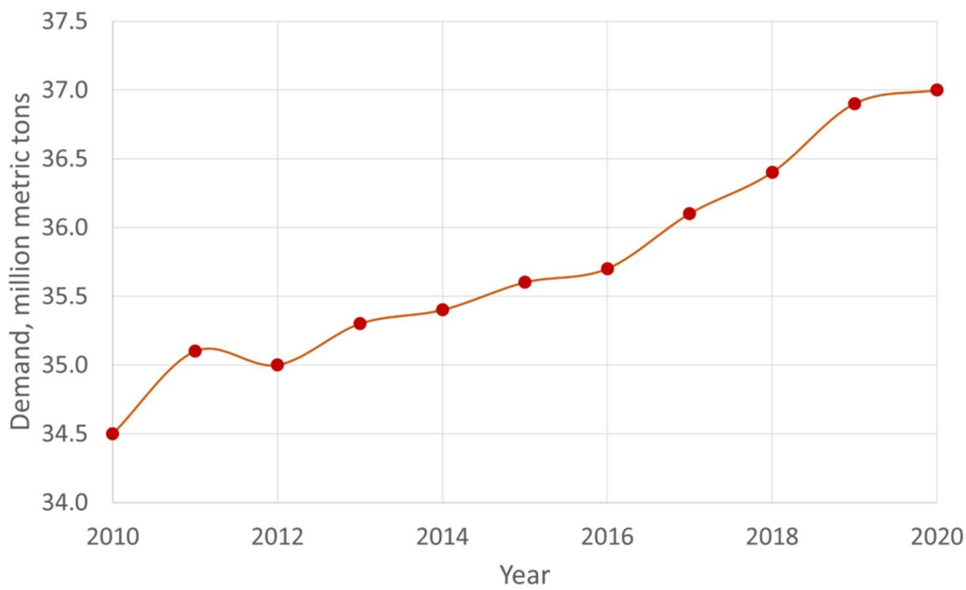

Figure 3. Global demand evolution for biolubricants in the last decade (source: [3]).

In parallel, lubricant production and demand can be broken down by region, as observed in Figure 4. It should be noted that the majority of lubricant demand (Figure 4a) and production (Figure 4b), exceeding 75%, is mainly concentrated in three regions that are, Asia-Pacific, Europe, and North America. On the contrary, lubricant production in Africa can be considered negligible for the time being. In that sense, the role of biolubricants can be doubly promising:

- On the one hand, considering the abovementioned concerns from international agencies and countries, the replacement for lubricants presents great potential in developed countries in Asia, Europe, and North America.
- On the other hand, considering the case of Africa, the use of biolubricants can meet the demands of developing countries, where the production of vegetable oils adapted to extreme climate conditions (such as cardoon or safflower) could contribute to an increase in industrial activity in a sustainable way, making these regions less dependent on energy or imported materials (like lubricants).

Thus, it is clear that there is great potential for biolubricant production based on vegetable oils. Even though there are some concerns related to energy crops (mainly based on oilseed species, both for edible and non-edible purposes) and their environmental impact or food competition, the sustainable use of poor soils, as well as the concept of crop rotation that could enhance soil alleviation have been widely studied as a sustainable way to take advantage of non-arable areas.

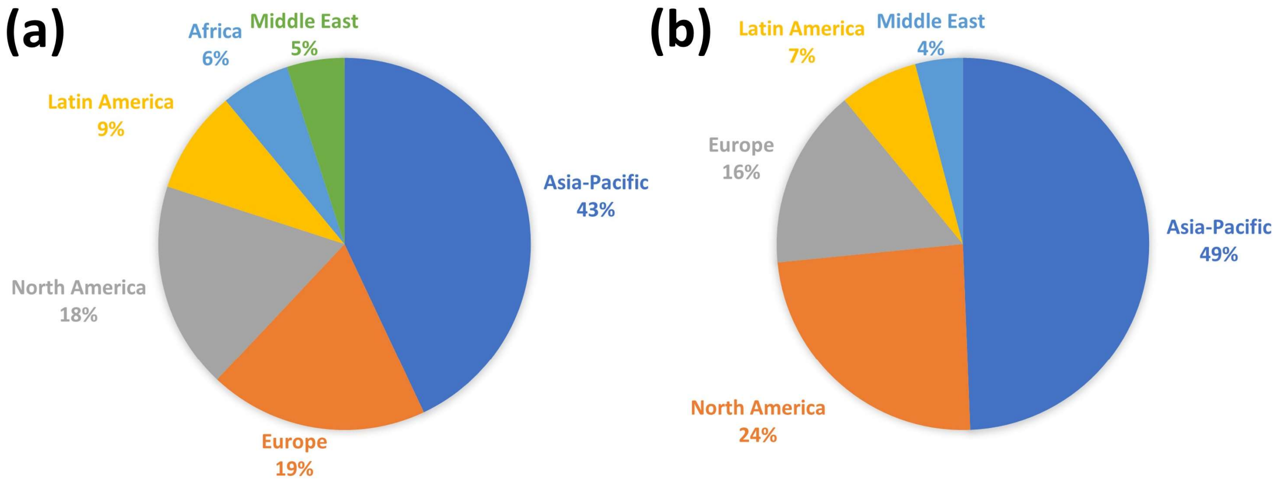

Figure 4. Lubricant demand (**a**) and production (**b**) shares by region in 2018 [23].

In that sense, some crops such as cardoon, rapeseed, or safflower [24–26] would be suitable for sustainable oil production, as they can be easily adapted to extreme climate conditions and poor soils that are not usually arable (which could be an advantage for developing areas where these conditions are usual) and present a long and deep tap root which can be used in rotation crops to recover superficial soils where typical crops such as corn, lettuce or garlic are used. Also, these crops are normally resistant to many plagues. In conclusion, if suitably managed, soils for oil production can be sustainable and would not imply any environmental concern.

Apart from that, there are some wastes related to the use of vegetable oils, especially after cooking and the subsequent frying oil generation, that should be properly managed to avoid environmental problems, especially related to soil and water pollution, where these wastes are especially pollutant. Thus, as commented in the following section, there is a real concern about frying oil management, which could be efficiently managed by its use as a biodiesel and biolubricant source. Equally, the use of these wastes to obtain biodiesel and biolubricants could also contribute to lower soil exploitation, implying a more sustainable production of biolubricants.

1.3. Waste Cooking Oil: A Real Challenge with Endless Opportunities (Such as Biolubricant Production)

Frying oils (FO), or waste cooking oils (WCO), which can be considered as used vegetable oils (UVO), is a waste that is increasingly generated in food and industrial sectors worldwide, which could imply a serious environmental problem if it is not suitably managed. Thus, about 200 million tons per year are produced, with 4 million tons in Europe (which constitutes around 2%, whereas the US, with 55%, and China, with 25%, are the majority of WCO generators) [27]. In any case, it should be noted that, in essence, WCO composition is relatively similar to the original vegetable oils used, presenting degradation compounds depending on many different factors such as frying cycles, temperatures used, etc., which could imply a relatively similar use of this waste compared to vegetable oils devoted, for instance, to biodiesel or biolubricant production (possibly adding some pre-treatments to remove solid residues or adjust pH).

Fortunately, there are plenty of ways to valorize this waste in order to obtain valuable products such as biofuels (like biodiesel), to produce energy, animal feeds, ecological solvents, composites materials, non-aqueous gas sorbent devices or, as in the case of the main subject of this review, biolubricants. For that purpose, new recycling processes have been developed, and the most traditional ones have been optimized to make the use of WCO a valuable chemical block (feasible and efficient), whereas other studies compared the environmental impact of multiple valorization options of waste cooking oil, showing low environmental impact and promising results for achieving circular economy goals [28–30]. Regarding biodiesel production (which is mainly carried out through a common chemical synthesis called transesterification, as will be explained in the following sections), it has proved the suitability of FO to be re-used in green chemistry or circular economy, whose market is expected to generate up to 8.88 billion dollars in 2026 [31].

As a result, WCO management is a matter that has attracted the attention of researchers. In that sense, our previous works have pointed out the possibility of using waste cooking oil as an interesting source for biodiesel and biolubricant production, with similar results to those obtained for equivalent vegetable oils such as corn, rapeseed, or safflower. Indeed, the only disadvantage of these productions was the short oxidative stability of final products, a challenge shared by the rest of the vegetable oils included in our experiences [32–34]. Apart from that, there are many examples of biolubricant production from WCO, offering interesting alternatives for the management of this waste [35]. Other authors have produced biolubricants from WCO through epoxidation, obtaining interesting products with high viscosity index values that could complement the standard ISO vegetable-grade lubricants in the market [36]. Moreover, from the same waste, some authors have synthesized an octylated branched biolubricant through hydrolysis, esterification, epoxidation, and a final reaction with octanoic acid, obtaining a product with better properties compared to mineral-based lubricants (for instance, improving friction coefficient and viscosity index) [37]. Furthermore, some experiences have assessed the possible implementation of double transesterification of WCO with methanol and trimethylolpropane to obtain biolubricants in a vertical pulsed column, carrying out an energy optimization through the surface response of the main operating parameters. As a result, an optimal reaction yield of around 83% was obtained, obtaining an interesting biolubricant with improved properties such as VI, flash point, and pour point [38].

But this interest has also been extended to global society and institutions, with the clear example of Europe, where there is a specific legislative framework about the management and the subsequent employment of this waste for the abovementioned industries, from disposal-collection to reconversion [28,31]. Thus, in the case of the United Kingdom, used cooking oil was the most resourceful feedstock for biofuel production, with 54% in 2020 [39]. But not only in Europe, there is a concern about WCO management. For instance, in 2021, there were more than 98% of biodiesel manufacturers in Japan whose main raw material was waste cooking oil, proving that the use of this waste is already a reality. Moreover, a high percentage of WCO comes from households (37.7%), proving the power of individuals to contribute to a change towards green and sustainable policies. That is, global change comes from local action [40].

Considering these facts, WCO “has earned the right” to be considered as valuable as any other vegetable oil for biolubricant production, being included throughout the discussion and reasoning of this work and playing a decisive role, as will be discussed later.

1.4. Scientific Interest in Biolubricants

In light of this evidence, it is quite clear that there is a real interest in the specific topic we are going to explain in this review work. In such a way, and according to Figure 5, there was a continuous interest in research about biolubricants, which implied an increasing number of published articles about this subject. Thus, especially from 2010, there was a considerable increase, reaching about 80 published articles per year about biolubricant production, application, or characterization. Among these publications, the use of vegetable oils through transesterification seemed to be popular, whereas epoxidation processes to obtain biolubricants were less researched.

As explained throughout this review, the higher interest in double transesterification could be due to the special characteristics of this chemical route, which could perfectly fit with the biorefinery concept, where biodegradable products and low quantities of wastes are obtained. In that sense, many studies about specific techno-economic aspects of biorefineries, as well as several patents about these subjects, have been developed (which will be further explored in the following sections), proving the increasing interest in double transesterification both at scientific and industrial level.

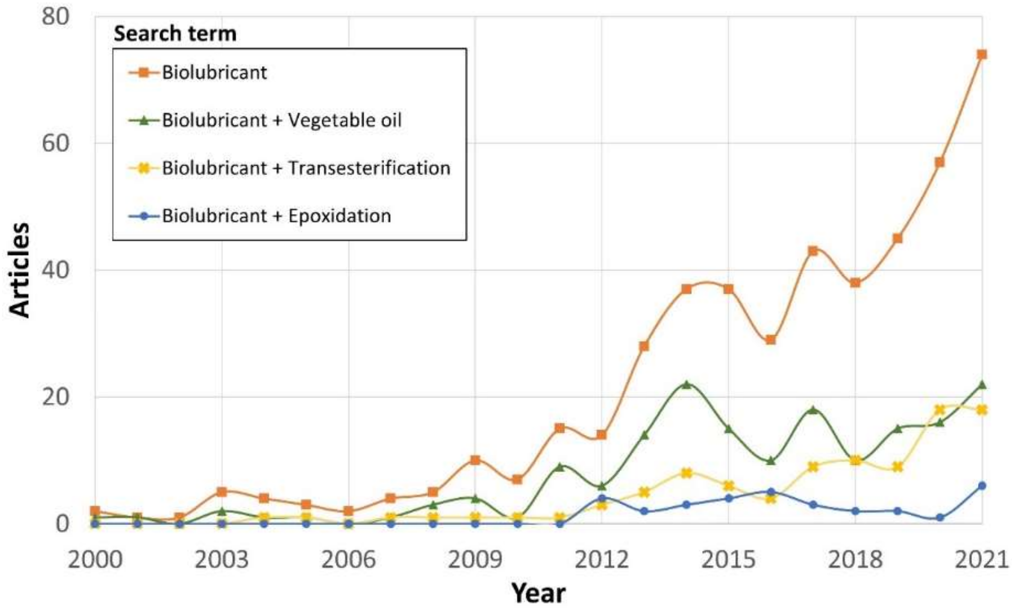

Figure 5. Current research trends on biolubricant (source: [41]). According to the following search criteria: "biolubricants"; "biolubricant" AND "vegetable oil"; "biolubricant" AND "transesterification"; "biolubricant" AND "epoxidation". Articles included research and review articles.

If published articles are broken down by country, the results obtained are included in Figure 6. As observed in this figure, Malaysia contributed the majority of articles about biolubricants based on vegetable oils (52), followed by India (46) and Spain (22). Interestingly enough, the two most important world players in research articles (the United States and China) were the fifth and seventh countries regarding article publication in this field, which is a relatively low position for such developed countries when it comes to research. This could be due to the fact that the former are countries with a long farming tradition, where some specific vegetable oils such as safflower or rapeseed, which are highly used as raw material for biodiesel or biolubricant production, are easily adapted to their climate. In other words, these oils are especially suitable for biolubricant production, and that is the reason why the research related to the main subject of this review is highly remarkable in the abovementioned countries at the expense of China or the United States.

Regarding the most cited articles about this subject (according to the search criterion "biolubricants" AND "vegetable" AND "oil"), the results are included in Table 1. These articles mainly dealt with the use of green chemical routes to obtain biolubricants, presenting their most representative characteristics (pointing out the sustainability of the process and their biodegradability) and focusing on tribological tests. In general, and even though there is room for improvement according to these works, the suitability of biolubricants has been proven, exploring the possibility of their production at the industrial level in a biorefinery context.

It should be noted the heterogeneous disciplines of the journals where these articles were published (from agriculture to tribology), which points out the interdisciplinary nature of the research teams that have carried out these research works. Also, these articles were recently published (many of them in the last 6 years), which proves the recent and great interest in this subject by the scientific community. Additionally, these recent works were highly cited (with almost 100 citations for one of the most recent articles, published in 2020, and up to 300 citations for the most popular work), proving the increasing interest in this subject by the scientific community.

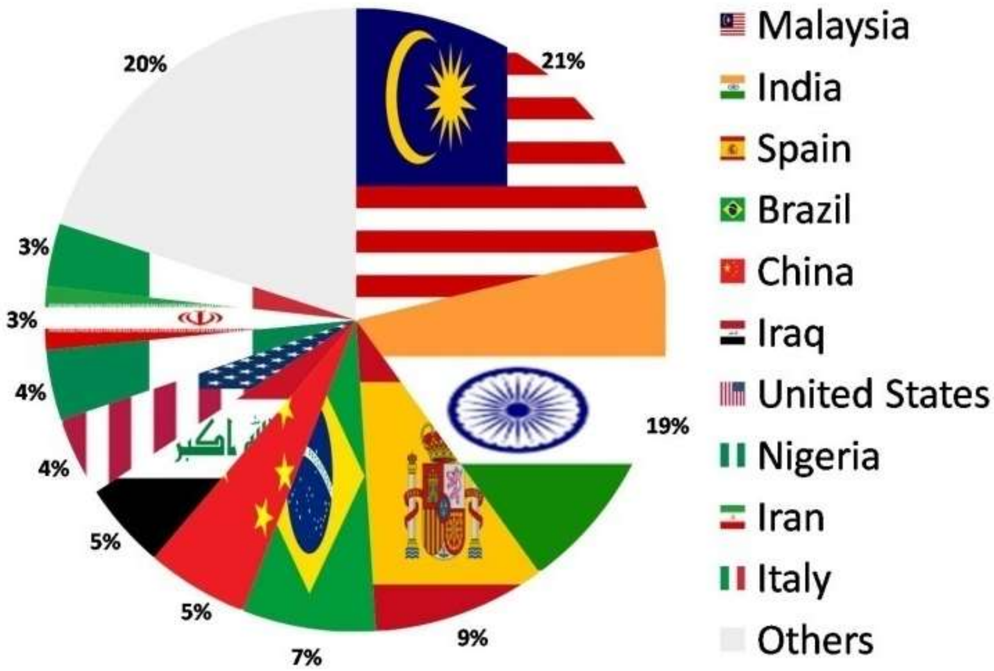

Figure 6. Articles about biolubricants based on vegetable oils by country [41]. According to the following search criterion: "biolubricant" AND "vegetable" AND "oil". Research and review articles were included.

Table 1. Top cited articles, and top cited authors dealing with scientific articles about biolubricants based on vegetable oils (source: [41]).

Article Title	Authors	Source	Year	Citations	Reference
The prospects of biolubricants as alternatives in automotive applications	Mobarak et al.	Renewable and Sustainable Energy Reviews	2014	304	[42]
Development of biolubricants from vegetable oils via chemical modification	McNutt et al.	Journal of Industrial and Engineering Chemistry	2016	218	[43]
Manufacturing of environment-friendly biolubricants from vegetable oils	Heikal et al.	Egyptian Journal of Petroleum	2017	171	[44]
Lubrication-enhanced mechanisms of titanium alloy grinding using lecithin biolubricant	Jia et al.	Tribology International	2022	148	[45]
Tribological behavior of biolubricant base stocks and additives	Chan et al.	Renewable and Sustainable Energy Reviews	2018	135	[46]
A review of biolubricants in drilling fluids: Recent research, performance, and applications	Kania et al.	Journal of Petroleum Science and Engineering	2015	129	[47]
Chemically modifying vegetable oils to prepare green lubricants	Karmakar et al.	Lubricants	2017	125	[48]
The physicochemical and tribological properties of oleic acid-based triester biolubricants	Salih et al.	Industrial Crops and Products	2011	122	[49]
Green synthesis of biolubricant base stock from canola oil	Madankar et al.	Industrial Crops and Products	2013	100	[50]
An overview of the biolubricant production process: Challenges and future perspectives	Cecilia et al.	Processes	2020	98	[51]

Table 1. *Cont.*

Article Title	Authors	Source	Year	Citations	Reference
Author Name	Published Articles about this Subject		Documents in Total		h-Index
Salimon, J.	11		207		35
Salih, N.	9		115		27
Yunus, R.	7		247		44
Yousif, E.	6		275		37
Freire, D. M. G.	6		284		52
Delgado, M. A.	6		50		22
Nogales-Delgado, S.	5		50		16
Habert, A. C.	5		63		20
Encinar, J. M.	5		80		36
Cavalcante, C. L.	5		164		41

Concerning the top publishing authors on this subject (also included in Table 1), it should be noted that their specific work about this research area was relatively short compared to their total published articles, pointing out that their careers are equally focused on other subjects and establishing, again, that researchers interested in this field come from multiple fields, focusing on biolubricant production from vegetable oils due to their scientific context and the great interest of this issue.

Also, it should be pointed out the great prestige and creativity of these top publishing authors, whose total publications (from 50 to 287 published works) and h-index (up to 52, which implies 52 papers with at least 52 citations each) are high, reflecting a great experience in research.

Regarding the subject area or field where these articles are focused on (according to the scientific journal where they were published), Figure 7 shows the distribution of the articles considered for this review:

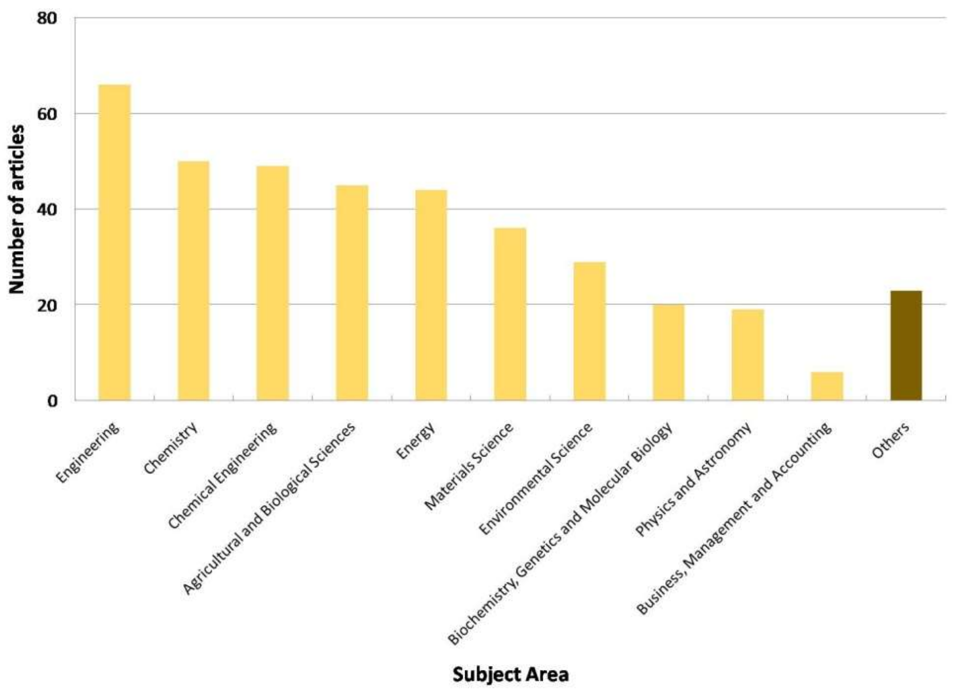

Figure 7. Main subject areas of the articles published about biolubricants obtained from vegetable oils [41]. According to the following search criterion: "biolubricant" AND "vegetable" AND "oil". Research and review articles were included.

As observed, most articles were focused on subject areas like engineering, chemistry, chemical engineering, agricultural and biological sciences, energy and materials, and environmental science. In that sense, the chemical routes for biolubricant production, as well as its industrial use and possible implementation in biorefineries (where products like biodiesel and glycerol can be used as fuels for different purposes), could explain the suitability of this research field for the abovementioned subject areas. As a result, biolubricants from vegetable oils offer a wide range of possibilities in research, implying the research work of multidisciplinary teams, with the subsequent synergy and enhancement of scientific production in this field.

Finally, concerning the role of catalysts during biolubricant production (which is essential to make the process efficient and competitive compared to traditional lubricant production), the evolution of published articles about this subject is included in Figure 8. As observed, the interest in catalytic conversion for biolubricant production arose in 2010, with a considerable increase in published works from then on. This could point out the fact that improvements in efficiency during this process are required, especially when the possible implementation at an industrial scale is considered. In that sense, the search for new catalysts (especially heterogeneous ones, in order to make the purification of biolubricant easier) could explain the increasing interest in this point. In addition, as observed in future sections, studies about techno-economic assessments and patents seem to show a special interest in the development of catalysts and the consequences on biolubricant production, especially when it comes to quality improvement of the final product and efficiency increase of the whole process mainly in a biorefinery context.

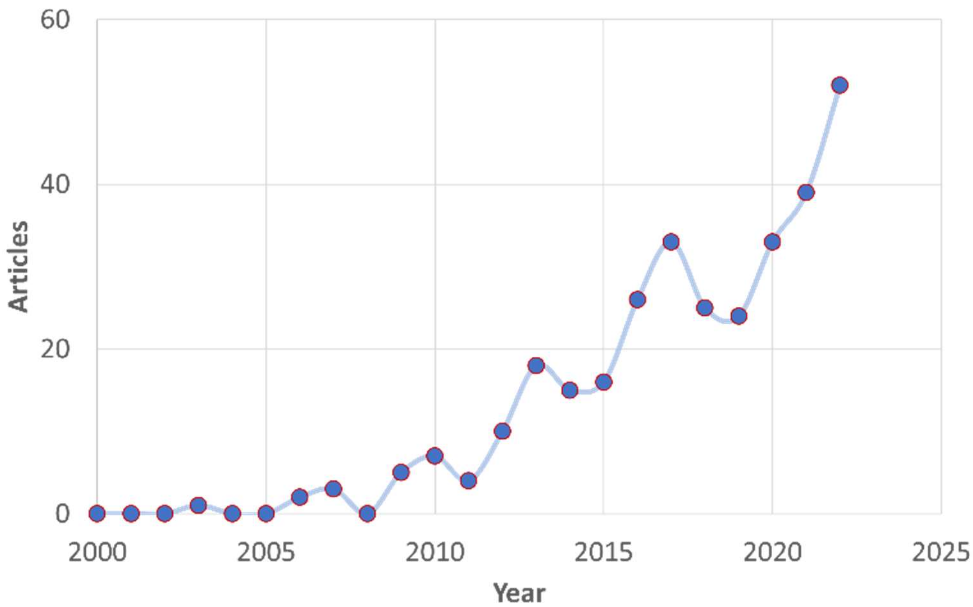

Figure 8. Articles published about catalytic biolubricant production (source: [41]). According to the following search criterion: "biolubricant" AND "catalysis". Research and review articles were included.

1.5. Aim of This Review

Considering the above, the aim of this review work was to carry out a state-of-the-art analysis of biolubricants based on vegetable oils, paying attention to the most recent developments in the following fields:

- Current use of vegetable oils in biolubricant production, especially concerning the possibilities related to the valorization of frying oil.
- Main biolubricant synthesis routes, paying special attention to transesterification processes, offer real potential for the implementation of biolubricant production in biorefineries based on vegetable oils.

- Use of catalysts, both homogeneous and heterogeneous, to make biolubricant production more competitive compared to the equivalent and traditional lubricant production.
- The main factors affecting quality during biolubricant production, with a special focus on viscosity and oxidative stability, are parameters that are vital to determining the use and service life of biolubricants. This way, the role of chemical conditions, as well as catalyst addition or additives such as antioxidants, will be especially enhanced.

For this purpose, a comparison of the most cited and interesting research works related to this field will be carried out in this review, trying to draw conclusions in this regard.

1.6. Scope and Bibliometric Analysis

To carry out this review, Scopus was investigated for all entries in the literature on the topics of biolubricant (including keywords such as vegetable oil, transesterification, epoxidation, and catalysts) for the last 20 years, with special attention to the last 5-year period (2018–2023), where there has been a considerable increase in published papers about this subject. The search, which was made from January to August 2023, returned 1560 results, from which up to 253 articles were considered for their inclusion in this work, including information about 152 published works (mainly research works and, to a lesser extent, proceeding papers and patents) in the final paper.

2. Biolubricants Based on Vegetable Oils: Main Sources and Characteristics

2.1. Biolubricants: Definition and Raw Materials

Biolubricants are a kind of lubricant based on plants (mainly from vegetable oils such as palm, safflower, or rapeseed oils), which makes them biodegradable and environmentally friendly. They mainly act as anti-friction media. Thus, the main purposes of this kind of product, as in the case of petroleum-based lubricants, are wear reduction by decreasing friction coefficient between two contacting surfaces, rust and oxidation prevention, and sealing effect against dirt, dust, or water [42,52].

In that sense, it is interesting to point out the versatility of biolubricants, as they can present different states of matter (solid, liquid, or semi-solid) obtained from different sources (from natural to synthetic oils), which make them suitable for multiple purposes such as automotive (engine or gearbox oils, transmission or brake fluids, etc.) or industrial oils (machine, hydraulic or compressor oils, for instance).

These products usually present some advantages compared to traditional lubricants based on petrol, like the following [52]:

- They are more sustainable and biodegradable, as raw materials are natural compared to oil. Also, there are no by-products with difficult management, as they can be used for other purposes or re-used in the same biolubricant production, as explained in further sections.
- Biolubricants usually have higher lubricity and viscosity index values (clearly exceeding 140–150, compared to the low values found for lubricants, at 90–100), which is important as it means that their viscosity is less dependent on temperature.
- They present, in general, higher flash and combustion points, which is a positive issue when it comes to safety during storage and shipping.

However, they also present some disadvantages or challenges, like the following:

- Due to the presence of saturated fatty acids, biolubricants might present a poor performance at low temperatures, which limits their worldwide marketability.
- Hydrolysis can take place in contact with moisture, increasing the possibility of corrosion in facilities by increasing free fatty acid levels.
- They usually have a short oxidative stability, which could imply a change in their properties during storage or oxidation, which is undesirable.

As mentioned above, there are plenty of oilseed crops that are easily adapted to extreme climate and soil conditions, and that can be suitable for biolubricant production, as the subsequent vegetable oil can be a perfect raw material for this purpose. These vegetable oils, along with the use of waste cooking oil, usually present homogeneous characteristics, although their fatty acid composition can present a considerable influence on the properties of these raw materials and, consequently, on the final biolubricant. Indeed, as many previous studies have pointed out, the role of fatty acids in some properties of biolubricants (for instance, viscosity or oxidative stability) is essential, as the presence of some functional groups such as hydroxyl groups (as in the case of ricinoleic acid) or even double bonds can alter these properties, as observed in Figure 9.

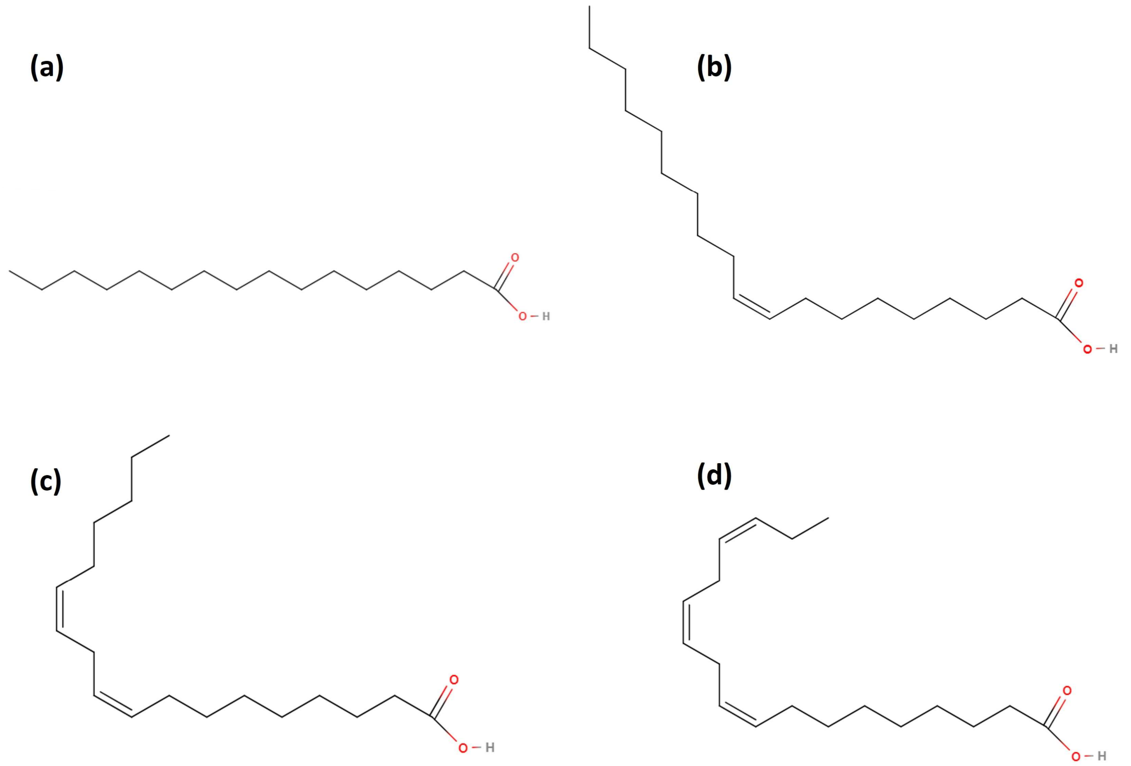

Figure 9. Molecular structure of some fatty acids: (**a**) palmitic acid, (**b**) oleic acid, (**c**) linoleic acid, (**d**) linolenic acid.

According to this figure, it can be observed how fatty acids basically differ from each other according to their molecular chain length and the presence of double bonds (which will be essential to understand the oxidative stability of biolubricants obtained through double transesterification). This way, a thorough knowledge of vegetable oils and their corresponding fatty acid composition is essential to assess, at least approximately, the main properties of the future biolubricant. It should be noted that the oil content in vegetable seeds might vary, according to the literature, from 20–36% for moringa to 45–70% for olive, with some representative crops such as rapeseed and palm presenting around 38–46% and 30–60%, respectively [42]. This fact should be considered in the final biolubricant yield as well as the agronomic performance of these crops.

Table 2 shows some examples of the main vegetable oils and their corresponding fatty acid composition, which will be an essential tool to understand some reasonings in this review work. As observed, some oils present a homogeneous fatty acid profile, whereas other crops (especially genetically modified) have a wide range of specific fatty acids, as in the case of safflower, whose oleic acid content can vary from less than 30% to up to 70%. In that sense, it is not a matter of "names" or "species", but a matter of fatty acid composition, as the fatty acid profile of some safflower oils could perfectly fit with the fatty acid profile of other vegetable oils like rapeseed.

Table 2. Potential raw materials for biolubricant production and their fatty acid composition (indicated in numerical symbol C:D, where C is the number of carbon atoms and D is the number of double bonds in their molecular structure). n.d. = not determined.

Vegetable Oil	16:0	16:1	18:0	18:1	18:2	18:3	Others	References
Castor	0.5–1.3	n.d.	0.5–1.2	4–5	2–8.4	0.4–1	83–88	[48,51,53–56]
Coconut	8–11	n.d.	1–3	5–8	0–1	n.d.	57–71	[48,51]
Corn	10.3–13	0.3	2–3	25–31	54–60	1	n.d.	[47,48,51]
Jatropha	13–16	n.d.	5–10.5	24–45	32–63	0.3–0.7	0.8–1.4	[48,51,57–59]
Olive	11.5–13.7	1.8	2.5	71–74	9.5–10	1.5	n.d.	[48,51,58]
Palm	37–47.9	0.4	3–8	37–45	1.9–10	0.3–0.5	1	[48,51,58,60]
Rapeseed	4–5	0.1–0.2	1–2	56–69.8	20–26	6.2–10	9.1	[48,51,54,61]
Safflower	5–7	0.08	1–4	10–21	73–79	n.d.	n.d.	[48,51,62]
Soybean	9.3–12	0.2–1.7	3–4.7	21–27.3	48.5–56.3	5.6–8	2.3	[48,51,56–58]
Sunflower	4.9–7	0.1–0.3	1.9–5	18.7–68	21–68.6	0.1–1.9	2.2	[48,51,55,57,63,64]
WCO	6.6–36.8	0.21–1.9	3–18.4	17.9–37.5	11.8–72.1	0.02–2.02	3.3	[33,57,65,66]

Thus, some interesting points can be inferred from this table:

- In general, palmitic, oleic, and linoleic acids are the majority of fatty acids found in most vegetable oils, which points out their vital role in some properties in the final biolubricant, as explained in further sections. In that sense, the presence of double bonds in their molecular structure (see Figure 9), which can be conserved in the molecular structure of the final biolubricant (especially in the case of double transesterification of fatty acids), could determine its oxidative stability. Thus, the knowledge of the ratio of some fatty acids (such as oleic/linoleic ratio) is usually interesting to understand oxidative stability in biodiesel or biolubricants.
- Nevertheless, there are some specific oils, such as castor oil, whose main fatty acid presents some special properties, as in the case of ricinoleic acid, with a hydroxyl group that can influence the properties of the final biolubricant regarding viscosity (as it promotes intermolecular interactions like hydrogen bonds, implying an increase in viscosity). In any case, there are other oils that present high quantities of other fatty acids, such as lauric and myristic acid in the case of coconut oil or icosenoic acid for rapeseed, which could imply changes in the properties of the corresponding biolubricants.
- The use of GM crops, as in the case of safflower, might vary the properties of the corresponding oil, with a considerable increase in oleic acid (exceeding 80%), improving some properties such as oxidative stability in the final biolubricant obtained [67]. Other studies point out the same aspect related to soybean oil, with a wide range of fatty acid contents depending on the gene technology used or the selection of soybean mutants [68]. Consequently, it is more interesting to consider FA profiles instead of kinds of vegetable oils, as it would give us a more exact idea about the raw material.
- The nature of WCO (and its subsequent fatty acid composition) might vary depending on the eating habits of the area where the research study was carried out. That is the reason why there was a wide range of oleic and linoleic acids in this table. In general, the main oils used for cooking are rapeseed, sunflower, soy, and olive oil, which can vary in the diet of some regions or areas. In any case, the fatty acid composition of this waste is relatively equivalent to the rest of vegetable oils, which supports the idea that its use as biodiesel and biolubricant source is feasible if a proper pre-treatment is carried out.

2.2. Main Characteristics of Biolubricants

It is clear that a biolubricant should present a series of characteristics that are essential for its use in lubrication processes. In that sense, there are plenty of requirements that should be accomplished to be a real alternative for lubricants [47,69]. In this review, we will focus on three main parameters such as viscosity, viscosity index, and oxidative stability.

- Viscosity: This is an essential parameter for a biolubricant, as it will determine its use for specific purposes. Thus, the resistance to the flow of a specific fluid (normally expressed in cSt) will influence many factors, such as the film thickness between the surfaces in contact or its permanence during lubrication (the higher the viscosity is, the thicker the film will be). Viscosity is influenced by factors such as temperature or pressure. It can be measured by dynamic or kinematic methods (by using Cannon-Fenske or Ostwald viscosimeters) at a specific temperature (normally 40 or 100 °C, which will be useful to determine VI) [70].
- Viscosity index (VI): This index indicates the changes in viscosity with temperature. Thus, a high viscosity index will imply a lower decrease in viscosity when temperature increases, which is a desirable effect as changes in temperature would not present a considerable influence on biolubricants [71,72]. High VI values will be obtained when the molecular structure of the final biolubricant is longer, and it will decrease with branching. That is the reason why the selection of a chemical route or specific reagents (like complex alcohols in double transesterification) will be vital to determine this parameter. It is calculated by measuring viscosity at 40 and 100 °C.
- Oxidative stability (OS): This parameter is related to the stability of biolubricants during oxidation processes, including storage. It is expressed in hours and determined through the induction point (IP) according to the Rancimat method [73,74]. This way, free radical generation (mainly due to the presence of double bonds in biolubricants) could start a chain reaction, where the propagation of free radicals could end up generating undesirable products such as free fatty acids (FFA) or polymers, among other decomposition compounds. The former could be related to the increase in acidity, which is an undesirable effect, especially when it comes to the maintenance of equipment and facilities. The latter is especially related to an increase in viscosity, as the polymerization of esters generates more complex molecules, which could imply an increase in molecular interactions such as Van der Waals or hydrogen bonds and, therefore, a higher resistance to the flow of biolubricants (that is, an increase in viscosity).
- Other parameters: in our opinion, the abovementioned properties are the most important ones to define the performance of a biolubricant, but there is a wide range of characteristics that should be considered, like pour point (the lowest temperature at which a biolubricant pours or flows, which is desirable to be as low as possible to be useful in cold climates), lubricity (that is, the reduction of friction between two surfaces in contact when the biolubricant is used), flash and combustion points (usually higher compared to traditional lubricants, which is a great advantage when it comes to safety during storage or shipping), hydrolytic stability (resistance of esters to hydrolyze, that is, to degrade in contact with water at high temperature) or biodegradability (which is considerably higher compared to petrol-based lubricants), among others.

Apart from the abovementioned properties, there are many other aspects that should be considered for the marketability of a biolubricant. For instance, acidity should be taken into account, as recently explained, whereas there are other parameters included in standards that should be considered. The changes in these parameters will be determined by different factors (such as raw materials used, the kind of chemical route selected for biolubricant production, or the chemical conditions that are chosen, including temperature, reaction time, reagents, etc.), as explained in further sections.

Thus, molecular factors such as functional groups and polarity (usually increase viscosity and tribofilm adhesion), numbers of branching (with a decrease in pour point and an improvement in oxidative stability), degree of unsaturation (with lower thermal and oxidative stabilities), or carbon chain length (improving viscosity and VI but with lower oxidative stability values) will determine the properties of a biolubricant, which are directly influenced by the abovementioned factors [46]

By way of example, Table 3 shows the most important characteristics of biolubricants mainly obtained through double transesterification (with methanol and the complex alcohol commented on in this table) from different sources.

Table 3. Some characteristics of biolubricants are obtained through double transesterification.

Biolubricant	Viscosity [1], cSt	VI	Pour Point, °C	Flash Point, °C	IP, h	References
Rapeseed-based 2-ethyl-1-hexyl-esters	7.97	n.d. [2]	n.d.	196	<6	[33]
Seed-based 2-ethyl-1-hexyl-esters	7.47	n.d.	n.d.	195	>3	[33]
WCO-based 2-ethyl-1-hexyl-ester	7.40	n.d.	n.d.	193	>3	[33,66]
WCO-based 2-ethyl-1-hexyl-ester	34.91	122	−1	216	n.d.	[66]
Mustard seed oil-based 2-ethyl-1-hexyl ester	8.6	n.d.	n.d.	n.d.	n.d.	[75]
Cardoon-based NPGE	18.85	184	n.d.	n.d.	<3	[76]
WCO-based NPGE	44.9	457	−1	238	n.d.	[66]
Palm-based PEE	68.4	188	−20	302	n.d.	[77]
High-oleic safflower-based PEE	77.7	155	n.d.	260	2.86	[67]
WCO-based PEE	68.5	144	n.d.	253	2.07	[34]
Palm-based TMPE	49.7	188	−1	n.d.	n.d.	[78]
High-oleic safflower-based TMPE	73.39	103	n.d.	216	6.7	[67]
High-oleic safflower-based TMPE	89.11	131	n.d.	220	>7	[79]
Rapeseed-based TMPE	75.5	128	n.d.	210	4.9	[80]
Jatropha-based TMPE	51.89	140	−3	n.d.	n.d.	[44]
Palm-based TMPE	38.25	171	5	240	n.d.	[44]
Sesame-based TMPE	35.55	193	−21	196	n.d.	[81]
WCO-based TMPE	30	179	n.d.	n.d.	n.d.	[82]
Palm kernel-based isoamyl ester	3-6	149	n.d.	n.d.	0.3	[83]

[1] at 40 °C. [2] not determined.

As inferred from this table, several factors should be pointed out, like the following:

- Viscosity values are mainly influenced by the alcohol used in the second transesterification, as it is the determining factor for the final molecular structure of the biolubricant. There are some exceptions where the raw material plays an important role, as in the case of castor oil, whose majority compound (ricinoleic acid) promotes a considerable increase in viscosity by itself. Thus, biolubricants obtained with complex alcohols usually present an increasing viscosity in that order: 2-ethyl-1-hexanol < NPG < TMP < PE.
- Another important factor is the conversion of the process. Thus, low conversions will imply a mixture with biodiesel (with a viscosity range between 3 and 6, in most cases). That is the reason why the role of catalysts is so important in order to obtain high conversion rates at mild reaction conditions.
- As previously explained, some properties of biolubricants are quite interesting, like high VI and flash points, which encourage the production of these compounds, as explained in the following section.

3. Biolubricant Production

As abovementioned in this review, there are different ways to produce biolubricants through specific chemical routes that will be explained in the following subsections. It should be noted that there are advantages and disadvantages for each route, mainly related to the properties of the final product or the technical/energy requirements.

3.1. Different Chemical Routes for Biolubricant Production

Among the main chemical routes to obtain biolubricants, there are some of them that have been widely studied, such as epoxidation, estolide formation, hydrolysis, hydrogenation (partial or complete), or transesterification/esterification [84].

- Epoxidation: This chemical route is carried out by using hydrogen peroxide proxy acids like formic or acetic acids, and the final product is a peracid that epoxidates double bonds included in fatty acids. This way, unsaturations are removed, which can increase the oxidative stability of biolubricants obtained by this chemical route.
- Estolide formation: These compounds are usually produced by using strong acids (sulphuric acid, methanesulfonic acid, or perchloric acids) as catalysts to activate alkene groups to produce estolides. Thus, they are generated by the bonding of a fatty acid's carboxylic acid functionality to an unsaturation of another fatty acid at relatively low temperatures (around 100 °C). This way, estolides usually have better cold flow properties and longer oxidative stability values compared to the original vegetable oil [43].
- Hydrolysis: It consists of the splitting of triglyceride molecules into fatty acids by using steam or water, implying an endothermic reaction. Some catalysts, such as metal oxides (ZnO), can be used to increase conversion and yield. Also, subcritical water is another interesting way to achieve hydrolysis of vegetable oils without catalyst addition [85].
- Hydrogenation: It normally implies the total or partial reaction with molecular hydrogen, taking place in an exothermic process. Partial hydrogenation can improve the oxidative and thermal stability of original vegetable oils or biolubricants, whereas other properties can be unaltered (such as low-temperature performance, viscosity, and VI, among others). It is usually carried out at relatively low temperatures (150–210 °C) and high pressures (21–35 bar), using some catalysts such as Ni, Pa, and Pt.
- Transesterification: This is the process generally used for biodiesel production from vegetable oils, removing glycerol from the triglyceride molecular structure. More details will be given later in this section.

To sum up, some of the advantages and disadvantages related to the most popular chemical routes to produce biolubricants are included in Table 4. As observed, every chemical route has its advantages and challenges, and in the case of double transesterification, the main problem is related to the possible low oxidative stability of the final product obtained if the raw material presents some specific characteristics like a fatty acid profile with a high percentage of linoleic or linolenic acids (at the expense of oleic or palmitic acids).

In any case, as explained in detail in further sections, these challenges can be easily overcome by the addition of low amounts of antioxidants, among other alternatives, and the possibility of implementing a biorefinery through double transesterification could offset these inconveniences in the long run, as the atom efficiency of these two processes is high, obtaining products that are highly biodegradable (such as fatty acid methyl esters and fatty acid esters). Moreover, other intermediate products obtained in the second transesterification, such as methanol, can be reused in the first transesterification, contributing to the abovementioned atom efficiency. Finally, according to Figure 5, where the publication trends were included, transesterification plays an important and increasing role in the scientific community, contributing to more published articles compared, for instance, with epoxidation. Regarding WCO, this double transesterification would be a suitable way to valorize this waste, as many valuable products are obtained, whose price will mainly depend on the raw material used. Thus, WCO, if collected properly, would be much cheaper than other raw materials studied in the literature (for instance, rapeseed oil), improving the abovementioned economic studies [80]. That is the reason why we will be focused on this chemical route in this review work.

Table 4. Main chemical routes for biolubricant production, including advantages and disadvantages [51,84].

Chemical Route	Details	Advantages	Disadvantages
Epoxidation	Double-bound removal and introduction of an epoxide functional group	Higher OS and lubricity	Viscosity, VO, and PP are usually low
Estolide formation	Estolide generation through different ways, reacting two acidic molecules	Low-temperature reaction, higher OS and lubricity, and better performance at low temperatures	Expensive
Esterification and Transesterification	Use of alcohols to transform fatty acids into fatty acid esters	High VI and flash point, improvement of low-temperature properties	High reaction temperatures. OS depends on the fatty acid profile of the raw material.
Hydrogenation	Reaction with molecular hydrogen	Better OS and lower unsaturation	Possible side reactions

Paying attention to the double transesterification process, Figures 10 and 11 present each transesterification route. Regarding the first transesterification, fatty acids react with methanol (or ethanol, but the former is preferred due to economic costs) to obtain fatty acid methyl esters and glycerol. It should be noted that the fatty acid composition might vary, with R_1, R_2, and R_3 representing the aliphatic chain of certain fatty acids such as palmitic, oleic, or linoleic acids. Thus, the presence of these chains might vary for each fatty acid depending on the nature of the original vegetable oil.

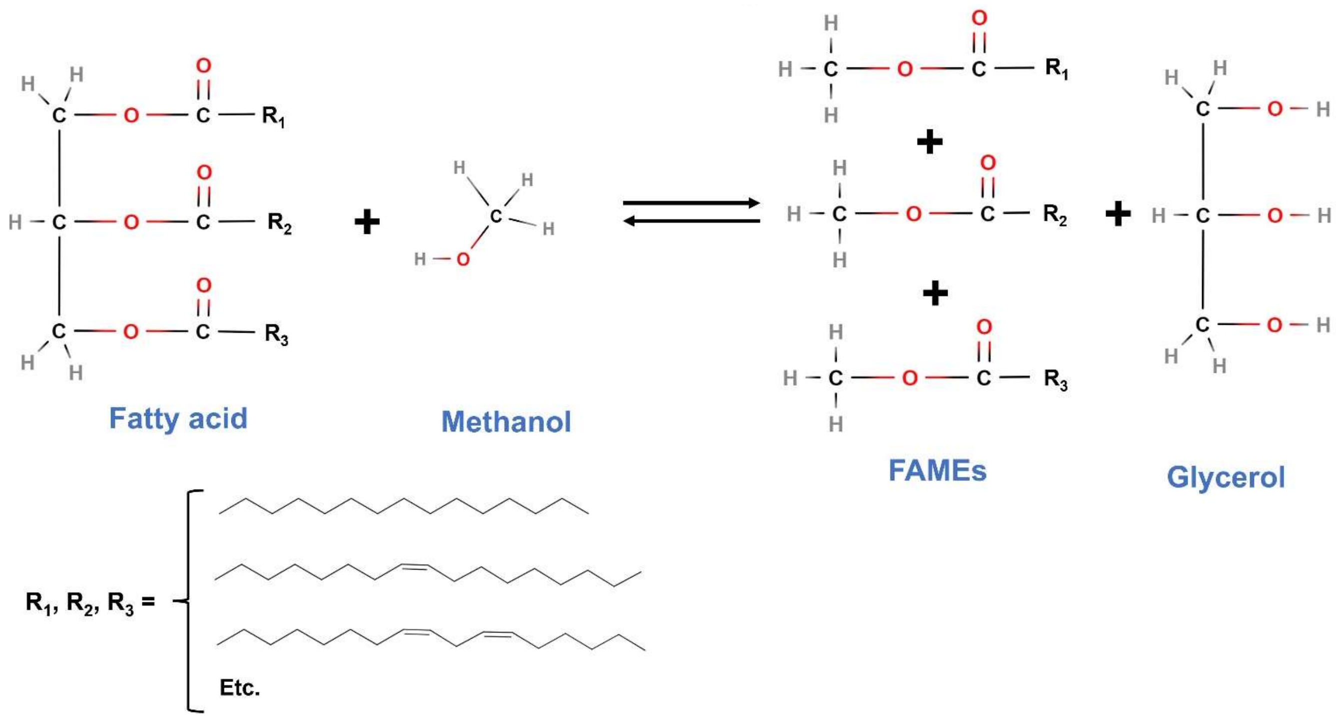

Figure 10. First, transesterification from fatty acids with methanol to obtain FAMEs as an intermediate step for biolubricant production.

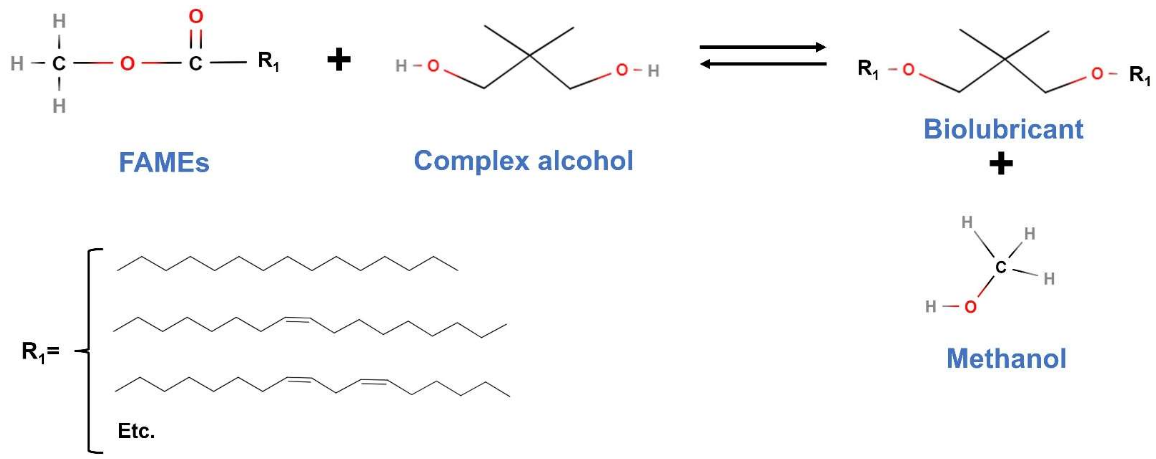

Figure 11. Example of the second transesterification from FAMEs to obtain biolubricants. The alcohol used was neopentyl glycol (2,2-Dimethyl-1,3-propanediol).

Regarding the second transesterification (Figure 11), it is similar to the abovementioned first stage, with the difference of using a more complex alcohol like those observed in Figure 12, which is widely used in the literature [86]. Thus, the final biolubricant is obtained, and methanol is released, which could be reused for the first transesterification process depending on the circumstances of this second transesterification and the recovery technique selected.

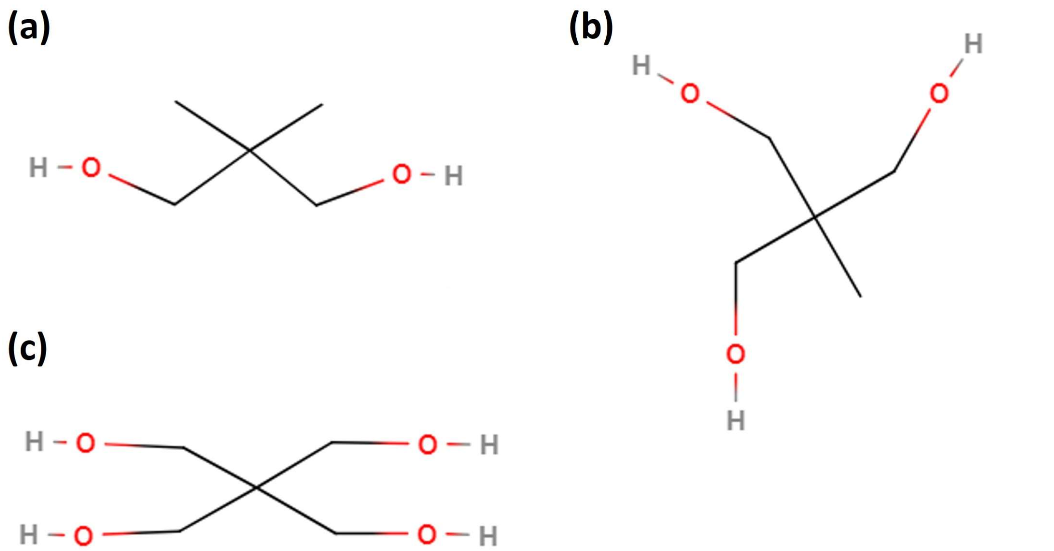

Figure 12. Molecular structure of main superior or complex alcohols used for biolubricant production during the second transesterification of fatty acid methyl esters: (**a**) neopentyl glycol; (**b**) trimethylolpropane; (**c**) pentaerythritol.

For this second transesterification, in order to promote the biolubricant generation, the use of a vacuum (that is, low working pressures) is recommended to remove methanol and shift the equilibrium towards product generation. However, as observed in Figure 12, some complex alcohols used for this purpose present low boiling points or a tendency to sublimation due to the spherical shape of their molecular structure. In that sense, the use of vacuum seems not to be suitable for NG, whereas TMP and PE seem to offer good results when working pressures below 300 mmHg are used.

In any case, the use of the alcohols included in Figure 12 (among others, as there is a wide range of products that can be used in this double transesterification) allow the production of biolubricants with endless opportunities, as it will be observed in further sections where the properties of biolubricants depending on the kind of alcohol (among other factors like conversion or the use of different raw materials) will be discussed, especially regarding viscosity and the subsequent use for industrial purposes of the biolubricant.

During the second transesterification, the complex alcohol must be dissolved in the reaction medium, that is, FAMEs, and due to dispersion phenomena and mixing, the reaction usually starts with a low reaction rate at the beginning. Once mixing is complete, the reaction rate will be increased, requiring the reaction a specific time to be carried out. If the reaction time is extended, it can proceed backward (that is, products can react to generate the reagents). That is the reason why factors such as temperature, reaction time, vacuum, etc., are essential to be optimized. Otherwise, low yields and efficiency can be found during the process.

As observed in Figures 10 and 11, these consecutive chemical routes can be perfectly coupled in a biorefinery context, obtaining several interesting products and reusing some intermediate by-products, as explained in the following section.

3.2. Double Transesterification as an Interesting Proposal for a Biorefinery Based on Vegetable Oils

As explained in the previous section, double transesterification presents a higher complexity compared to other simpler chemical routes. Nevertheless, apart from fatty acid esters that can be used as biolubricants, many different products are obtained during the whole process, which can be used for different purposes (see Figure 13):

- Fatty acid methyl esters: As a result of the first transesterification, FAMEs are obtained, which can be used as fuels in Diesel engines, being the perfect replacement for traditional fuels used for that purpose. In that sense, compared to the UNE-EN 14,214 standard [87], many of its requirements are clearly complied with by biodiesel, especially concerning key aspects such as viscosity or cold filter plugging point (CFPP), which are essential for the correct performance in a Diesel engine. However, in many cases, and due to the same factors affecting biolubricants, the oxidative stability of FAMEs is not high enough [88,89] (not reaching 8 h, which is the lower limit of the European standard, for instance), requiring the use of alternatives such as antioxidant addition (mainly TBHQ, PG or BHA) or genetically modified (GM) crops, among others [63,90,91]. In any case, it is a very important product obtained in this process, which can increase the valorization of the whole biorefinery [92].
- Glycerol: It has been one of the most abundant and versatile by-products obtained during biodiesel production. Comparing the similarities of biodiesel and biolubricant production (indeed, FAME production is the initial stage for further biolubricant synthesis), it is no wonder that glycerol could play an important role in this case. Depending on the degree of purity of glycerol, it can be used in different ways, such as an energy source (through dry or steam reforming) or the precursor of interesting products like acrolein, propanediols, or carboxylic acids, along with other products with a great interest in the pharmaceutical industry) obtained from routes such as hydrogenation, oxidation, or esterification [93–96]. If the recent trend in biodiesel generation, along with the possible incorporation of biolubricant production through double transesterification, glycerol production is expected to increase, with the subsequent opportunity for its valorization through the abovementioned chemical routes. This way, a feasible technology applied to glycerol could be synthesis gas generation (a mixture of hydrogen and carbon monoxide at different ratios), which could produce green fuels as glycerol is generally obtained from raw materials [97].
- Methanol: One of the byproducts generated during the second transesterification to produce biolubricants is equally interesting, as it can be reused in the first transesterification process, where it is one of the reagents used. Thus, the concept of circular economy is really connected to this process, which could make a biorefinery based on vegetable oils more efficient. However, some factors should be taken into account during this process, like the possibility of using a vacuum for a high biolubricant

production yield, which could make the recovery of methanol more difficult or less economically feasible.

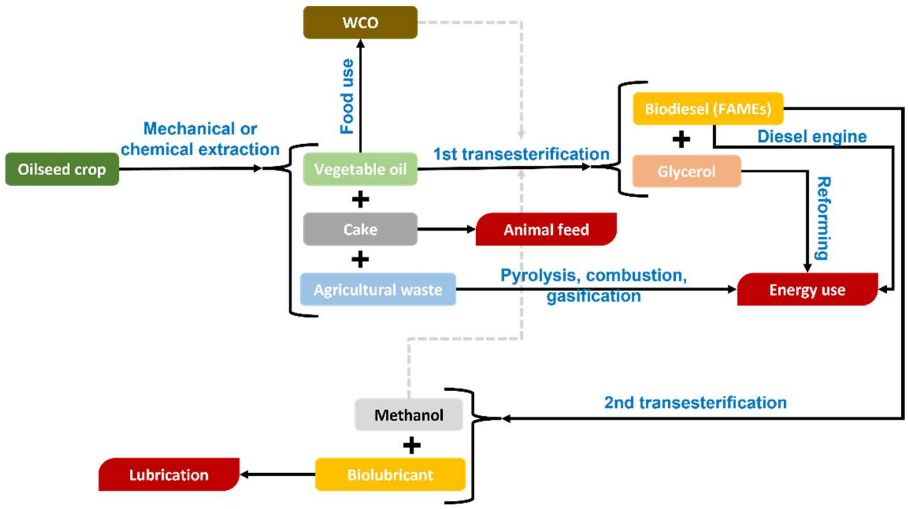

Figure 13. Biorefinery proposal according to the possibilities of oilseed crops. Dashed lines indicate the reusability of some products, whereas red boxes indicate the final use of each product taking part in this process. In blue are the main steps for each product.

Consequently, double transesterification could be a suitable solution for the implementation of a biorefinery from oilseed crops (or vegetable oils, VO), where plenty of products (apart from the abovementioned ones) can be valorized. In that sense, this process presents some similarities compared to other biorefineries, like the following [98]:

- Natural raw materials or wastes obtained in agricultural practices or food industries are normally used.
- Different products that are normally biodegradable are generated, as the raw materials are naturally obtained. The chemical transformations do not normally imply considerable changes in the molecular structure of the subsequent products (biodiesel and biolubricants), which makes these products (in case of spillage) easily assimilable by microorganisms.
- These products can be directly used for energy production or further synthesis, or they can be upgraded to different degrees. Thus, the versatility of this technology is a strong point to compete with traditional refineries.
- Some of the byproducts generated can be directly (or indirectly through purification processes) reused in the same process, which is one of the key points of the circular economy.
- With regard to these points, a biorefinery with these characteristics would perfectly fit the concept of green chemistry and circular economy, which is highly regarded by governments and society in general.

These particularities are essential to understand the role of biolubricants in sustainability and green policies, as it contributes to a circular economy production, with a high atom efficiency as most products can be directly used or reused in the process, with a considerable decrease in evolved products (or pollutants) to the environment. In that sense, some works have pointed out the potential of soy for its implementation in a biorefinery context, whereas food waste valorization (where WCO could be included) has also been assessed in previous studies [99–102]. It should be noted the possibility of implementation of this technology in previous biodiesel industries, as double transesterification could share equivalent processes and facilities that could be suitable for the industrial growth of traditional biodiesel plants, as previously considered by other authors [103].

One of the essential points of this review is the use of a catalyst to improve the efficiency of biolubricant production (in a biorefinery context) to compete with the equivalent and traditional processes to obtain lubricants. In that sense, high conversion of the two main reactions taking place in Figure 13 (that is, the first and second transesterification) at low reaction temperatures and times are required, which can be achieved by the use of catalysts. It should be noted, even though this is not the main purpose of this review, that catalysts are also present in other chemical routes included in this biorefinery, as in the case of pyrolysis, combustion, and gasification of agricultural waste or steam reforming of glycerol. In these cases, heterogeneous catalysts are generally used, with popular catalysts such as nickel catalysts supported on alumina with different promoters to increase their useful life and performance [104,105]. In the following section, a thorough study of this subject will be carried out, as catalysts play an essential role in the improvement of competitiveness of this technology compared to refineries based on petrol.

4. The Use of Catalysts in Biolubricant Production

As in any technology, production, or process, there are some aspects that should be considered to make them economically effective and efficient. In the case of green chemistry routes or circular economy procedures, effectiveness is especially important, as this will be the determining factor to make these processes competitive compared to previous or traditional technologies (for instance, based on petrol). That is the reason why economic and life-cycle assessments are so important in these cases. Consequently, every detail counts to make the process more efficient, and the role of catalysts in that sense is essential.

Biolubricant production through transesterification could take place in supercritical conditions, but the use of catalysts is generally accepted for this purpose. Thus, catalysts can contribute to a decrease in activation energy, which in turn could afford a decrease in chemical reaction conditions related to energy costs, mainly having to do with temperature. Regarding the main catalysts used in transesterification, there are three kinds of catalysts: homogeneous, heterogeneous, and biochemical (mainly lipases).

- Concerning homogeneous catalysts, they are usually classified as acidic and alkaline catalysts, which are normally more effective and provide faster reaction rates. Some examples of acidic catalysts are hydrochloric, sulfonic, sulfuric acids, etc., whereas examples of alkaline catalysts are sodium and potassium hydroxide and methoxide, among others. In the case of the latter, low moisture and FFA content in biodiesel is recommended to avoid a decrease in yield or side reactions. Figure 14 shows the main mechanism taking place when basic homogeneous catalysts are used. This way, the role of the catalyst was to generate the corresponding alkoxide (from neopentyl glycol, for instance) to carry out a nucleophilic substitution in the carboxyl group, with the final generation of the biolubricant and the release of methoxide and, subsequently, methanol.
- As far as heterogeneous catalysts are concerned, there are also acid and base catalysis, such as metal complexes, metal oxides, zeolites, membranes, or resins [106]. In this case, mass transfer phenomena, along with some important properties of the heterogeneous catalyst (such as porosimetry or reusability), should be taken into account in industrial design.
- Regarding lipases, their natural function is the hydrolysis of oils and fats to produce glycerol and free fatty acids, being one of the most resourceful enzymes in biocatalysis, as they are present in all organisms and their variety can offer different characteristics. Lipases can be used for different purposes and chemical routes, such as esterification, transesterification, acidolysis, or amidations, among others, being stable in different solvents, such as aqueous, organic, or ionic [107–109]. In that sense, as explained in previous studies, transesterification with methanol to produce biodiesel has been successfully carried out, offering satisfactory results [64,110,111]. This way, considering the equivalence between this chemical route and double transesterification to produce biolubricants, its possible use for this purpose seems to be feasible, as explained later on.

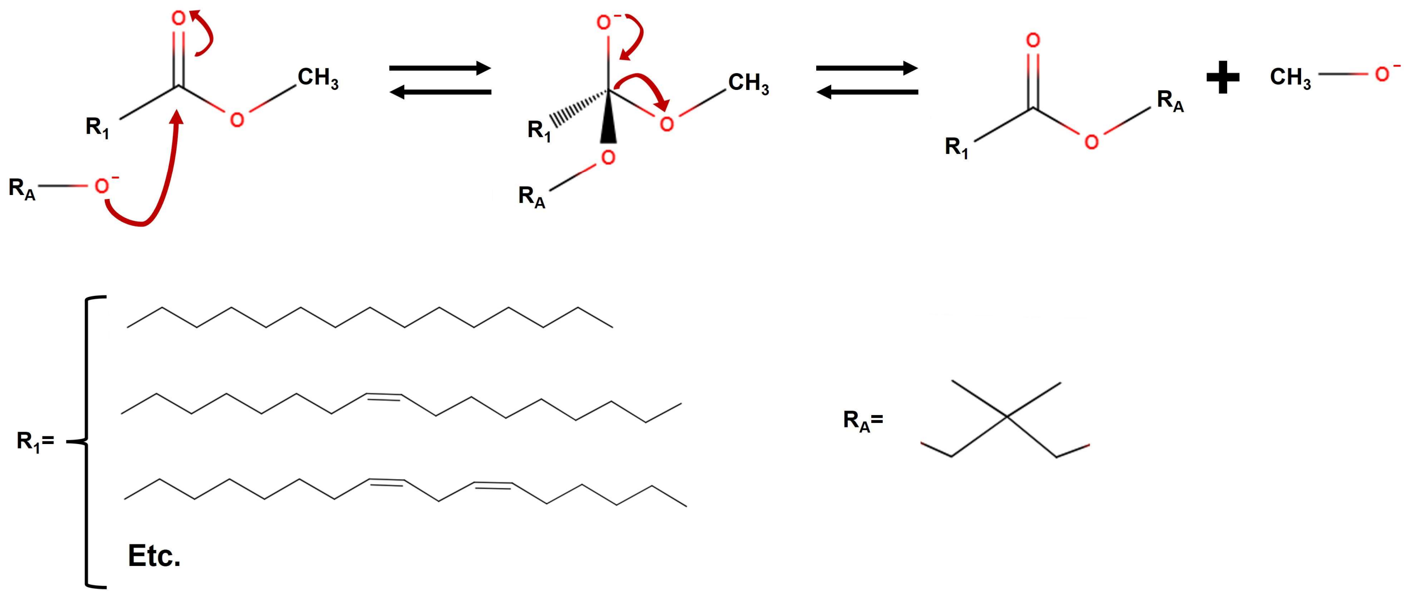

Figure 14. Mechanism of homogeneous basic catalysis for the second transesterification (FAME conversion to biolubricants).

This way, many research works carried out comparative studies with different kinds of catalysts or catalyst doses, proving the suitability of their use in biolubricant production and obtaining high production yields, as observed in Table 5 (homogeneous catalysis) and 6 (heterogeneous catalysis) for the case of double transesterification. As observed, different kinds of catalysts have been used for biolubricant production, but chemical reactions with heterogenous catalysts usually require longer reaction times and higher catalyst concentrations, not reaching, in some cases, high conversions compared to homogeneous catalysts. As previously explained, these catalysts were used for a wide range of raw materials, including WCO, which was successfully used in homogeneous and heterogeneous catalysis, proving the utility of this waste to be used to produce biolubricants.

One of the main issues related to the use of catalysts during biolubricant production is the subsequent purification process. It should be taken into account that, depending on the kind of catalyst (homogeneous or heterogeneous), this process could be drastically different:

- Regarding homogeneous catalysts, their removal from the final biolubricant might be complicated, as they are easily dissolved in the final product, increasing their level in some metal elements that could contribute to the acceleration of some degradation phenomena that can take place during storage (for instance, Na and K content due to catalyst addition could contribute to auto-oxidation acceleration). Thus, if a typical biodiesel purification (through successive washing steps) is considered an equivalent process to be carried out in this case, it should be noted that hydrolysis could take place, which is an undesirable effect. In that sense, some alternatives could be chosen, like the avoidance of catalyst removal by adding some additives to increase the oxidative stability of biolubricants or the use of more expensive alternatives, such as ion exchange columns.
- In the case of heterogeneous catalysts (see Table 6), the separation process is quite simple, mainly through filtration after biolubricant production. In that sense, porous catalysts could be an interesting starting point, as their interaction with raw materials is higher [60,112,113]. However, the use of these catalysts is usually related to some inconveniences, such as lower effectiveness compared to homogeneous catalysts or the low current reusability of these products, which presents considerable room for improvement in biodiesel and biolubricant synthesis.

Table 5. Studies related to catalytic conversion of vegetable oils to obtain biolubricants through double transesterification (using homogeneous catalysts).

Raw Material and Catalyst	Chemical Conditions [1]	Conversion, %	Reference
Rapeseed, corn, and sunflower mixture, and WCO with titanium isopropoxide	Transesterification with 2-ethyl-1-hexanol at 160 °C, 1.5% catalyst, and 1:1 molar ratio for 60 min	>96.5	[33]
Palm oil with H_2SO_4	Esterification of palm oil fatty acids with NPG at 138 °C, 1.12% catalyst, and 1:2.26 molar ratio for 4.79 h	87.6	[114]
Elaeis guineensis kernel oil with H_2SO_4	Transesterification with di-TMP at 150 °C, 1.7% catalyst, and 1.6:1 molar ratio for 4.6 h	79	[115]
Methyl oleate with K_2CO_3	Transesterification with TMP at 120 °C, 1.5% catalyst, and 4:1 molar ratio for 240 min	95.6	[116]
Babassu oil with sodium methoxide	Transesterification with TMP at 65 °C, 1.0% catalyst, and 3:1 molar ratio for 6 h at 700 mmHg	>90	[117]
Palm oil and sodium methoxide	Transesterification with pentaerythritol at 158 °C, 1.19% catalyst, and 4.5:1 molar ratio for 60 min	40.13	[77]
High-oleic safflower and sodium methoxide	Transesterification with pentaerythritol at 160 °C, 1.0% catalyst, and 1:1/3 molar ratio for 120 min (working pressure 400 mmHg)	>94	[67]
WCO and sodium methoxide	Transesterification with pentaerythritol at 160 °C, 1.0% catalyst, and 1:1/3 molar ratio for 120 min (working pressure 260 mmHg)	92.6	[34]
WCO and zinc acetate	Transesterification with different alcohols (1-heptanol, 2-ethyl hexanol, and neopentyl glycol) at 160 °C, 3.0% catalyst, and different molar ratio for 240 min	n.d.	[66]
Cardoon oil and sodium methoxide	Transesterification with NG at 130 °C, 1.5% catalyst, and 1:1 molar ratio for 120 min	>95	[76]
High-oleic safflower and sodium methoxide	Transesterification with TMP at 140 °C, 1.0% catalyst, and 1:1 molar ratio for 90 min (working pressure 400 mmHg)	>92	[118]
Jatropha oil and sodium methoxide	Transesterification with TMP at 200 °C, 1.0% catalyst, and 3.9:1 molar ratio for 3 h (working pressure 10 mbar)	47	[119]
Rapeseed and sodium methoxide	Transesterification with TMP at 120 °C, 1.5% catalyst, and 1:1 molar ratio for 90 min	>99	[80]
High-oleic safflower and sodium methoxide	Transesterification with TMP at 100 °C, 0.3% catalyst, and 1:1 molar ratio for 120 min and a working pressure of 210 mmHg	>94	[79]
Fish oil residue with sodium ethoxide	Transesterification with TMP at 100–140 °C under vacuum	84	[120]
Litsea cubeba kernel oil with KOH	Transesterification with TMP at 130 °C, 1/4:1 molar ratio for 60 min, and different working pressures	92	[121]
Cottonseed oil with sodium methoxide	Transesterification with TMP at 144 °C, 0.8% catalyst, and 1/4:1 molar ratio for 10 h at 25 mbar	>90	[122]
Jatropha oil with sodium hydroxide	Transesterification with ethylene glycol at 150 °C, 1.2% catalyst, and 2:1 molar ratio for 120 min and vacuum	98	[57]
Mustard seed oil with KOH	Transesterification with 2-ethyl-1-hexanol at 70 °C, 2% catalyst, 2:1 molar ratio for 65 min at 0.05 bar	93	[75]

[1] Otherwise explained, these transesterifications are with FAMEs. Alcohol/FAME ratios are expressed.

Table 6. Studies related to catalytic conversion of vegetable oils to obtain biolubricants through double transesterification (using heterogeneous/biochemical catalysts).

Raw Material and Catalyst	Chemical Conditions [1]	Conversion, %	Reference
Castor oil and lipase	Transesterification with TMP at 40 °C, 0.4% catalyst, and atmospheric pressure, using a pervaporation membrane to remove CH_4	59	[123]
Soybean oil and lipase	Esterification with NG and TMP at 45 °C, 4% catalyst, and 6 h	90	[124]
Palm oil and solid acid catalyst	Esterification with NG at 180 °C, 2% catalyst, 0.5:1 molar ratio and 4 h	85	[125]
Palm kernel oil with lipase	Transesterification with isoamyl alcohol at 45 °C, 4:1 molar ratio for 54 h	99	[83]
Palm oil and lipase	Esterification with TMP at 130 °C, 3% *w*/*w* catalyst, 3.45:1 molar ratio, 15.25 mbar for 48 h	82	[126]
WCO with CaO derived from waste cockle shell	Transesterification with TMP at 130 °C, 4% *w*/*w* catalyst, 3:1 molar ratio for 4 h	97	[82]
WCO with CaO	Transesterification with ethylene glycol at 130 °C, 1.2% catalyst, 3.5:1 molar ratio for 1.5 h	94	[127]
Palm oil with mixed oxides of Ca and Sr on CaO	Transesterification with TMP at 180 °C, 1% *w*/*w* mixed oxides of Ca and Sr catalyst with 5% *w*/*w* SrO on CaO, 2 mbar and 240 min	88	[128]
Soybean oil with Zn Al hydrotalcites	Transesterification with TMP at 140 °C, 5% catalyst, 4:1 molar ratio for 2 h	77	[129]
WCO with K_2CO_3-hydrotalcite	Transesterification with TMP at 160 °C, 2% catalyst, 3:1 molar ratio and 300 Pa for 2 h	80.6	[130]

[1] Otherwise explained, these transesterifications are with FAMEs. FAME/alcohol ratios are expressed.

It should be noted that there are other works dealing with the transesterification of vegetable oils (castor, coconut, and palm kernel oils) with methanol to obtain fatty acid methyl esters (that is, biodiesel), but for a different purpose, as thanks to the use of some additives biolubricants with different viscosity values were satisfactorily obtained [131]. In that sense, the biolubricant obtained from castor oil presented the highest viscosity value due to the high percentage of ricinoleic acid in the original oil, whose OH- group contributed to the increase in viscosity.

5. Influencing Factors on Quality Parameters of Biolubricants

As explained in previous sections, there are some quality parameters that are vital to understanding the right performance of biolubricants for industrial applications. Thus, a good biolubricant should present repeatable or stable properties once it is produced, stable properties during storage, and specific industrial use (unalterable due to circumstances such as auto-oxidation). Figure 15 shows the main influencing factors on biolubricant quality parameters, which are closely related to each other, usually presenting opposite effects depending on the circumstances. For instance, the use of a catalyst can contribute to a higher biolubricant yield, which is positive regarding a product with a stable composition, whereas high amounts of homogeneous catalysts can imply further auto-oxidation effects if they are not properly removed from the final product, with the subsequent decrease in oxidation stability. Additionally, some vegetable oils could present functional groups or molecular structures (such as branching), which could provide an interesting viscosity value for a specific industrial use, whereas the presence of unsaturations could worsen the oxidation stability of the final biolubricant.

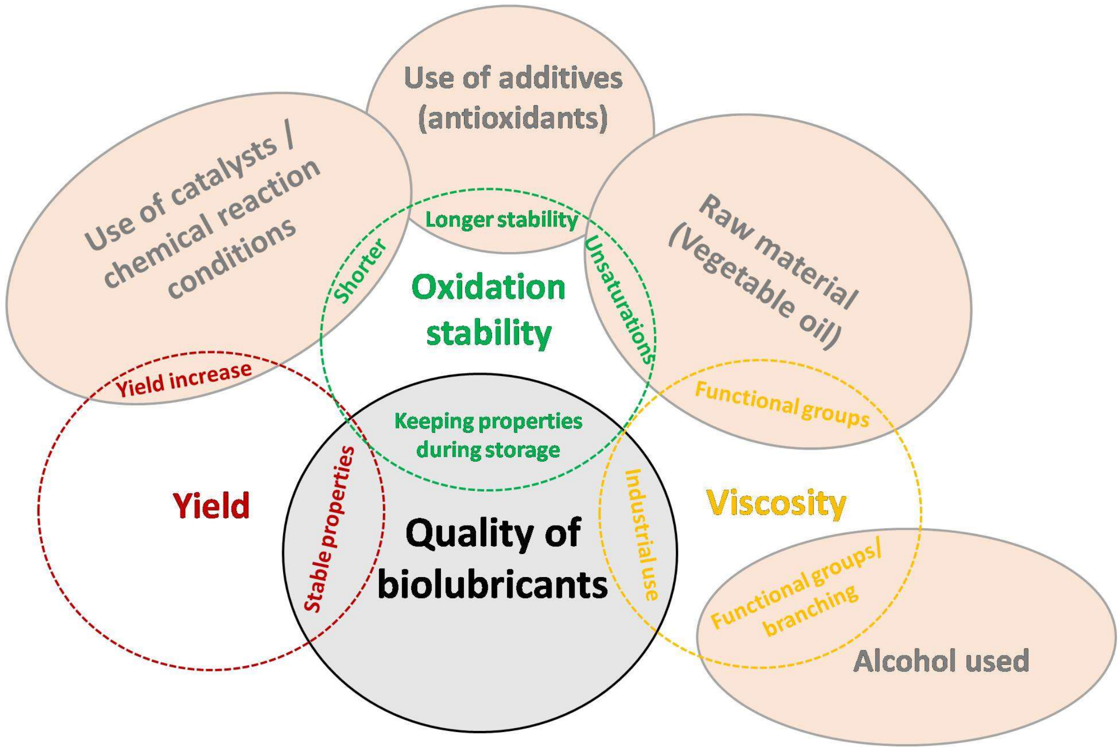

Figure 15. Main factors (in orange circles) affecting quality parameters of biolubricants obtained through transesterification.

A thorough explanation of Figure 15 is included in the following subsections. This way, the main quality parameters considered were yield or conversion, oxidation stability, and viscosity, which are vital to understanding the performance of a biolubricant:

5.1. Yield or Conversion

It is important to obtain a high conversion of biolubricant from vegetable oil or biodiesel, as its separation from the corresponding raw material is difficult, obtaining a mixture with combined properties like viscosity. Indeed, in previous studies, there was a good correlation between conversion and viscosity in the reaction medium for biolubricant production from some vegetable oils like high-oleic safflower biolubricant [118]. This way, high conversion of biodiesel or vegetable oil can provide more fixed viscosity values and, therefore, the characteristics of a biolubricant can be more predictable. On the other hand, the presence of biodiesel in the final biolubricant could imply a drastic decrease in viscosity in the medium, as the differences between biodiesel and biolubricant viscosities (much lower for the former, with 3.5 to 5.0 cSt) are considerable. That is the reason why high conversions are especially important in biolubricant production.

5.2. Oxidative Stability

As thoroughly explained, it is another important parameter that is vital to keep the main properties of biolubricant during storage, where auto-oxidation processes can take place. Thus, auto-oxidation can generate by-products like free fatty acids or polymers, which increase acidity (and the subsequent corrosion in containers or machines) and viscosity (with the subsequent change in its specific use), respectively. In that sense, as observed in the case of cardoon biolubricant (obtained through double transesterification with methanol and 2,2-dimethyl-1,3-propanediol) during storage, its viscosity increased up to 16% during storage for 12 months at room temperature, with a considerable decrease in viscosity index (which is also an undesirable effect) [76].

5.3. Viscosity

As previously stated, viscosity is highly related to the specific use of biolubricants in industry. Indeed, it can be considered the most important characteristic of a biolubricant, as viscosity can affect some functions, such as lubrication or sealing. Thus, depending on its viscosity, a biolubricant can be used in different areas, such as Diesel engines or machines in the textile industry.

Some of the key factors affecting these quality parameters are the chemical reaction conditions (where the use of catalysts plays a vital role), the use of additives, the raw material, and the alcohol selected. These factors can affect these quality parameters in different ways, or they can affect multiple quality parameters. For instance, the raw material can affect oxidation stability or viscosity, mainly depending on fatty acid composition.

5.4. Use of Catalysts/Chemical Reaction Conditions

As expected, the use of catalysts promotes the decrease in activation energy of a chemical reaction, which facilitates the completion of transesterification. Thus, on the one hand, the use of catalysts is positive as conversion increases, making the composition of the final biolubricant stable and predictable.

As explained in previous sections (see Tables 5 and 6), the use of catalysts might vary (from homogeneous to heterogeneous, with a wide range of compounds for each case), and in the case of esterification and transesterification, there seems to be a clear trend about the use of catalysts, with a special preference for homogeneous catalysts including sodium methoxide and ethoxide or sodium and potassium hydroxides, which are relatively cheap and easily obtained. These catalysts are usually added at low concentrations (from 0.3 to 2% w/w of total mass), which contributes to a low-cost impact in biolubricant production, obtaining high yields (at least 90% in most cases).

However, the use of homogeneous catalysts (usually containing Na and K), which are normally difficult to remove from the final biolubricant, can worsen the oxidative stability of biolubricants, as the presence of metal traces can act as catalysts for oxidation during storage. In that sense, the use of heterogeneous catalysts can present an additional advantage, like their easy removal from the chemical medium. Thus, the use of lipases, hydrotalcites, or CaO could avoid this problem, and even though their addition is relatively low (from 1% to 5% w/w, see Table 6), their costs are usually higher compared to homogeneous catalysts (which can explain the lower amount of research works about this matter). Nevertheless, they present an interesting advantage, like the total removal from the reaction medium, which would avoid the presence of catalysts in the final biolubricant and the abovementioned problems. However, the yields by using these catalysts are relatively low (up to 90% in many cases), and their reusability is limited, which is an interesting research line in the future, as their advantages could offset these inconveniences.

On the other hand, chemical reaction conditions (apart from catalyst concentration) can affect the final characteristics of the biolubricant. For instance, high temperatures during biolubricant production can affect its oxidative stability, as explained in previous studies. To avoid that, the use of a vacuum, when possible, is recommended to remove methanol released during the second transesterification, with the subsequent shift towards product generation at lower temperatures or catalyst concentrations [79].

5.5. Use of Additives (Antioxidants)

Apart from other additives that can improve the tribological performance of a biolubricant, as in the case of nanoparticles (for instance, Fe_3O_4 nanoparticles) to reduce the coefficient of friction between surfaces [132,133], we should pay attention to the use of antioxidants in final formulations. Thus, these antioxidants (both natural and synthetic) mainly affect oxidation stability in biodiesel and biolubricant samples. The use of products like propyl gallate (PG) or tert-butylhydroquinone (TBHQ) could increase oxidation stability, delaying some processes like free fatty acid generation or polymerization, which alter acidity and viscosity, respectively [67]. Thus, the use of TBHQ in WCO biolubricant showed a considerable increase in oxidative stability up to 10 h of induction point with very low quantities of antioxidants (2500 ppm) [34]. Figure 16 shows the molecular structure of some of the most popular antioxidants according to the literature in order to enhance the oxidative stability of biodiesel and biolubricants. As observed, all of them share one thing in common, that is, the aromatic ring that is responsible for free radical neutralization and the subsequent disruption (or delay) of the auto-oxidation process. It should be noted that once they react with free radicals, their molecular structure and effectiveness decrease, with the subsequent need to assess the amount of these compounds in biodiesel and biolubricant through analytical techniques. In that sense, the use of voltametric techniques seems to be effective in understanding the effect of antioxidant addition during oxidation processes [34,63,134].

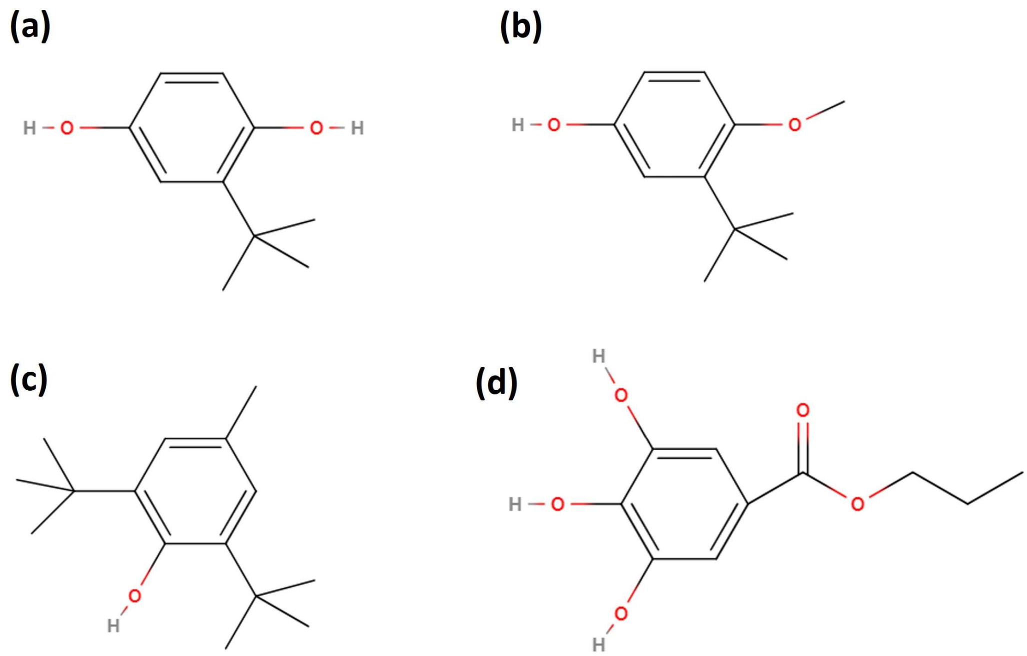

Figure 16. Molecular structure of some antioxidants used to extend the oxidative stability of biodiesel and biolubricants: (**a**) tert-butylhydroquinone (TBHQ); (**b**) butylated hydroxyanisole (BHA); (**c**) butylated hydroxytoluene (BHT); (**d**) propyl gallate.

In that sense, the use of antioxidants could offset the negative effect of trace metals included in biolubricants after the purification process, mainly due to homogeneous catalyst addition, although some removal techniques would be recommended to reduce Na and K content in biolubricants, such as the use of exchange-ion columns.

5.6. Raw Material (Vegetable Oil)

The raw material mainly affects, among other characteristics, the oxidation stability of the final product obtained. This is due to the fatty acid composition of vegetable oils, which are transformed into fatty acid methyl esters or fatty acid esters. Thus, the presence of double bonds can promote the generation of free radicals, the main starting point for auto-oxidation, decreasing oxidative stability. For instance, in the case of biolubricants obtained through double transesterification with methanol and 2-ethyl-1-hexanol from different vegetable oils (rapeseed, corn, and sunflower mix "seed oil" and WCO), different oxidative stability values were observed (with the following order from most to less stable: rapeseed, seed oil, and WCO) due to the different fatty acid content of the raw materials (rapeseed oil presented high oleic content, exceeding 60%, whereas seed oil and WCO had 31% and 27%, respectively [33]. Also, if fatty acids present some special functional groups like hydroxyl in the aliphatic chain (as in the case of ricinoleic acid), the final product obtained during the first transesterification could present a considerable viscosity, which can be used as a biolubricant for specific purposes [55].

5.7. Alcohols Used

Concerning transesterification, the superior alcohol used (usually trimethylolpropane and pentaerythritol, among others) plays an important role, as it is usually a polyol that, after transesterification with fatty acid methyl esters, generates a polyester that increases the viscosity of the final substance obtained. This way, the presence of more functional groups like hydroxyl in the polyol promotes the generation of more complex esters, increasing the possibility of higher intermolecular interactions and, therefore, a higher resistance to flow (in other words, a higher viscosity). Additionally, the stereochemistry of this second transesterification can make the reaction between hydroxyl groups in the superior alcohol and the corresponding fatty acid methyl ester require higher amounts of catalysts or temperature. In essence, the kind of alcohol equally affects the chemical conditions of the second transesterification and the yield of this chemical reaction.

As observed, these conditions are interrelated, and intermediate solutions might be advisable for sustainable and efficient biolubricant production. Indeed, in the following section, a brief exposition of works dealing with this subject (that is, techno-economic analyses and patents) is included to enhance the possibility of a real implementation of double transesterification at an industrial scale.

6. Techno-Economic Analyses Applied to Biolubricant Production in a Biorefinery Context and Patents

The role of a biorefinery can be attractive from an economic point of view if the efficiency of the process is comparable to equivalent industries based on petroleum. For that purpose, a correct design of a biorefinery should involve accurate data to estimate capital costs, using adequate indicators (especially for capital cost estimations) to carry out a suitable economic assessment [135].

Even though the industry of biobased products shows multiple economic and environmental benefits, there are still some challenges (especially in emerging industrial and developing countries) that should be addressed, like possible high production costs, lack of funds to invest in these kinds of technologies, inadequate policy support, fluctuating oil or feedstock prices, logistic performance, industrial competitiveness, etc. [136,137], considering several aspects such as logistics, existing infrastructure, feedstock supply chains, market opportunities, socio-economic issues and political context [137]. To overcome this inconvenience and concerning the feasibility of the implementation of biolubricant production based on vegetable oils, there are recent studies that assess the technical and economic issues that this green process must face to compete with equivalent processes based on petroleum.

As expected, the versatility and wide variety of biolubricant production processes implied the publication of dispersed works focused on specific aspects related to techno-economics. In any case, and even though there is a lack of these kinds of studies (which could imply an interesting research niche to contribute to the spread of knowledge), these research works share some points in common, like the following:

- The role of raw materials is essential to determine the marketability of biolubricants, as the costs related to agricultural practices (such as harvest), along with vegetable oil production and purification, usually imply a considerable percentage of fixed costs in a biorefinery based on vegetable oils. For instance, when it comes to estolide synthesis from oleic acid, the raw material implied 23.7% of total operating costs (around $6742 \cdot 10^3$ US$ to produce 1000 tons per year) [138], whereas, in the case of branched-chain glycerides production, this percentage was 18.2%, with total operating costs of $2247 \cdot 10^3$ US$ per year to produce 100 MT [139]. With this regard, again, the characteristics of WCO could be interesting, as many of the above-mentioned steps could be skipped, considerably reducing the costs related to the raw material.

- One of the main strong points of biolubricant production at an industrial scale is its integration in a biorefinery context, where multiple products can be obtained with the aim of adapting the performance of the biorefinery according to environmental policies or demand, among other factors.
- Another interesting aspect to consider is the reaction temperature (among other operating conditions), which usually takes a considerable percentage of energy consumption during biolubricant production and, therefore, is an important contribution to production costs. In that sense, a simple decrease of a few degrees could result in large savings. As proved in some abovementioned works (where the optimum reaction temperature was decreased at least 20 °C for biolubricant production from high-oleic safflower oil), reaction temperature can easily be reduced by using some improvements such as the vacuum (when this technique is possible, as in many cases it can remove some reagents in the reaction medium like complex alcohols that tend to sublimate due to their molecular structure, such as 2,2-dimethyl-1,3-propanediol for double transesterification) or the use of catalysts (both heterogeneous and, homogeneous, where a considerable decrease in reaction temperature was observed) [80].
- Indeed, the use of catalysts and their improvement related to their use in chemical routes to produce biolubricants has been widely studied in the literature. In that sense, their contribution to an increase in efficiency could be related to three aspects: First, the study of their optimum addition to avoiding extra costs; Second, the possibility of reuse (especially in the case of heterogeneous catalysts) or the purification process of biolubricants to remove homogeneous catalysts; Third, the effectiveness in reducing or improving chemical parameters that can contribute to energy or cost saving.
- Another interesting aspect to be considered is the possible real implementation of this technology by using pre-existing ones. Specifically, the use of double transesterification seems to be an interesting choice, as many of the facilities used for biodiesel production (that is, the first transesterification of fatty acids) could be perfectly adapted to the second transesterification process by adding some specific changes depending on the desired kind of biolubricant. Therefore, as similar facilities are required, the equipment acquisition would be easier and cheaper compared to other specific or customized facilities. Also, other chemical routes, such as epoxidation, could be easily adapted to this purpose, as explained to produce a biolubricant based on soybean oil [103].
- Finally, and even though some biolubricant productions could not be economically feasible at the industrial level, there is one interesting and favorable point to tilt the balance in favor of this green technology: the high environmental value and the favorable policies carried out by national and international agencies. Thus, the market value of these products could be higher compared to traditional lubricants, as there is an increasing demand for green products by customers in general. This fact could offset the initial and disadvantageous cost balance when these kinds of large-scale facilities are used.

Thus, Table 7 shows the main works related to techno-economic assessment applied to biolubricant production, even though it plays a secondary role within the biorefinery context of the corresponding vegetable oil.

As observed, these works point out the feasibility of biorefineries based on vegetable oils or agricultural wastes such as vegetable pulp, showing promising results that will encourage further studies in the near future.

Another remarkable point is the knowledge about the current patents about biolubricant production (see Table 8), specifically dealing with transesterification processes. In that sense, this is an interesting way to assess the practical application of a scientific subject or field, as patents are traditionally linked to the profitable exploitation of interesting findings, exploring their possible implementation at the industrial level.

In general, many of the chemical routes mentioned in this review are equally covered in patent registration (such as hydrolysis, epoxidation, and, especially, estolide formation, whose production was expensive, and these works are devoted to obtaining cheaper ways to exploit this concept), which points out the parallelisms with the scientific literature. Also, the use of multiple raw materials proves the versatility of this process. In this case, it should be noted the use of WCO, an interesting waste as explained in the introduction section, that is equally attractive to industrial processes (not only at the research level).

Table 7. Studies devoted to techno-economic assessment related to biolubricant production from vegetable oils.

Description	Details	References
Biolubricant production from rapeseed oil through double transesterification with methanol and TMP	High conversions were obtained for first (97%) and second (99%) transesterification and a reactor was designed (12 m^3) for industry level (production = 5550 $tm \cdot y^{-1}$)	[80]
Techno-economic analysis of biolubricants through different chemical routes	Non-edible oils (karanja, jatropha, WCO) through transesterification with TMP were proved as one sustainable way to obtain biolubricants for food lubrication and as automotive oils	[138]
Study of different biorefineries (based on first to fourth-generation raw materials, including edible and non-edible oils) for their design at different scale levels	The authors point out the importance of a suitable design of biorefineries depending on the purity and use of the final product obtained. Thus, high-quality products such as pharmaceutics are more adequate for small scales, whereas energy products could be useful at industrial scale	[140]
Biorefinery based on non-food agricultural feedstocks (vegetable pulp).	High lifecycle greenhouse gas savings can be obtained (up to 80%) if biofuels and biolubricant production are coupled in a biorefinery context	[141,142]
Biorefinery based on castor oil to produce biodiesel and multiple products, including a biolubricant	This biorefinery was mainly based on biodiesel production (exceeding 40% of total production) as well as other products, pointing out that multi-objective optimization is essential to obtain the optimal feedstock distribution and operating conditions to upgrade its performance	[143]

Table 8. Recent patents about biolubricant production through esterification or transesterification.

Description	Details	References
Preparation of heterogeneous catalyst for transesterification	It can be used for manufacturing commercial-grade biodiesel, biolubricant, and glycerol	[144]
Production of lubricating bio-oils	Use of soaps, WCO, and animal fats with initial hydrolysis to react with several alcohols and produce biolubricants	[145]
Production of biolubricants catalyzed by fermented solid	The reaction of methyl esters or free fatty acids with a polyhydroxylated alcohol is catalyzed by a fermented solid containing lipases	[146]
System for making biolubricants	A process for continuous preparation of biolubricants is described, including the use of acidic heterogeneous catalyst	[147]
Method for making biofuel and biolubricant	A process for producing biofuels and biolubricants from lipid material, pointing out the possibility of a biorefinery	[148]
Biolubricant production using fly ash as a catalyst	The reaction of fatty acids with different alcohols for the production of alkyl esters with C5 to C12 alcohols in the presence of fly ash as a catalyst	[149]
Method for producing neopentyl glycol diester as a biolubricant	Neopentyl glycol and vegetable fatty acids react using immobilized lipase	[150]

Thus, critical aspects such as high biolubricant conversion or catalyst durability are covered in these patents, which usually offer biolubricants for very specific uses.

7. Conclusions and Prospects

After carrying out a review of the most recent literature about the synthesis and characterization of biolubricants, the following remarks can be made:

- A definition of biolubricants, apart from the main chemical routes for their production (paying attention to double transesterification), has been shown. According to the literature, it has been proved the feasibility of biolubricant production from vegetable oils, obtaining high yields of this product regardless of the chemical route selected, and presenting some properties that are even better compared to traditional lubricants obtained from oil.
- Specifically, biolubricants through double transesterification present, in general, a higher viscosity index, which makes them more suitable to keep viscosity values under temperature changes.
- However, these products also present some challenges, like the short oxidative stability, which could imply a change in very characteristic properties such as viscosity during storage or auto-oxidation processes. Nevertheless, there are accessible alternatives to avoid this problem, like the use of antioxidants such as TBHQ, BHA, or PG, widely used in the scientific literature to increase the service life of this product.
- Regarding the possibility of implementation of this technology, it should be noted the potential of some wastes derived from VO, such as WCO, whose management would be difficult otherwise. As a matter of fact, the properties observed for biolubricants based on WCO are equivalent to those obtained from vegetable oils, with a slight decrease in oxidative stability in some cases, which could be easily solved by antioxidant addition, as explained above. This fact points out the versatility of biolubricant synthesis, being able to compete with traditional lubricant production.
- Considering the above, the possible integration of biolubricant production in biorefineries, or even the implementation of a biorefinery based on vegetable oils, could be an interesting starting point for this technology, especially in the case of double transesterification from fatty acids, as many bioproducts and byproducts that are easily reusable can be obtained, implying a green process that should replace traditional ones.
- In that sense, the role of catalysts is becoming more and more important in biolubricant production, as their use contributes to the higher efficiency of the process, which is an essential part of the real implementation of this technology at an industrial scale. This way, plenty of studies have been focused on the use of new and innovative catalysts, mainly heterogeneous and porous catalysts with the possibility of re-use in several cycles, to make the process more attractive when it comes to techno-economic analyses, especially by reducing the purification process to obtain the final biolubricant.
- Consequently, apart from the use of catalysts, the chemical conditions to carry out double transesterification usually have a strong influence on the final quality of biolubricants. Thus, "every detail counts", which should be pointed out especially in the case of temperature, catalyst addition, or reaction time, among other factors. Indeed, many studies addressed the use of milder reaction conditions, which will present a positive effect on techno-economic assessment, especially in biolubricant quality (especially concerning viscosity and oxidative stability). In other words, it would be the greatest exponent of sustainability, as it would be possible to obtain better products (in this case, biolubricants) under mild reaction conditions and the subsequent energy and material cost, implying a more attractive process for its implementation at an industrial scale.
- Finally, and according to the techno-economic assessments carried out by the scientific literature and recently published patents (where the role of catalysts is essential), the industrial scale implementation of biolubricant production is feasible, pointing out the high added-value product obtained, apart from other by-products equally interesting or reusable, and showing a promising starting point for the contribution to green chemistry and circular economy. In any case, due to the wide variety of processes, further studies would be advisable to cover this subject.

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Abbreviations

Abbreviation	**Term**
BHA	Butylated hydroxyanisole
CFPP	Cold filter plugging point
FA	Fatty acid
FAE	Fatty acid esters
FAME	Fatty acid methyl ester
FFA	Free fatty acids
FO	Frying oil
GM	Genetically modified
IP	Induction point
NG	Neopentyl glycol
NGE	Neopentyl glycol ester
OPEC	Organization of the Petroleum Exporting Countries
OS	Oxidative stability
PE	Pentaerythritol
PEE	Pentaerythritol ester
PG	Propyl gallate
PP	Pour point
SDG	Sustainable development goal
TBHQ	Tert-Butylhydroquinone
TMP	Trimethylolpropane
TMPE	Trimethylolpropane ester
UN	United Nations
VI	Viscosity index
UVO	Used vegetable oil
VI	Viscosity index
VO	Vegetable oil
WCO	Waste cooking oil

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