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Research review paper

Biocatalytic production of biolubricants: Strategies, problems and future trends

Rodolpho R.C. Monteiro [a], Ángel Berenguer-Murcia [b], Javier Rocha-Martin [c,*], Rodrigo S. Vieira [a,*], Roberto Fernandez-Lafuente [d,*]

[a] Departamento de Engenharia Química, Universidade Federal do Ceará, Campus do Pici, 60455760 Fortaleza, Brazil
[b] Departamento de Química Inorgánica e Instituto Universitario de Materiales, Universidad de Alicante, 03080 Alicante, Spain
[c] Departamento de Bioquímica y Biología Molecular, Facultad de Biología, Universidad Complutense de Madrid, 28040 Madrid, Spain
[d] Departamento de Biocatálisis, ICP-CSIC, Campus UAM-CSIC, 28049 Madrid, Spain

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ABSTRACT

The increasing worries by the inadequate use of energy and the preservation of nature are promoting an increasing interest in the production of biolubricants. After discussing the necessity of producing biolubricants, this review focuses on the production of these interesting molecules through the use of lipases, discussing the different possibilities (esterification of free fatty acids, hydroesterification or transesterification of oils and fats, transesterification of biodiesel with more adequate alcohols, estolides production, modification of fatty acids). The utilization of discarded substrates has special interest due to the double positive ecological impact (e.g., oil distillated, overused oils). *Pros* and *cons* of all these possibilities, together with general considerations to optimize the different processes will be outlined. Some possibilities to overcome some of the problems detected in the production of these interesting compounds will be also discussed.

1. Introduction

1.1. Lubricants: general concepts, importance and concerns

Tribology is the science and technology of friction, wear, and lubrication of interacting surfaces (Meng et al., 2022; Wakelin, 1974). Strictly, lubricants are substances (liquid, solid, semi-solid or gaseous) employed to control the friction and, thus, to mitigate wear losses; furthermore, lubricants are employed to dissipate frictional heat from a system (Berman et al., 2014; Rahman et al., 2022). Moreover, lubricants may act as a sealing agent against dirt, dust, and water, so that they protect the material from corrosion and/or oxidation (Shahnazar et al., 2016; Singh et al., 2017). Depending on the film separating the surfaces, lubricants may operate in the (i) boundary lubrication regime, (ii) mixed lubrication regime, or (iii) hydrodynamic lubrication regime, as depicted by the Stribeck curve in Fig. 1. Accordingly, there is a direct contact between the protected surfaces in the boundary and mixed lubrication regimes whereas the surfaces are fully separated by the lubricant in the hydrodynamic lubrication regime (Nyholm and Espallargas, 2023).

In general, lubricants may be categorized into mineral ones and biolubricants, depending on the nature of the base oil (Karmakar et al., 2017). Lubricants have been used since ancient Egypt, in which olive oil was used to lubricate wood to facilitate the moving of construction stones; yet, the basic concepts of lubrication were only later explained by Leonardo da Vinci in the XV century (Sawyer, 2021). Until the middle of the 19th century, vegetable oils and animal fats were the main sources of lubricants; however, the demand for lubricants increased rapidly due to the industrial development during the 19th century (Boyde, 2002). Meanwhile, the development of the petroleum industry provided a new and cheaper material to be used as lubricant: mineral oils (Zainal et al., 2018). The lower price and high performance of mineral oil allowed it to be used as the standard lubricant in most industries (Nyholm and Espallargas, 2023; Zainal et al., 2018). In general, a high-performance lubricant should possess high viscosity index, high boiling point, low freezing point (to remain liquid at low temperatures), high thermal and oxidative stabilities and corrosion prevention capability (Singh et al., 2017). Moreover, suitable lubricants for specific applications must increase the lifespan of systems as well as the overall efficiency and reliability of the systems (Shahnazar et al., 2016; Zainal et al., 2018).

Lubricants are widely employed in many important industrial sectors

* Corresponding authors.
E-mail addresses: javrocha@ucm.es (J. Rocha-Martin), rodrigo@gpsa.ufc.br (R.S. Vieira), rfl@icp.csic.es (R. Fernandez-Lafuente).

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(e.g., transportation, manufacturing, energy, food, and pharmaceuticals) as a solution to friction and wear (Nyholm and Espallargas, 2023). Despite the technological advances in tribology over the last centuries, the losses due to friction and wear still account for approximately 23% (119 EJ) of the global total energy consumption (Holmberg and Erdemir, 2017). Lubrication conserves energy consumption by mitigating frictional and wear losses, thereby reducing fuels consumption (Marlinda et al., 2023); in fact, approximately 8.7% of the global energy consumption could be reduced if energy losses due to friction and wear were reduced to 40% (Holmberg and Erdemir, 2017). In this context, lubricants are essential to the development of mankind in the 21st century, especially with the growing concerns on energy and resources consumption. The industrial development and population growth have been leading to the depletion of petroleum reserves. According to the International Energy Agency (IEA), the world is facing an unprecedented energy crisis due to the Russian invasion of Ukraine, with consequences in affordability and security of energy supply (International Energy Agency, 2022). As the energy crisis in the 1970s, the current energy crisis has revealed underlying fragilities and dependencies in the energy system. Even though the current world energy system is less dependent on fossil fuels than it was in the 1970s, the fossil fuels demand might reach a high point in the mid-2030s, accounting for approximately three-quarters of the total world energy supply (International Energy Agency, 2022). By 2030, the global lubricant market is projected to grow at a compound annual growth rate (CAGR) of 3.7% in terms of revenue, compared to the 2022 market (Grand View Research, 2022). Overall, in addition to its intrinsic financial advantages of protecting surfaces of probable damages, further developments in tribology may mitigate energy consumption and, consequently, carbon dioxide emissions due to the burning of fossil fuels.

Currently, mineral oils remain the most used lubricants in industry due to their low cost, easy availability, and adequate performance (Karmakar et al., 2017; Pinheiro et al., 2021; Rosenkranz et al., 2021). Mineral oils are heavy hydrocarbons (C_{20}–C_{50}) manufactured from the distillation and refinement of crude oil, containing a range of linear and branched alkanes, alicyclic, olefinic and aromatic species, together with molecules containing significant concentrations of heteroatoms, mainly sulfur (Panchal et al., 2017; Shahnazar et al., 2016; Shao et al., 2022). Despite their useful physicochemical properties, mineral-based lubricants are very toxic to the environment and are obtained from non-renewable sources (Zhao et al., 2022).

Lubricants may be expelled to the environment through leakages and/or spillages, thus leading to soil and water contaminations (Singh et al., 2017; Zainal et al., 2018). Furthermore, the long-term utilization of lubricants produces their degradation, and their final disposal produces contamination or requires high investments to fully degrade them (Singh et al., 2017; Zainal et al., 2018). The improper disposal of mineral lubricants into the soil may: (i) induce anaerobic zones by filling the pores between soil particles and hindering the access to oxygen of the living beings, (ii) lead to metabolic and growth inhibition for most plant species due to high concentration of toxic metals and (iii) lead to the uptake of polycyclic aromatic hydrocarbons (which are toxic to humans) by vegetables (Nowak et al., 2019; Pinheiro et al., 2021; Singh et al., 2017). Moreover, the improper disposal of mineral oils into water bodies may: (i) prevent the oxygenation of living organisms on the water surface due to the formation of low-density organic films, (ii) stress and changes in the community of microorganisms and (iii) cause adverse effects on human health by ingestion/contact (Nowak et al., 2019; Pinheiro et al., 2021; Singh et al., 2017). Beyond the poor biodegradability, the combustion of mineral lubricants releases metal traces (e.g., calcium, cadmium, chromium, iron, magnesium, platinum and zinc) if the burning is performed without a proper pretreatment; in addition, the combustion of mineral lubricants may produce other harmful compounds (e.g., dioxins, sulfur oxides, nitro compounds, hydrochloric acid, nitrogen oxides, phosphates and carcinogenic hydrocarbons of polycyclic type) (Nowak et al., 2019; Pinheiro et al., 2021; Singh et al., 2017).

In this scenario, there have been increasing efforts by academia and industry to minimize the leakage/spillage/improper disposal and combustion/evaporation in operation of mineral lubricants; however, it may be a very difficult task to avoid or even minimize the environmental issues related to the use and disposal of mineral lubricants. Consequently, the United States Environmental Protection Agency (EPA) has been encouraging the use of alternative feedstocks to synthesize non-toxic and biodegradable lubricants (Pinheiro et al., 2021). Synthetic lubricants have been used before the internal combustion engine existed; however, the first 100% synthetic lubricant was developed by AMSOIL and certified by the American Petroleum Institute in 1972 (Nagendramma and Kaul, 2012). Remarkably, synthetic lubricants were firstly developed to be used under high temperatures in military and aero engines, despite their high cost (Nagendramma and Kaul, 2012). Beyond the non-toxicity and biodegradability, synthetic lubricants may be rationally designed to produce compounds with predictable properties and performance in the target application. In the following section, the general features (feedstocks, production, advantages and drawbacks) of synthetic biodegradable lubricants (known as biolubricants or green/eco lubricants) will be highlighted.

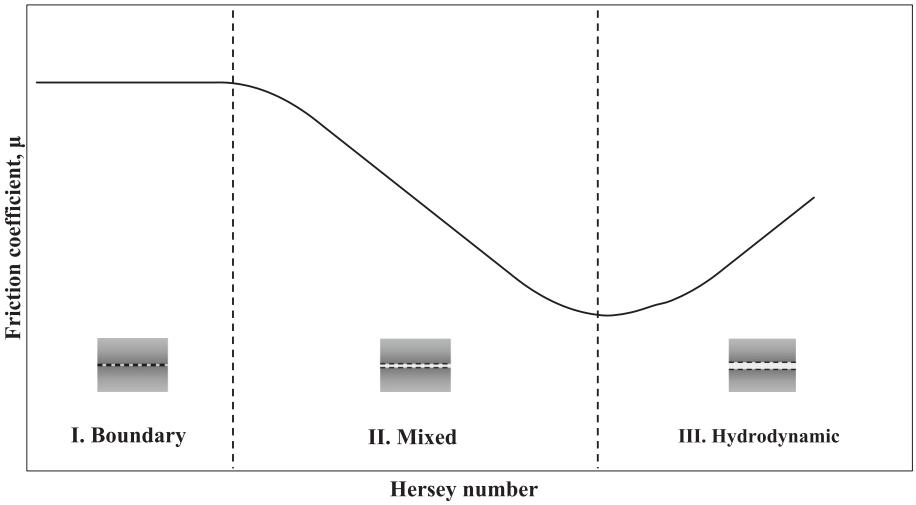

Fig. 1. Stribeck curve (Hersey number = viscosity × speed/load).

1.2. Biolubricant: general concepts

As stated in the previous section, the depletion of petroleum reserves and the potential environmental problems of mineral-based lubricants have promoted the concepts of green tribology. Green tribology is the science and technology specially concerned with the sustainable aspects of friction, wear, and lubrication of interacting surfaces (Pawar et al., 2022). The green tribology principles were introduced by Nosonovsky and Bhushan (Nosonovsky and Bhushan, 2010) as a broader approach for the concept of eco-lubrication introduced by Sasaki (Sasaki, 2010). The twelve principles of green tribology are as follows (Freschi et al., 2022): (i) minimization of heat and energy dissipation; (ii) minimization of wear; (iii) reduction or complete elimination of lubrication, and self-lubrication; (iv) natural lubrication; (v) biodegradable lubrication; (vi) sustainable chemistry and green engineering principles; (vii) biomimetic approach; (viii) surface texturing; (ix) environmental implications of coatings; (x) design for degradation; (xi) real-time monitoring; (xii) sustainable energy applications. To meet the principles of green tribology, government regulations have been limiting the use of mineral lubricant and, thus, encouraging the use of biolubricants by subsidies, tax incentives, and national and international labeling systems, especially in Europe (Raof et al., 2022a). Consequently, the biolubricant market has been increasing over the years, reaching a CAG of 5.2% from 2016 to 2024 (Grand View Research, 2022); similarly, the interest in the production of biolubricants by academia has been increasing over the years as reflected by the increasing number of publications (Fig. 2).

Regarding the feedstock, biolubricants are lubricants derived from several bio-based feedstocks (e.g., vegetable oils, animal fats, algae lipids and renewable hydrocarbons) (Ho et al., 2019; Mobarak et al., 2014; Syahir et al., 2017). Nowadays, lubricants are mainly produced from vegetable oils. Edible and non-edible vegetable oils may be extracted from approximately 360 oil-bearing crops available worldwide (e.g., palm, soybean, rapeseed, sunflower, peanut, cottonseed, coconut, sunflower, canola, corn, castor, jatropha curcas, karanja, rubber seed, neem) (Pawar et al., 2022; Uppar et al., 2022). Nevertheless, non-edible vegetable oils are more suitable to produce biolubricants since they do not compete with food demands and may have special interest if the crops can be cultivated under harsh environments; furthermore, they are usually relatively low-priced (Pawar et al., 2022; Uppar et al., 2022). Overall, vegetable oils may possess suitable properties to be used as biolubricants without any further modification as they possess excellent lubricity, high viscosity index, high flash point and are renewable and biodegradable; however, vegetable oils possess some negative features, such as low thermal oxidation stability, poor cold flow behavior, poor atomization, and confer poor corrosion protection (Pawar et al., 2022; Uppar et al., 2022). The properties of vegetable oils may be enhanced by genetic modification of the producer microorganisms or the chemical/biological of the oil; furthermore, they can be tuned by using the proper additives (Pawar et al., 2022; Uppar et al., 2022). Strictly, chemical/biological modification of vegetable oils may result in biolubricants with good lubricity/viscosity, high viscosity index, high flash point, and good resistance to shear compared to mineral oils (Barbera et al., 2022; Narayana Sarma and Vinu, 2022; Syahir et al., 2017).

Viscosity is the resistance of the biolubricant to flow. It depends on temperature and pressure; furthermore, viscosity is related to the ability of the lubricant to form a film on the surface to be protected (i.e., highly viscous lubricants tend to form thicker films) (Barbera et al., 2022; Syahir et al., 2017). The viscosity index (VI) measures the dependency of viscosity upon temperature and, thus, high VI values infer that the viscosity of the lubricant will be slightly affected by temperature changes (Narayana Sarma and Vinu, 2022). Biolubricants possess higher VI than most mineral lubricants (Narayana Sarma and Vinu, 2022; Syahir et al., 2017). Flash point is another temperature-dependent remarkable property to be considered in a biolubricant. Flash point is the temperature where ignitable vapor is formed in the presence of air, conditions where it can burn (Syahir et al., 2017). Moreover, as it has been stated so far, biodegradability is one of the outstanding properties of biolubricants. Biodegradation is the aerobic or anaerobic processes of decomposition of a biolubricant by microorganisms (Freschi et al., 2022; Narayana Sarma and Vinu, 2022). For instance, the biodegradability of mineral lubricants is 20-40% whereas the biodegradability of biolubricants is 90-98% for those derived from vegetable oils (Mobarak et al., 2014). In general, the biodegradability of biolubricants is mainly dependent upon the chemical composition of base oil; however, the biodegradability of the base oil may be changed by the lubricant modification or by the usage conditions (e.g., temperature, pressure, humidity, presence of air or metals) (Narayana Sarma and Vinu, 2022).

Despite the advantages of biolubricants, their price and performance have hindered their massive implementation. The cost of the feedstock accounts for 70-80% of the total production costs of biolubricants (Athaley et al., 2019); therefore, the costs of production of biolubricants must be reduced by the employment of low-priced feedstocks (e.g., non-edible oils or waste cooking oils) (Joshi et al., 2023b). Regarding their performance, the poor cloud and pour points and low thermo oxidative stability are the main concerns of using vegetable oils as feedstocks to

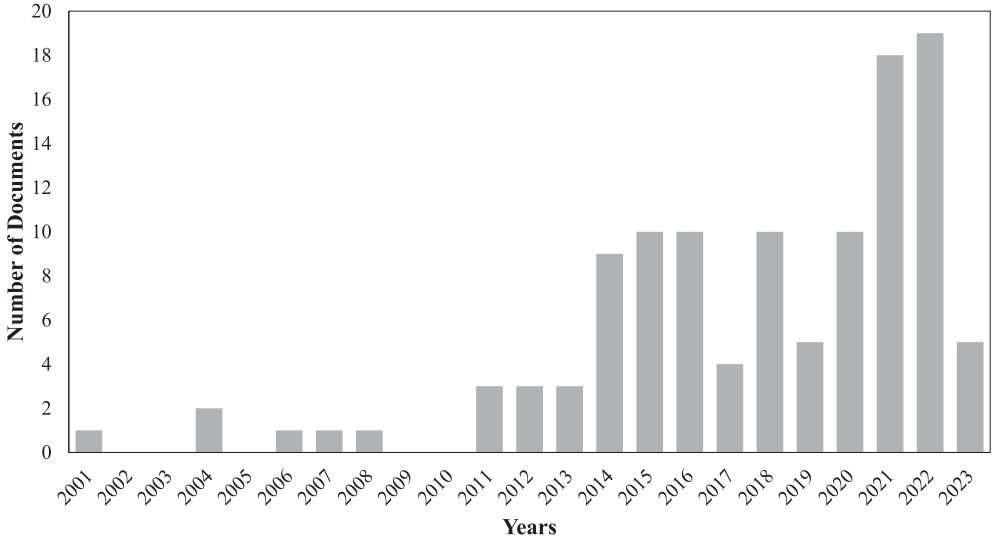

Fig. 2. Bibliometric trends for biolubricant research. Search algorithms on Scopus: (TITLE-ABS-KEY (bio-lubricant* OR biolubricant*) AND TITLE-ABS-KEY (enzym* OR lipas*)).

produce biolubricants (Raof et al., 2022a). Cloud point is the minimum temperature of the biolubricant to start forming solids whereas pour point is the temperature below cloud point at which the biolubricant loses its flowability (Barbera et al., 2022; Narayana Sarma and Vinu, 2022). The thermo oxidative modification of the biolubricants is promoted due to exothermic auto-oxidation and endothermic pyrolysis reactions, thereby altering the viscosity and performance of the biolubricant (Narayana Sarma and Vinu, 2022). Synthetic biolubricants usually exhibit better cloud and pour points and higher oxidative stability than the corresponding vegetable oil (Cecilia et al., 2020). In the following subsections, the optimal features of the feedstock (oil and alcohol) to synthesize biolubricants with suitable properties will be highlighted. There are many recent papers and reviews listing the properties of the final products obtained using different feedstocks (Cecilia et al., 2020; Joshi et al., 2023a; Kurre and Yadav, 2023; Mendes et al., 2022; Narayana Sarma and Vinu, 2022; Owuna et al., 2020; Pawar et al., 2022; Perera et al., 2022; Raof et al., 2022b; Syahir et al., 2017), here we focus on the general features of the "ideal" biolubricant.

1.2.1. Optimal features of the oil

The main feedstock employed to produce biolubricants are vegetable oils, which are mainly composed of triacylglycerols (i.e., three fatty acids molecules linked to one molecule of glycerol by an ester bond) with a fatty acid carbon chain length varying usually from C_{12} to C_{24} (McNutt and He, 2016; Pawar et al., 2022). The fatty acid composition of vegetable oils greatly influences the performance of biolubricants. For example, a high degree of unsaturation of the fatty acids of vegetable oils may result in biolubricants with lower viscosity, melting point, and thermo oxidative stability (Pawar et al., 2022; Syahir et al., 2017). To address the problems of the unsaturation of fatty acids, the hydrogenation of the double bonds has been proposed as a solution, but this makes the process more complex (Cecilia et al., 2020; Hájek et al., 2021). The epoxidation followed by oxirane ring-opening is another alternative to address the unsaturation of vegetable oils. On the other hand, the saturation of fatty acid of vegetable oils may result in biolubricants with unsuitable cloud and pour points (Barbera et al., 2022). Therefore, the optimal degree of saturation of vegetable oils should increase the oxidative stability and, at the same time, maintain acceptable properties of the biolubricant at low temperature (Chan et al., 2018). In this sense, vegetable oils with high content of monounsaturated fatty acids (e.g., oleic acid and ricinoleic acid) are the most adequate feedstocks to produce biolubricants, the unsaturated positions may be more susceptible to oxidations but the resulting product stacking of molecules and crystallizationc is disrupted, and advantages supress the problems, always that the unsaturatio is only moderate (Chan et al., 2018; Reeves et al., 2015). Moreover, a vegetable oil with fatty acids of long carbon chain length may result in biolubricants with high melting point and viscosity (McNutt and He, 2016; Pawar et al., 2022). Esterification or transesterification of the free fatty acids (FFAs) or triacylglycerols with fatty alcohols are the most employed strategy to increase the chain length of the biolubricant (Barbera et al., 2022; Ho et al., 2019), as it will be further discussed in the following section. The epoxidation and oxirane ring-opening is also employed to increase the melting point, viscosity and thermal oxidative stability of biolubricants; however, the excessive molecular branching at the oxirane ring-opening sites may lead to steric hindrances, ultimately resulting in impoverished tribological properties (Chan et al., 2018). The condensation of hydroxyl FFAs to form estolides is another strategy employed to produce high molecular weight biolubricants with higher viscosity and better pour point (Barbera et al., 2022; Chan et al., 2018). Overall, the selection of the suitable vegetable oil to be used in the production of biolubricants is ultimately dependent upon the final application. Section 3 will discuss the different possibilities.

1.2.2. Optimal features of the alcohol

The selection of an alcohol is another critical step to define the properties of a biolubricant. Vegetable oils (i.e., triacyclglycerols) are natural esters; however, the substitution of the glycerol moiety by another alcohol may result in a biolubricant with improved properties since the substitution of the glycerol backbone by a polyol, for example, eliminates the β-hydrogen of glycerol, thereby enhancing the thermo oxidative stability of the biolubricant (Barbera et al., 2022; Raof et al., 2022a). Synthetic esters are the most widespread market biolubricants, being employed in the automobile, industrial, metalworking, marine and aviation sectors (Ho et al., 2019). Synthetic esters of vegetable oils may be synthesized by the transesterification of vegetable oils or by the esterification of the corresponding FFAs with different alcohols, usually fatty alcohol or polyols (Barbera et al., 2022). Neopentylglycol (NPG), trimethylolpropane (TMP), pentaerythritol (PE) or dipentaerythritol (diPE) may enhance the thermal and hydrolytic stabilities of vegetable oils (Barbera et al., 2022; Raof et al., 2022a). Among the polyols, TMP has been more widely employed due to its availability and lower cost (Raof et al., 2022a). Oligoesters may be used in green tribology as well; however, they are usually utilized as additives to improve the performance of mineral or bio-based lubricants, not as base biolubricants as conventional esters are (Ho et al., 2019). Oligoesters may be produced by the esterification of di- or polyacids with polyols or by the condensation of the carboxyl/hydroxyl moiety of hydroxy-FFAs or hydroxyl-fatty esters, the final esterification/transesterification of the unreacted carboxyl moiety with a fatty alcohol (e.g., 2-ethyl-1-hexanol) can reduce the undesired acidity of the final product (Ho et al., 2019). The general features of the catalysis of the chemical modification of vegetable oils to produce high-performance biolubricants will be assessed in the following section.

1.2.3. Chemical production of biolubricants

As previously commented, vegetable oils must be modified to enhance their properties to be used as biolubricants; hence, there have been reported several catalytic-mediated modifications of vegetable oils, such as esterification, transesterification, hydroesterification, oligomerization, epoxidation and oxirane-ring opening (Barbera et al., 2022; Cecilia et al., 2020; Hájek et al., 2021; Pawar et al., 2022; Uppar et al., 2022).

The esterification of FFAs with fatty alcohol or polyols has been mainly performed by chemical catalysts (homogenous and heterogenous), especially acid (e.g., sulfuric, hydrochloric, p-toluenesulfonic, phosphoric acids as homogenous catalysts and WO_3 and sulfonated active carbons as heterogenous catalysts) catalysts to avoid the formation of soaps produced if using alkaline catalysts (Appiah et al., 2022; Langeveld et al., 2010; Qin et al., 2019). Similarly, the transesterification of triacylglycerols with fatty alcohols or polyols has been mainly performed by alkali chemical catalysts (e.g., potassium or sodium ethoxide as homogenous catalysts and calcium or magnesium methoxide and calcium oxide as heterogeneous catalysts); however, the feedstock requirements (i.e., water content and acidity index) of these processes are high to avoid saponification (Appiah et al., 2022; Shrivastava et al., 2023; Xie et al., 2022). The esterification/transesterification of acid vegetable oils with acid catalysts is another interesting strategy to produce biolubricants since it uses unrefined vegetable oils, waste cooking oils, and acid sludge vegetable oils as feedstocks (Bolina et al., 2021). The hydrolysis of the feedstock with high acidity index followed by the esterification of the corresponding FFAs (formally, hydroesterification) may be another strategy employed to avoid saponification in the production of biolubricants; however, there are no reports in the scientific literature on the full chemically catalyzed hydroesterification of vegetable oils to produce biolubricants. In general, the esterification of FFAs and transesterification of vegetable oils performed by chemical catalysts are conducted under high temperature (high energy demand) to reduce medium viscosity and, thus, improve mass transfer (Bolina et al., 2021; Kurre and Yadav, 2023).

The production of estolides is another strategy employed to enhance the properties of vegetable oils (or the corresponding FFAs) to be used as

biolubricants. Estolides may be produced by the reaction of hydroxy fatty acids (e.g., ricinoleic acid) with vegetable oils (triacylglycerols) or FFAs or by the reaction of two FFAs – at least one of them must contain a hydroxy, double-bond or epoxide functional group (Chen et al., 2020). Homogenous (e.g., hydrochloric, phosphoric, nitric, and perchloric acids) and heterogenous (e.g., clays, aluminosilicates) catalysts are employed in the oligomerization of fatty acids to produce estolides, especially in the esterification of the hydroxy moiety of one FFA with the carboxyl moiety of another FFA (Chen et al., 2020). As for the esterification, transesterification and hydroesterification of vegetable oils to produce high-performance biolubricants, the oligomerization of fatty acids to produce estolides is performed under high temperatures; in addition, chemically catalyzed production of estolides presents poor stereoselectivity, thus resulting in side reactions (Chen et al., 2020). On the other hand, the epoxidation of vegetable oils (or the corresponding FFAs) must be performed under milder reaction temperatures due to the unstable nature of double bonds (Yan et al., 2022). Homogenous (e.g., peracid and protonic acid) and heterogenous (e.g., Ti-, W-, Al-, Zr-, Mo-, Nb-, V-, Co-, Cu- and Mn-based) are employed in the epoxidation of vegetable oils, using H_2O_2 as an oxidant (Yan et al., 2022). Similarly, the oxirane ring-opening to modify epoxidated vegetable oils is performed under mild reaction conditions due to the high reactivity of the oxirane group, even in the absence of a catalyst (Bolina et al., 2021; Panchal et al., 2017).

Lipases are the most widely used biocatalysts to perform the modification of vegetable oils to produce high performance biolubricants, as it will be discussed in the Section 3, making it the main body of this review.

2. Lipases

The natural function of lipases is the hydrolysis of oils and fats to produce glycerol, free fatty acids and mono or diglycerides (Herrington, 1954; Robinson, 1963). These are among the most utilized enzymes in biocatalysis for several reasons. They are present in all living beings, that way nature can offer a wide diversity of lipases, bearing different features (Borrelli and Trono, 2015; Chandra et al., 2020; Chen and Sih, 1989; Jaeger and Eggert, 2002; Reetz, 2002; Villeneuve et al., 2000). Moreover, they can catalyze many different reactions, such as ester hydrolysis (Goswami et al., 2013; Murty et al., 2002), esterification (Hari Krishna and Karanth, 2002; Soumanou et al., 2013; Stergiou et al., 2013), transesterification (Bajaj et al., 2010; Santaniello et al., 1993; Toldrá-Reig et al., 2020), acidolysis (Akil et al., 2020; Fomuso and Akoh, 2002; Sahin et al., 2005), amidations (Slotema et al., 2003; Vongvilai and Ramström, 2009), etc. They are also among the enzymes able to catalyze a wider diversity of promiscuous reactions (Kapoor and Gupta, 2012; Li et al., 2008; Svedendahl et al., 2005).

Lipase substrate specificity is also very wide, accepting very different compounds as substrates (from aromatic to aliphatic acids or alcohols, primary or secondary alcohols) and permitting their use in many different processes (Borrelli and Trono, 2015; Chandra et al., 2020; Chen and Sih, 1989; Jaeger et al., 1999; Reetz, 2002; Villeneuve et al., 2000). There are very stable lipases that can be utilized in a wide range of reaction media, e.g., aqueous media, solvent-free media (Chang and Wu, 2009; Sousa et al., 2021), organic solvents (Kobayashi and Adachi, 2004; Kumar et al., 2016), ionic liquids (Elgharbawy et al., 2018; Šibalić et al., 2023), deep eutectic solvents (Durand et al., 2013; Tan and Dou, 2020), supercritical fluids (Dias et al., 2018; Fan and Qian, 2010). That way, these enzymes may be utilized in a huge diversity of areas, such as food (Coelho and Orlandelli, 2021; Reyes-Reyes et al., 2022; Salgado et al., 2022), fine chemistry (de Miranda et al., 2015; Ghanem and Aboul-Enein, 2005) or energy industries (Hama et al., 2018; Tan et al., 2010; Zhao et al., 2015; Zhong et al., 2020).

Lipases have a common feature that distinguishes them from standard esterases, their capacity to act in the interfaces (Schmid and Verger, 1998; Verger, 1997). This is necessary considering the extremely low solubility of triglycerides in water. To fulfil this necessity, lipases have a peculiar mechanism of action, called interfacial activation. In the closed conformation, the active center of most lipases is isolated from the medium by a polypeptide change called lid (Brzozowski et al., 1991; Brzozowski et al., 2000; Grochulski et al., 1993; Martinelle et al., 1995; van Tilbeurgh et al., 1993; Wang et al., 2021). This lid may be small, and that way unable to fully isolate the active center (as it is the case of the lipase B from *Candida antarctica*) (Uppenberg et al., 1994) or very large and complex, like the double lid exhibited by the lipase BTL2 from *Geobacillus thermocatenulatus* (Carrasco-López et al., 2009) (Fig. 3). In the open form, this lid is shifted and exposes a large hydrophobic pocket to the media, unstable in aqueous media. Both conformations are in equilibrium, and in the presence of a hydrophobic surface, the open conformation becomes adsorbed via the huge hydrophobic pocket, shifting the conformational equilibrium (Schmid and Verger, 1998; Verger, 1997). This is called interfacial activation, because lipases use to increase its activity when the substrate concentration exceeds that of their solubility and form insoluble drops. This mobility of the lipase active center causes them to be easily tunable, being relatively simple to alter their activity, selectivity or specificity (Izquierdo et al., 2014; Matsuda et al., 2003; Quirós et al., 2001; Tacias-Pascacio et al., 2016; Tomin et al., 2011). However, it also involves some drawbacks, as they tend to form lipase-lipase dimers (Fernández-Lorente et al., 2003; Palomo et al., 2003a; Palomo et al., 2005; Palomo et al., 2004; Wilson et al., 2006) or to interact with hydrophobic components of the extract (Palomo et al., 2003b; Wang et al., 2016), making comparison between free lipases from different microorganisms complex, or even between those extracts simply submitted to different treatments.

2.1. Potential problems of using lipases in the production of biolubricants

Although lipases have a wide specificity, they still may have preference for some specific free fatty acids or they cannot recognize some of them as substrates, and even some of these fatty acids (as acids or esters) can act as some lipase inhibitors (Arana-Peña et al., 2020a). When transforming a pure fatty acid into a biolubricant, it is possible to find an "optimal lipase" for the process, as the substrates are unique. However, using oils, free fatty acids obtained from the oils, biodiesel, etc., we should consider that they are not a single substrate, but a collection of substrates with different chemical compositions (different fatty acids) (Arana-Peña et al., 2020a). In the case of glycerides, the reaction can start mainly using triglycerides (many different ones), but during reaction diglycerides and monoglycerides (still very different ones) will be formed. That way, in these instances, to propose an optimal lipase may not be a good idea, as it is hard to think that a specific lipase can be the best *versus* all the diversity of possible substrates (Arana-Peña et al., 2020a). Using initial rates, the researcher will select the lipase that modifies the main component of the substrate mixture faster. However, literature has shown how it may be better to use a mixture of different lipases to perform these reactions, combining enzymes with different specificities. This may permit not only to reach higher yields, but also at a higher reaction velocity. This problem is usually ignored in the optimization of the processes of biolubricant production, while it is more considered in the production of biodiesel (Cesarini et al., 2014; Guan et al., 2010; Jin et al., 2013; Lee et al., 2006; Lee et al., 2011; Lee et al., 2010; Liu et al., 2010; Poppe et al., 2018a; Poppe et al., 2018b; Poppe et al., 2015; Sangkharak et al., 2022).

2.2. Lipase immobilization

The use of immobilized enzymes was initially proposed to solve the problems of enzyme recovery and reuse (Sheldon and van Pelt, 2013). Nowadays, the prices of enzymes, and even more so of some lipases, have decreased to a degree that they are proposed for their use in a one-off batch in its free form in the production of products as cheap as biodiesel, accounting only for the 5% of the final expenses of the

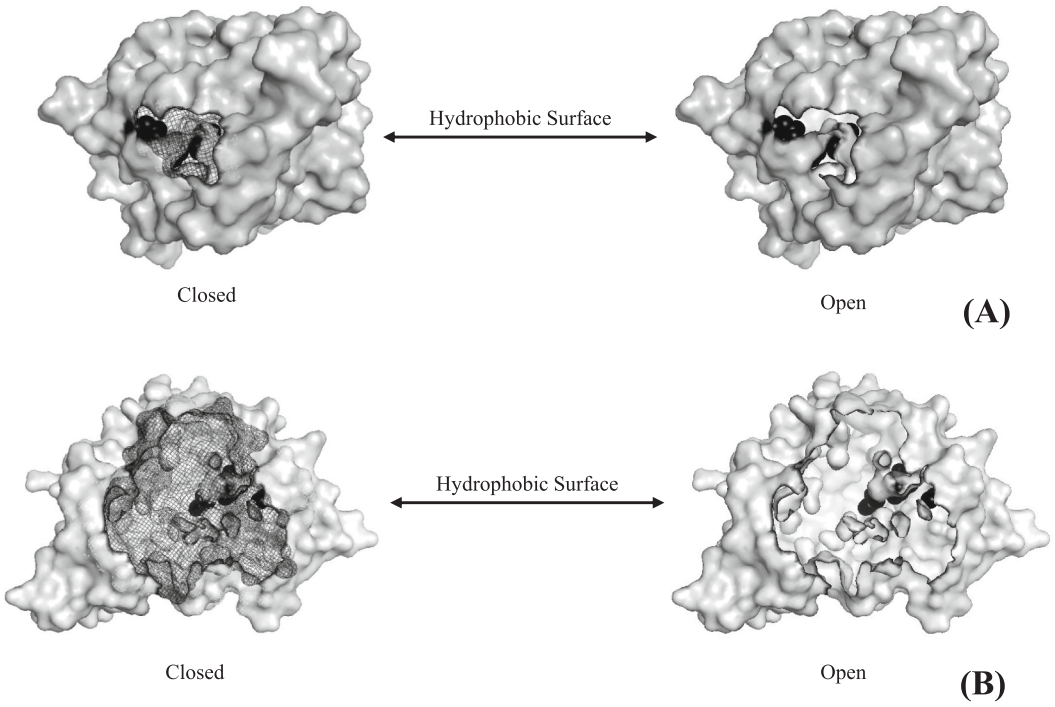

Fig. 3. Structure of the closed and open forms of (A) lipase B from *Candida antarctica* (PDB code: 1LBS) (B) lipase BTL2 from *Geobacillus thermocatenulatus* (PDB code:1J13). Lid: black mesh; active site: black spheres.

biodiesel production (although later it may promote some difficulties in down-stream) (Bhatt et al., 2022; Monteiro et al., 2021; Wancura et al., 2020). However, a proper enzyme immobilization has shown to be far more than a mere way to permit enzyme recovery, as it may permit to greatly improve many enzyme features (Bolivar et al., 2022). The most studied improvement of enzymes features due to their immobilization is its stabilization (Guisan et al., 2020; Klibanov, 1979; Mateo et al., 2007). This may be accomplished due to many different causes, as recently reviewed (Rodrigues et al., 2021), but it should be considered that only a proper immobilization will have this effect. An incorrect immobilization (including support, active group nature and density, and immobilization protocol) can lead to an enzyme with even a lower stability that the free counterpart (Bolivar et al., 2022). Stabilization of the enzyme means not only the possibility of using the enzyme for more reaction cycles, but also to widen the operation ranges of the enzymes, making it easier to find conditions where good parameters of the reaction can be found (Bolivar et al., 2022). Immobilization may be also coupled to enzyme purification, compensating the costs of the immobilization by the savings in enzyme purification (Barbosa et al., 2015). Enzyme immobilization usually means that the enzyme is partially distorted due to the enzyme-support interactions, and thus, immobilization can also alter enzyme selectivity, specificity, inhibitions, etc. (Garcia-Galan et al., 2011; Rodrigues et al., 2013). By placing the enzyme in a confined space (the pores of a solid), some benefits/problems can be observed due to diffusional limitations (Bolivar et al., 2022). These advantages will have a cost, which is derived from the immobilization process itself, the materials used in the immobilization (supports, chemicals, etc.), its storage and discarding when the catalyst is inactivated, and any possible loss of enzyme activity (Bolivar et al., 2022). The use of very simple immobilization strategies that can permit to take the most of the expected benefits of immobilization will be preferred when the final product value is just moderately high, like in the case of biolubricants. Fortunately, for lipases there is a simple method that permits to achieve the one step immobilization, purification, stabilization and hyperactivation of lipases (Palomo et al., 2002; Rodrigues et al., 2019), the immobilization of lipases in hydrophobic supports at low ionic strength via interfacial activation (Manoel et al., 2015). This method is very rapid and permits to reach many of the expected advantages of immobilization (Rodrigues et al., 2019). Usually, a physical immobilization of enzymes can hardly produce a large stabilization (dos Santos et al., 2015a), but the open form of the lipases stabilized by adsorption on a hydrophobic surface is more stable than the enzyme in open/closing equilibrium (Cygler and Schrag, 1999; Jaeger et al., 1993; Kim et al., 1997) and usually gives higher enzyme stability than the immobilization of enzymes via multipoint covalent attachment (dos Santos et al., 2015b; dos Santos et al., 2015c; dos Santos et al., 2015d). Moreover, when using a hydrophobic support, usually one not recommended for immobilization of standard enzymes, this may become an advantage in the production of biolubricants (see Section 3).

While this physical adsorption is very strong, it is also reversible. This reversibility of immobilization via lipase interfacial activation may be an advantage, as it permits the enzyme release after its inactivation and the reuse of the hydrophobic support (Virgen-Ortíz et al., 2017a). However, it may become a problem if the enzyme is released during operation. This is favored at high temperature and in the presence of detergents, and free fatty acids may be considered a weak detergent, able to favor this undesired enzyme release (Hirata et al., 2016a; Hirata et al., 2016b; Rueda et al., 2015; Virgen-Ortíz et al., 2017b). To solve this, there are some solutions. One possibility is to perform an intermolecular crosslinking, covalently (that means the loss of the reversibility) (Cejudo-Sanches et al., 2020; Fernandez-Lorente et al., 2011; Pizarro et al., 2012; Zaak et al., 2017) or physically (not as efficient, but maintaining the reversibility) (Fernandez-Lopez et al., 2017; Fernandez-Lopez et al., 2018), using different polymers. The use of ionic polymers may be taken as an opportunity to coimmobilize different lipases, enabling the enzyme release of the least stable enzyme that should be ionically exchanged in this polymeric bead (Arana-Peña et al., 2020b; Carballares et al., 2022; Peirce et al., 2016). In this regard, the interest of the simultaneous use of different lipases to combine different enzyme specificities as discussed above should be considered. The other strategy is to use heterofunctional supports. If the support, together with the hydrophobic groups, contains ionic groups, metal chelates, etc., the

enzyme will be immobilized via a mixed adsorption and the enzyme release will be more difficult, but it will still be possible (enabling the support recovery and reuse) (Rueda et al., 2016b). This is the cheapest solution, the support will be more expensive but the immobilization protocol remains very simple. The use of chemically reactive moieties (epoxy, glyoxyl, vinyl sulfone) (Albuquerque et al., 2016; Bernal et al., 2014; Bernal et al., 2018; Guajardo et al., 2015a, 2015b; Rueda et al., 2016a; Rueda et al., 2015) combined with the hydrophobic groups fully prevents the enzyme release, but makes the immobilization protocol more sophisticated and prevents support reuse (although it may be compatible with enzyme reactivation) (Suescun et al., 2015). These supports have also been proposed to coimmobilize different lipases enabling the recovery and reuse of the most stable enzymes to build a new combi-lipase when the least stable ones have been inactivated (Arana-Peña et al., 2019; Carballares et al., 2022; Rios et al., 2019).

3. Enzymatic production of biolubricants

3.1. Esterification

The simplest strategy to produce biolubricants is esterification, the opposite of the hydrolysis reaction that lipases catalyze in nature (Fig. 4). Following this strategy, a free fatty acid and the desired alcohols without any further modification are the raw materials (Fig. 4). This is a thermodynamically (or equilibrium) controlled synthesis (Kasche, 1986; Kasche et al., 1987). Following this strategy, at first glance, the catalysts can only accelerate the reaction but cannot alter the final yields, which are exclusively determined by the thermodynamic constant of the process (Marsden et al., 2020). A way to shift the yields towards the ester is to reduce water activity (a by-product of the reaction) (Fig. 4). For this reason esterifications are traditionally performed in media with very low water activity (e.g., organic (Janssen et al., 1999; Kumar et al., 2016; Valivety et al., 1991), ionic liquids (Alvarez et al., 2019; Barahona et al., 2006; Lozano et al., 2012; Lozano et al., 2003; Yuan et al., 2006), deep eutectic solvents (Nian and Li, 2022; Tan and Dou, 2020), supercritical fluids (Lozano et al., 2004; Mandari and Devarai, 2022; Marty et al., 1992), or solvent-free media (Liu et al., 2016; Sandoval et al., 2002; Sousa et al., 2021; Zhong et al., 2013). Water activity should be controlled throughout the process, for example capturing the formed water using molecular sieves or promoting its evaporation (Barahona et al., 2006; Colombié et al., 1998; Kwon et al., 1995; Zulkeflee et al., 2022) (Fig. 4). However, if the biocatalyst activity is very high, the fast formation of water may cause some water molecules to remain inside the biocatalyst particle and form a water phase, surrounding the enzyme molecules, and leading to their inhibition (because hydrophobic substrates cannot reach the active center of the enzyme) or inactivation (because the acid can lead to a very low pH value in this water layer). This problem was marked by the group of Prof Marty (Castillo et al., 1997; Colombié et al., 1998; Dossat et al., 1999, 2002; Marty et al., 1997) that proposed the use of very hydrophobic supports to reduce the water tendency to remain in the biocatalyst particle (Séverac et al., 2011). This was later confirmed by other researchers (Friedrich et al., 2013; Graebin et al., 2012; Martins et al., 2013a; Poppe et al., 2013; Rodrigues et al., 2015). The use of ultrasounds, able to "stir" even inside the biocatalysts particle, was another successful solution to prevent the inner water layer formation (Alves et al., 2014; Fallavena et al., 2014; Martins et al., 2013b; Paludo et al., 2015; Todeschini et al., 2016). Using polyols (Fig. 5), the situation can become more complex, as the enzyme selectivity (with the possibility of modifying up to all hydroxyl groups) and specificity (recognition of partially poly-acylated esters) can alter the number of final products, that way the yields can be modified by using different enzymes or exposed to different modifications (genetic modifications, chemical modification or different immobilization protocols) (Rodrigues et al., 2013).

According to the authors bibliographic search, the first report on the production of biolubricants using lipases as biocatalysts via esterification was published in 2004 by Koszorz and coworkers (Koszorz et al., 2004). In this first report, Novozym 435, a commercially immobilized lipase B from *Candida antarctica* (CALB), was employed in the esterification of oleic acid with isoamyl alcohol, producing isoamyl oleate, an ester with biolubricant properties (Koszorz et al., 2004). In this paper, a membrane reactor was utilized to integrate a pervaporation system to remove the water formed from the reaction medium and, that way, to shift the reaction equilibrium in the direction of the ester formation (Koszorz et al., 2004). In a similar approach, a pervaporation system was integrated to an esterification system to remove water from the esterification of oleic acid catalyzed by immobilized CALB (Dörmő et al., 2004). The researchers found that a water content under 0.1% may reduce enzyme activity whereas a water content above 0.5% may favor the equilibrium of the reaction towards hydrolysis (Dörmő et al., 2004). As previously stated, the use of molecular sieves is another technique to remove the water excess from the reaction medium in this kind of processes. This was the strategy to control the water in the enzymatic esterification of sebacic acid with octanol, where 3Å molecular sieves were used (dos Santos Corrêa et al., 2016). The use of molecular sieves must be carefully analyzed. For example, it may decrease the available water at the beginning of the esterification, and thus it can lead to lipase deactivation due to dehydration (dos Santos Corrêa et al., 2016). Moreover, the use of molecular sieves means the addition of a new solid to the system (together with the immobilized enzyme), and this can lead to the generation of diffusional limitations and problems in solid dispersion. Besides pervaporation and the addition of molecular sieves, water has been removed from lipase-mediated esterification in the production of biolubricants by vacuum (dos Santos Corrêa et al., 2016) or dry air (Tao et al., 2015).

As stated in the general introduction, the selection of the alcohol plays an important role in the design of synthetic esters with biolubricant properties. In this sense, branched and straight-chain alcohols have been evaluated in the esterification of oleic acid using immobilized CALB as biocatalyst (Yao et al., 2008). The melting point of the branched ester (isopropyl oleate) was lower than that for its straight-chain counterpart (propyl alcohol) while the viscosity was not really affected, making this ester more appropriate as biolubricant (Yao et al., 2008). Polyols have also been employed in the design of synthetic esters with

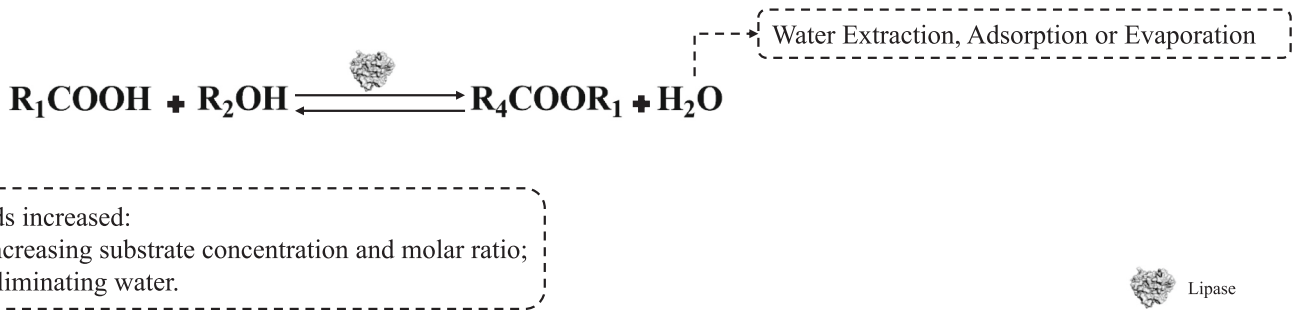

Fig. 4. Scheme of the esterification reaction, a thermodynamically controlled synthesis.

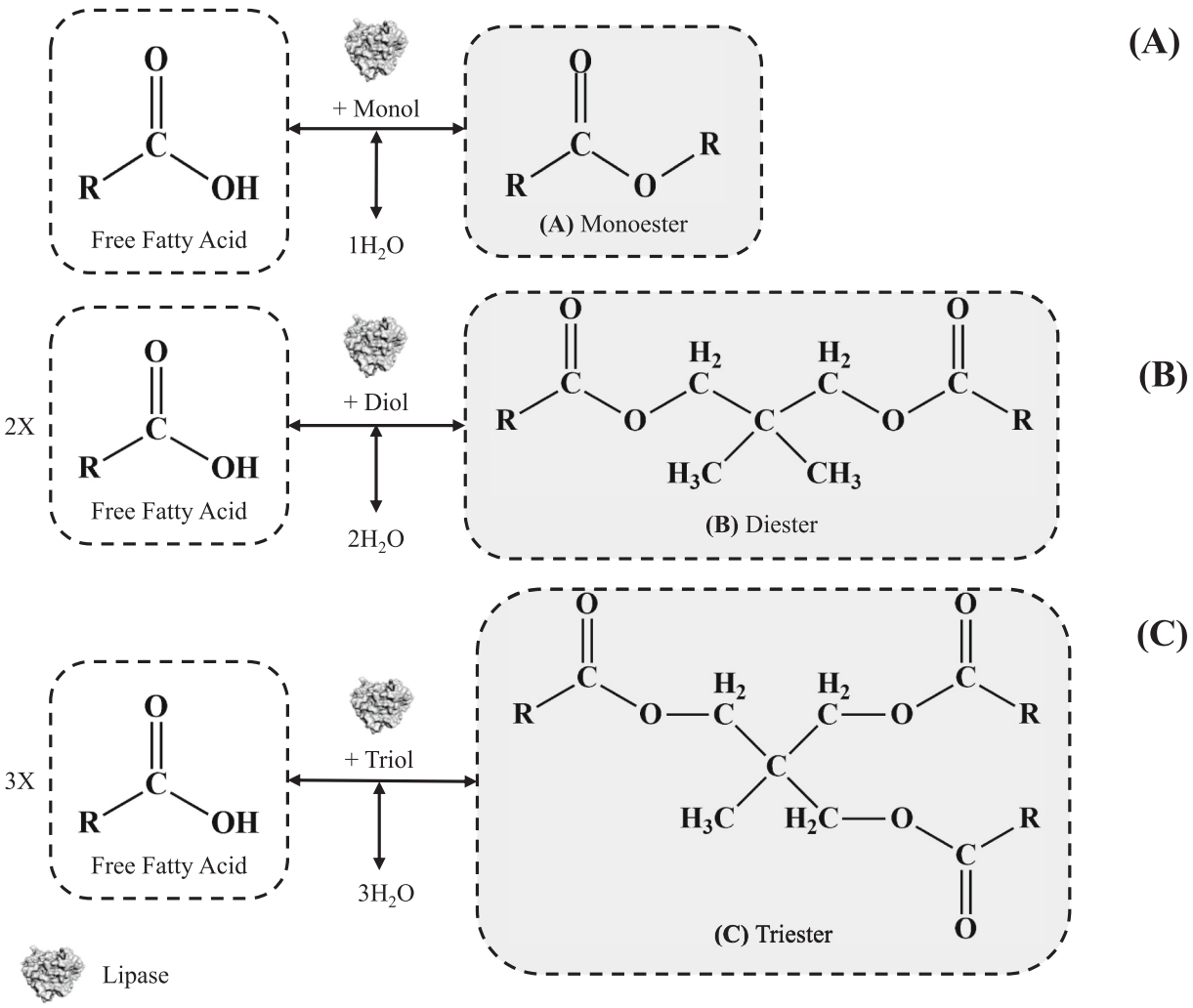

Fig. 5. Lipase-catalyzed esterification of (A) one molecule of free fatty acid with one molecule of mono-hydroxy alcohol, (B) two molecules of free fatty acid with one molecule of a diol compound and (C) three molecules of free fatty acid with one molecule of a triol.

biolubricant properties. For example, immobilized CALB was used as biocatalyst in the esterification of oleic acid with TMP, presenting 3 hydroxy groups (Åkerman et al., 2011b). It was found that the higher the content of tri-ester in the final product, the lower the pour point of the biolubricant. The same biocatalyst was employed in the esterification of levulinic acid with TMP, with the resulting tri-ester exhibiting a good viscosity index (49), a low pour point (−27 °C), and a high flash point (223 °C), all of them very adequate parameters for a lubricant (Zhu et al., 2020). PE was also evaluated as raw material to produce biolubricants via esterification reaction using lipases as catalysts. For example, it was esterified with oleic acid using Novozym 435 as biocatalyst (Happe et al., 2014). Researchers found that the biocatalyst preferred to produce monooleates, and this selectivity was not dependent upon temperature (Happe et al., 2014). Some research is focused on the effects of the alcohol in the enzymatic activity. The kinetic study of the esterification of oleic acid with furfuryl alcohol catalyzed by Novozym 435 showed a significant inhibition effect of the alcohol into the enzyme (Sengupta et al., 2012).

As it has been stated so far, Novozym 435 is the most employed lipase in the esterification of FFAs to produce biolubricants. The high operational stability of this immobilized-CALB biocatalyst to perform such reaction may explain its widespread use (Gómez et al., 2023). However, it presents some limitations (Ortiz et al., 2019). For this reason, some home-made immobilized lipases have also been evaluated in the esterification of FFAs to produce biolubricants. For example, lipase from *Thermomyces lanuginosus* (TLL) was immobilized on a mesoporous polymethacrylate hydrophobic support (PMA) via physical adsorption (Lage et al., 2016), where the support stabilized the open form of the lipase that became interfacially activated (Manoel et al., 2015). The home-made immobilized TLL was employed in the esterification of oleic acid with isoamyl alcohol, reaching 85% of conversion into biolubricants ester under optimized conditions (45 °C, 200 rpm, 0.5h, 20% of biocatalyst) and fully retaining its initial activity after twenty-two reaction cycles (Lage et al., 2016). Later, TLL, lipase from porcine pancreatic (PPL), lipase from *Mucor javanicus* (MJL), lipase from *Candida sp*. (CALA) and lipase from *Rhizomucor miehei* (RML) were immobilized on the same support (Bassi et al., 2016). TLL-PMA was the most active in the esterification of oleic acid with *n*-octanol, reaching 95.1% of conversion after 1 h under optimized reaction conditions (45 °C, 240 rpm, 10% of biocatalyst and molar ratio oleic acid/*n*-octanol of 1:1.5) and fully retaining its original activity after twelve cycles of esterification (Bassi et al., 2016). In another research, CALB was covalently immobilized onto a nanocomposite of Fe_3O_4 and lignin from cashew apple bagasse activated with glutaraldehyde and utilized as biocatalyst in the esterification of oleic acid and 2-ethyl-1-hexanol, reaching a conversion of 76.7% (Serpa et al., 2021). The immobilized biocatalyst retained up to 40% of its activity after 5 cycles of esterification (Serpa et al., 2021). The use of iron para-magnetic nanoparticles (Fe_3O_4) was regarded as a way to facilitate the biocatalysts recovery from the high viscous media (Serpa et al., 2021). However, the authors

did not confirm the covalent immobilization of the enzyme, that could be just physically immobilized considering the heterofunctionality of the support (Barbosa et al., 2014).

One enzyme frequently utilized to produce biolubricants is the commercial lipase named Eversa Transform 2.0 (ETL). This enzyme was obtained by genetic modification of TLL, and commercialized to be used as a low-cost liquid formulation in the production of biodiesel (Monteiro et al., 2021). This is also a production of esters of FFAs but using small alcohols. However, free and immobilized ETL have been employed in the esterification of FFAs to produce biolubricants, despite the alcohols being much larger and more complex than in the case of biodiesel. For instance, free ETL was used in the esterification of oleic acid with oleyl alcohol, octanol, hexanol, 3,7-dimethyloctan-1-ol and 2-ethyl-1-hexanol (Trivedi et al., 2015). Curiously, ETL activity increases with the chain length of the alcohol (Trivedi et al., 2015). In another research effort, free ETL was utilized in the esterification of oleic acid with isoamyl alcohol or octanol; however, a low conversion (~40% for isoamyl alcohol and ~20% for octanol) was observed (Cavalcante et al., 2022). Isoamyl alcohol is able to form stronger hydrogen bonds with the active site domain of ETL, according to the molecular docking and molecular dynamics studies performed by the authors (Cavalcante et al., 2022). In another approach, ETL was immobilized on a glutaraldehyde-activated hybrid support of chitosan and agarose; then, the immobilized biocatalyst was employed in the esterification of oleic acid with 2-ethyl-1-hexanol, reaching a conversion of approximately 40% (Germano de Sousa et al., 2022). Later, ETL was immobilized on macroporous hydrophobic resin (Lewatit VP OC 1600) (via interfacial activation) and, then, the immobilized biocatalyst was employed in the esterification of FFAs with NPG (Kim et al., 2021). This immobilized ETL biocatalyst was the most effective one for the synthesis of NPG esters when compared to commercially immobilized CALB, RML and TLL (Kim et al., 2021).

Although the esterification of FFAs to produce biolubricants is usually performed in stirred batch reactors, some efforts have been made to use other reactors configurations. In this regard, a microwave barrel reactor (MBR) was used in the esterification of oleic acid with TMP (Happe et al., 2012). At 25 °C, TMP is a solid alcohol, so that the esterification of FFAs with TMP is usually performed in the presence of organic solvents, which may lead to the denaturation of the lipase. The MBR-assisted enzymatic esterification of FFAs with TMP may be performed in a solvent-free medium; in addition, microwave-assisted processes are more energy efficient than the conventionally heated ones (Happe et al., 2012). This paper compared 8 commercial lipases and found that Novozym 435 was more active than the other ones, reaching more than 90% yield. In another research effort, a solvent-free enzymatic esterification was conducted in a continuous microfluidic reactor (Madarász et al., 2015). The esterification of oleic acid with isoamyl alcohol catalyzed by Novozym 435 packed in microchannel reactors reached almost full conversion (98%) (Madarász et al., 2015). Ultrasound-assisted esterification is another strategy to enhance the enzymatic production of biolubricants. For instance, the esterification of stearic acid with 2-ethyl-1-hexanol was catalyzed by Novozym 435 under ultrasound irradiation (Gawas and Rathod, 2020). Remarkably, the ultrasound-assisted esterification reduced the reaction time to 3 h from the 7h that required the process when using mechanical stirring (Gawas and Rathod, 2020). In another research effort, after a previous lipase selection, CALB and lipase from *Rhizopus oryzae* (ROL) were individually immobilized onto a hydrophobic support (styrene–divinylbenzene) via interfacial activation (Manoel et al., 2015); the immobilized biocatalysts were evaluated in the esterification of oleic acid with fusel oil in a packed bed reactor (de Lima et al., 2022). Conversions of 90-93% and high productivities (3,144 mmol g^{-1} min^{-1}) were obtained. Later, the same ROL biocatalyst was employed in in the esterification of oleic acid with fusel oil in a two-stage packed-bed reactor coupled to a water extraction column filled with molecular sieves (Vilas Bôas et al., 2021). The authors used isooctane as solvent and reported a conversion of >90% in 24 h of reaction, using (1) fusel oil and (1.5) oleic acid molar ratio, achieving a productivity of 292.20 ± 18.46 μmol g^{-1} min^{-1}. The estimated biocatalyst half-life was 179.6 h (Vilas Bôas et al., 2021). In another approach, the FFAs from linseed were enriched with oleic acid or ricinoleic acid and, then, esterified with NPG by Novozym 435, aiming to improve the properties of the feedstock (Dutta et al., 2023). The NPG-biolubricants presented enhanced oxidative onset temperature (290 °C for the oleic acid-enriched biolubricant and 270 °C for the ricinoleic acid-enriched biolubricant) than using the individual feedstocks (206 °C for oleic acid, 221 °C for ricinoleic acid and 203 °C for linseed oil) (Dutta et al., 2023). In another example, TLL was immobilized onto Duolite A568 (an anion exchange resin) and employed in the esterification of the high oleic fatty acid from palm oil with TMP, reaching a conversion of 95% under optimized reaction conditions (60 °C, 6.7 kPa, 9h, 15 wt.% of biocatalyst and 0.53 of water activity) and with a performance similar to commercial TMP triester prepared by chemical catalyst (Kim et al., 2019).

In some instances, researchers have tried to utilize discarded materials as raw substrates for the production of biolubricants, with the undoubtable ecologic interest that this can have because it avoids the discarding of these materials in nature. For example, the discarded materials from the molecular distillation of vegetable oils have a high FFAs content, and they have been employed to produce esters with biolubricant properties. In one example, palm fatty-acid distillate (PFAD) was esterified with NPG and TMP by lyophilized lipase from *Candida rugosa* (CRL, for short) (Fernandes et al., 2018). PFAD-TMP biolubricants exhibited better properties than PFAD-NPG biolubricants: higher viscosity index (187 against 166) and higher oxidative stability at 140 °C (17.5 h against 3.0 h) (Fernandes et al., 2018). In another research effort, CRL was immobilized into a commercial hydrophobic support (Accurel) and a home-made core-shell matrix of poly (methyl methacrylate) (PMMA) via interfacial activation (Fernandes et al., 2021). This biocatalyst was employed in the esterification of soybean fatty acid distillate (SFAD) with NPG and TMP. The performance of lyophilized and immobilized (Accurel and PMMA) CRL was similar when producing the NPG esters; however, CRL-PMMA was not very active to produce TMP esters (Fernandes et al., 2021).

Some papers compared chemical and biological catalysis. For example, the esterification of different FFAs (C_5–C_{18}) with TMP was evaluated using silica–sulfuric acid, Amberlyst-15 and Novozyme 435 (Åkerman et al., 2011a). The chemical catalysts were more efficient, especially in the esterification of short chain acids; however, the performance of CALB was similar to that of silica–sulfuric acid in the esterification of C_{18} acids (Åkerman et al., 2011a). It becomes noteworthy that the chemical esterification produced unwanted dark color compounds in the biolubricants, requiring further post-treatment (bleaching and deodorization); steps that can be skipped using lipases as catalysts. Moreover, biological esterification presented the lowest environmental impact (Åkerman et al., 2011a).

3.2. Hydroesterification

Hydroesterification (Fig. 6) is an ester production strategy closely related to the previous one (Folster et al., 2021; Li and Shi, 2022; Pourzolfaghar et al., 2016). This strategy starts with the oils or fats, which are submitted to a step of hydrolysis (that can be chemically or enzymatically catalyzed) to produce FFAs and glycerin (Fig. 6). After purification of the FFAs, they are esterified with the desired alcohol, again, with the option of using a chemical or enzymatic strategy (Fig. 6). The main advantage of the use of this strategy regarding to the strategies described below (transesterification using the glycerides directly) is the lack of a competitive alcohol for the production of the target ester, as glycerin is eliminated.

There are many examples of the employment of this strategy. One interesting option is the use of waste cooking oil (WCO), as this way a contaminant by-product is transformed into a valuable product, coupling the ecological interest of biolubricants with the prevention of

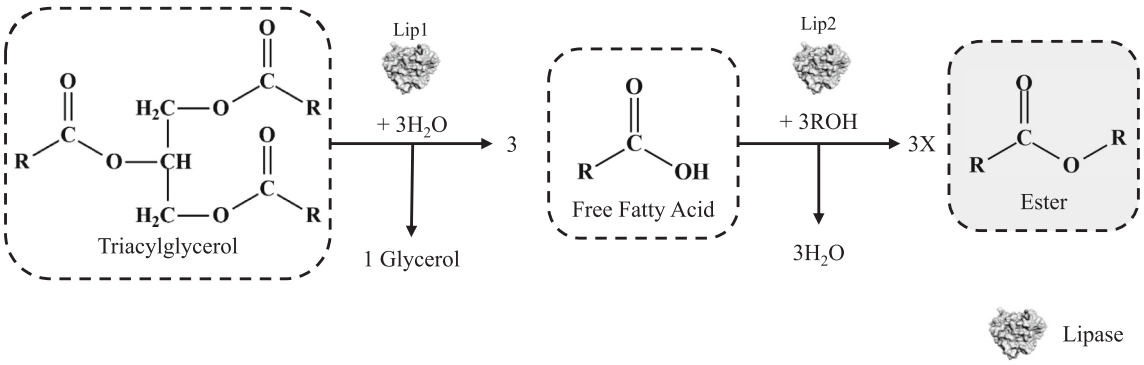

Fig. 6. Hydroesterification: (A) hydrolysis of triacylglycerol followed by the (B) esterification of the released fatty acids with an alcohol. The process may be catalyzed by one or two different lipases.

the contamination by discarding these used wasted oils into the natural environment. For example, WCO was hydrolyzed by the lipase from *Candida rugosa* (CRL) and, then, the obtained FFAs were purified and esterified with octanol by Amberlyst 15H (Chowdhury et al., 2013; Chowdhury et al., 2016). The chemoenzymatically produced ester presented good features as biolubricant (Chowdhury et al., 2013; Chowdhury et al., 2016). In another research effort by the same group, the produced FFAs were esterified with octanol utilizing Novozym 435 as biocatalyst (Chowdhury et al., 2014b). Both chemical and biological esterifications gave high conversions (> 95%); however, the biological esterification was performed at lower temperature (60 °C *versus* 80 °C); and CALB was three-fold more active than Amberlyst 15H under their respective optimal conditions (Chowdhury et al., 2013, 2014b). The researchers investigated the kinetics of the process of Novozym 435 and found that the system follows a Ping-pong bi-bi kinetics with no inhibition by substrates or products (Chowdhury and Mitra, 2015). Furthermore, the influence of reaction parameters (biocatalyst content, molar ratio, temperature and time) on the esterification of the FFAs from WCO with octanol was evaluated by the Taguchi orthogonal array method (Chowdhury et al., 2014a). Under optimized conditions (5 wt% CALB, 1:2.5 (FFAs/octanol), 60 °C and 3 h), the highest conversion into ester was approximately 95% (Chowdhury et al., 2014a). The synthetic ester presented improved viscosity index, pour point, flash point and oxidation stability when compared to WCO (Chowdhury et al., 2014a). In another example, TLL was immobilized onto citric acid modified paramagnetic Fe_3O_4 nanoparticles (prepared using an ecofriendly procedure) and employed as biocatalyst in the hydrolysis of WCO and, subsequently, in the esterification of the resulting FFAs with NPG (Sarno et al., 2019). Noteworthy, the immobilized biocatalyst retained approximately 90% of conversion after seven cycles of esterification (Sarno et al., 2019). In another research effort, WCO was first hydrolyzed by free CRL; then, the produced FFAs were esterified with TMP, evaluating CRL, TLL, ETL and the lipase from *Pseudomonas fluorescens* (PFL) immobilized via interfacial activation on a hydrophobic support (polystyrene-divinylbenzene) (Rodrigues et al., 2015) as biocatalysts of this second step (Carvalho et al., 2021). Immobilized ETL was the most active immobilized biocatalyst in the esterification of the FFAs from WCO with TMP, reaching a conversion of approximately 97% under optimized reaction conditions (55 °C, 1:3.25 (TMP/FFAs), 240 rpm, and 15 wt.%). Furthermore, the immobilized biocatalyst retained approximately 90% of its initial activity after thirteen cycles of esterification (Carvalho et al., 2021). Interestingly, the immobilized biocatalyst presented a similar performance for waste and refined cooking oils, and it was more active than Novozym 435 (Carvalho et al., 2021). In another paper, WCO was hydrolyzed by free CRL and the resulting purified FFAs were esterified with ethylene glycol using ETL immobilized in a similar support and employed in the esterification of the FFAs from WCO (Guedes Júnior et al., 2022). The esterification of the FFAs from WCO with ethylene glycol was optimized by a central composite rotatable design (CCRD), reaching an almost full conversion of the alcohol to the ester under optimal conditions: 65 °C, 1:3 molar ratio (alcohol/FFA) and 18 wt.% of immobilized biocatalyst after only 40 min of reaction (Guedes Júnior et al., 2022). Furthermore, the immobilized ETL was more active than its free counterpart under these conditions (100% of alcohol conversion utilizing the immobilized enzyme as catalysts *versus* only 32.5% of conversion employing free ETL), and it retained approximately 37% of its initial activity after seven cycles of esterification (Guedes Júnior et al., 2022). In addition, the synthetic esters presented a similar performance to commercial synthetic neopolyol esters (Guedes Júnior et al., 2022). In another interesting research effort, WCO was hydrolyzed by free CRL and, then, the FFAs from WCO were esterified with decanol, using TLL that was immobilized by interfacial activation on silica particles prepared from rice husk (an agricultural waste, reinforcing the ecological interest of the strategy) coated with octyl or phenyl groups (Sabi et al., 2022). The performance of TLL immobilized on the octyl-silica support was similar to that of TLL immobilized on the non-functionalized-silica support, while both were more active than TLL immobilized on the phenyl-silica support. However, octyl-silica immobilized TLL presented a better operational stability than the non-funcionalized silica immobilized TLL, retaining 90% of its initial activity after fifteen cycles of esterification (Sabi et al., 2022). The solid waste resulting from *Moringa oleifera* Lam oil extraction (WMO), silica and silica-WCO were evaluated as supports to physically immobilize CRL (the real cause for immobilization was not investigated) (Barbosa et al., 2021). CRL immobilized on silica-WCO was the most active biocatalyst in the esterification of isoamyl alcohol with the FFAs obtained by hydrolysis catalyzed by free CRL of crude oil from *Moringa oleifera* Lam, (Barbosa et al., 2021). After optimization, a conversion into esters of approximately 95% was achieved at 40 °C, employing a substrate equimolar molar ratio (FFAs/alcohol) and 22.6 mg FFAs/g of immobilized protein loading, maintaining its initial activity after eight cycles of esterification (Barbosa et al., 2021). It must be highlighted that the synthetic biolubricants presented a performance similar to commercial lubricants (Barbosa et al., 2021).

Chicken tallow is rich in fat content and may be an interesting but usually discarded feedstock from slaughterhouses, restaurant chains, and from food processing industry (Hernández-Cruz et al., 2017; Toldrá-Reig et al., 2020) that can be used for biolubricant synthesis. For example, the influence of reaction parameters (temperature, biocatalyst content, temperature and molar ratio) on the CRL esterification of TMP with the FFAs obtained after CRL catalyzed hydrolysis of chicken tallow, using Response Surface Methodology (RSM) has been studied (Islam et al., 2023). Under the optimized reaction conditions (3 wt% of CRL, 1:4 (TMP/FFAs), 35 °C and 2 h), the highest conversion of FFAs into ester was approximately 60% (Islam et al., 2023).

In another research, castor oil (without interest as feed) was hydrolyzed by castor seeds endogenous lipases to produce FFAs, which were later esterified with different polyols (NPG, TMP and PE) by

lyophilized CRL (Greco-Duarte et al., 2017). The hydrolysis step released approximately 93% of the fatty acids after 1h of reaction, whereas the esterification of the FFAs using lyophilized CRL was able to decrease the acidity index in approximately 90% for NPG and TMP and 75% for PE after 96 h of reaction (Greco-Duarte et al., 2017). The NPG- and TMP-esters were characterized regarding viscosity index (111 and 112, respectively), oxidative stability (50 and 54 min, respectively) and pour point (– 42 °C and – 39 °C) (Greco-Duarte et al., 2017).

Other oils without human food interest have been employed. CRL was also employed to synthesize NPG- and TMP-esters with biolubricant properties but using the FFAs from microbial oil (from *Rhodosporidium toruloides* and *Cryptococcus curvatus*) as feedstock after hydrolysis by the same enzyme (Papadaki et al., 2018). NPG resulted in higher conversion for both microbial oils. The NPG and TMP-esters were further characterized by viscosity index (183.0 and 181.0 respectively), pour point (3.0 °C and 2.0 °C, respectively), cloud point (4.0 °C and 6.0 °C) and oxidative stability (3.3 h and 4.2 h) (Papadaki et al., 2018). Similarly, the microbial oil from *Rhodotorula glutinis* was hydrolyzed by lyophilized *Candida sp*. 99–125 and, then, the FFAs were esterified by the same lipase (Ma et al., 2021). Remarkably, the microbial oil-based biolubricant presented excellent low-temperature lubrication performance (pour point = – 54 °C) (Ma et al., 2021).

Microalgae oil is another alternative feedstock used as a source of FFAs to produce biolubricants. In this regard, the oil from the microalgae *Chlorella protothecoides* was enzymatically hydrolyzed by TLL and, then, the produced and purified FFAs were enzymatically esterified with TMP (Kutluk and Kutluk, 2022). The enzymatic esterification was optimized by univariate design of experiment, reaching the highest conversion (93%) at 60 °C using 5.5% of biocatalyst and 1:3 molar ratio (TMP/FFAs) (Kutluk and Kutluk, 2022).

In some instances, fresh food oils are utilized, although this can generate some collision between energy and food human demand, in fact, there are just some few examples. For example, soybean oil was hydrolyzed by free CRL and, then, the produced purified FFAs were esterified with NPG and TMP by Lipomod 34MDP (free lipase from *Candida rugosa*), Lipozyme RM IM (immobilized lipase from *Rhizomucor miehei*, RML) and Novozym 435, reaching the best results when using free CRL (Cavalcanti et al., 2018). Next, CRL was immobilized on Accurel MP1000 (a microporous hydrophobic support) via interfacial activation (Manoel et al., 2015), further improving the results (Cavalcanti et al., 2018). A conversion of 99% into NPG-esters and 92% into TMP-esters was achieved (Cavalcanti et al., 2018). Remarkably, the home-made immobilized CRL maintained the conversions for both NPG and TMP after six cycles of esterification, whereas the commercially immobilized RML decreased the conversion from 92 to 56% after six cycles of esterification (Cavalcanti et al., 2018).

3.3. Transesterification

The transesterification is a popular strategy of production of esters, and in a more general view it is a kinetically controlled process synthesis (Kasche, 1986; Kasche et al., 1987; Marsden et al., 2020) (Fig. 7). Conceptually, it is fully different from the esterification that we have described previously. In this process, we try to convert a hydrolase (in this case, a lipase) into a transferase. The main features of this strategy make it significantly different compared to the thermodynamically controlled synthesis (Fig. 4). These are (Kasche, 1986; Kasche et al., 1987; Marsden et al., 2020):

- An activated acyl donor is necessary, that will form the acyl enzyme.
- The maximum yields are transient, as they can be over the equilibrium of the global system.
- These maximum yields are the result of the kinetic properties of the enzyme, the ratios “esterification activity/hydrolysis of the activated acyl donor activity” and “esterification activity/hydrolysis of the formed ester activity” determine their values

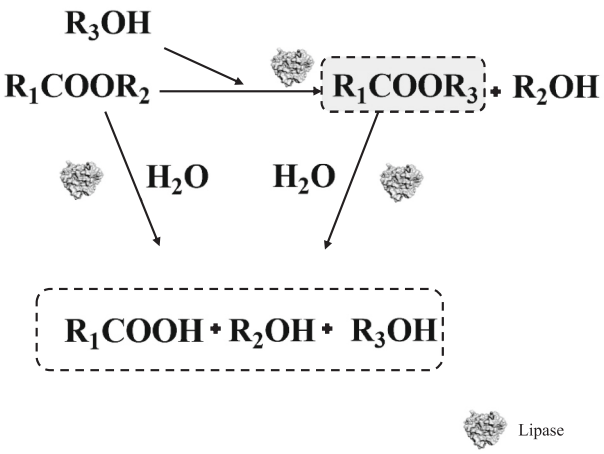

Fig. 7. General scheme of the kinetically controlled synthesis (transesterification).

- That way, the maximum yields are strictly dependent on the kinetic features of the enzyme, which can be altered by changing the enzyme source, chemical modification, genetic modification or immobilization.
- Although in the synthesis of peptides and antibiotics these reactions are performed in media with high water activity (Fernández-Lafuente et al., 1996; Hernández-Justiz et al., 1999; Kasche, 1986; Kasche et al., 1987; Schellenberger and Jakubke, 1991), in the case of lipases these reactions are performed at low water activity. That way, the differences between thermodynamic yields and the maximum yields in kinetically controlled synthesis may not be very high, mainly if the produced alcohol is eliminated. However, it should be considered that in the thermodynamic equilibrium the new target alcohol and the alcohol forming part of the initial ester substrate will both participate. Similarly, the released alcohol can make a competition with the target alcohol (behaving also like a competitive inhibitor). To overcome this, in some kinetically controlled synthesis the activated acyl door is activated with a vinyl group, as it will not participate on the equilibrium (Barbosa et al., 2011; Kolodiazhna et al., 2013; Lozano et al., 2002; Pomeisl et al., 2019). This is not utilized in the production of biolubricants, since the costs would most probably become excessive.

The simplest activated acyl donor in these reactions is to use the glycerides forming the oil and fats (Fig. 8). In most cases, some free acids will be also presented (Fig. 9). In the case of the use of lipase, this is not a problem, as lipases are able to also perform esterification (Hama et al., 2018; Toldrá-Reig et al., 2020; Zambare et al., 2021), but it should be considered that the global reaction will be a mixture between a kinetically controlled synthesis (for all fatty acids forming part of the glycerides) and a thermodynamically controlled process (for the fraction of free fatty acids) (Figs. 4, 8 and 9). Thus, this can be a really a complex process, since additional requirements pile up on the usual problems derived from the heterogeneity of the substrate described above (Arana-Peña et al., 2020a), that makes complex to find an “optimal enzyme”. In this instance, we have two different reactions simultaneously occurring, very likely with the optimal enzyme being different for each reaction. However, this is usually not discussed in most papers. Using 1,3 specific enzymes full modification of the substrate can be achieved if acyl migration occurs and the 2-monoglycerides spontaneously become 1-monoglycerides (Li et al., 2010; Sánchez et al., 2016; Wang et al., 2008) (Fig. 10).

That way, there are some examples of this direct modification of vegetable oils by enzymatic transesterification to produce high-performance biolubricants. For example, castor oil was transesterified with methanol in a reaction catalyzed by Novozym 435 (Hajar and

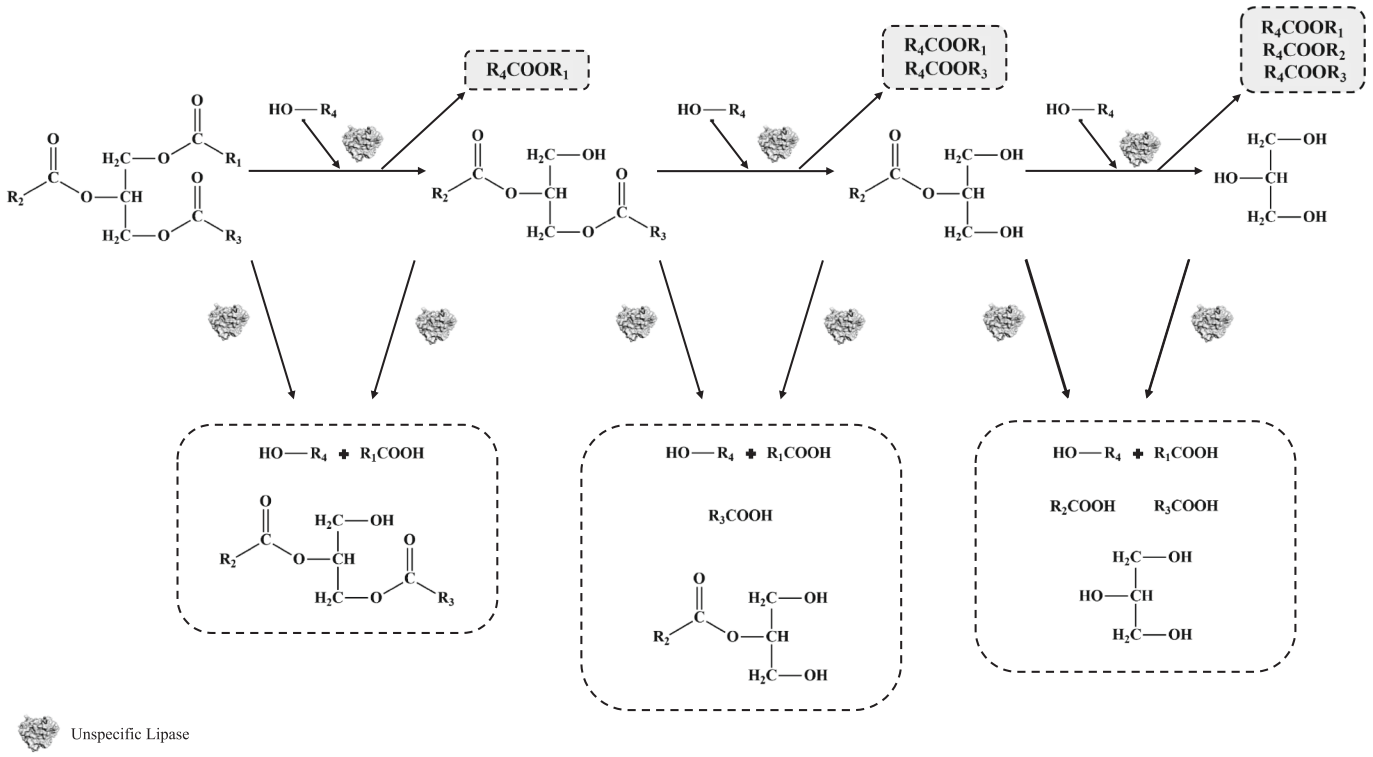

Fig. 8. Kinetically controlled synthesis catalyzed by an unspecific lipase using a triacylglycerol as activated acyl donor.

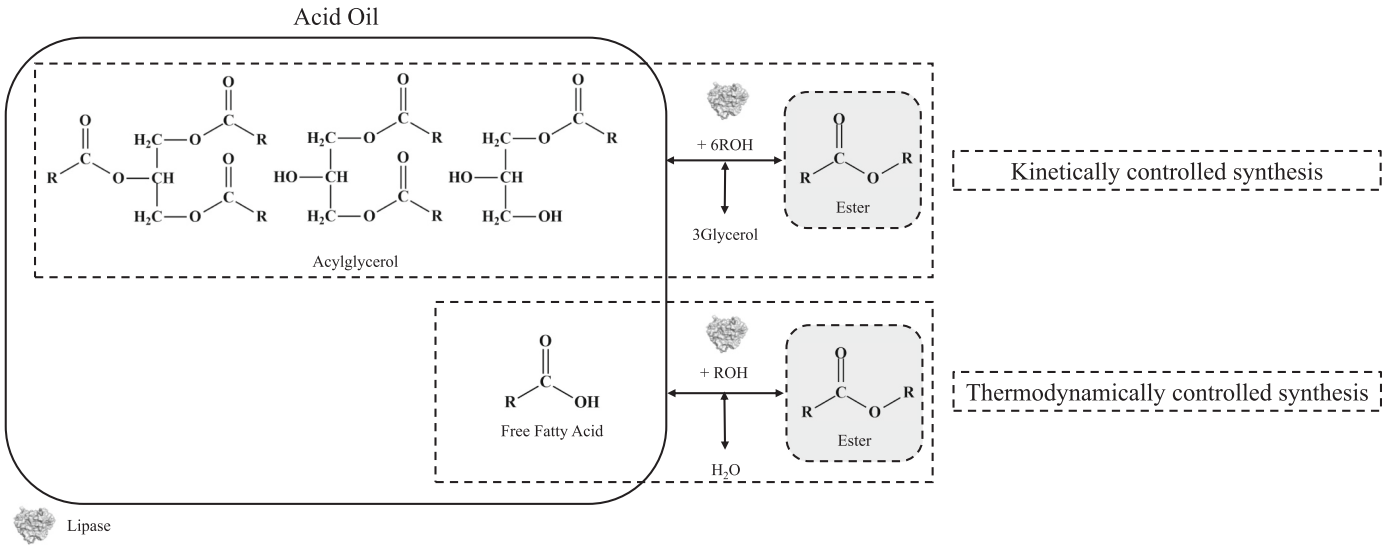

Fig. 9. Simultaneous transesterification/esterification of an acidic oil (containing acylglycerols and free fatty acids) catalyzed by an unspecific lipase.

Vahabzadeh, 2014a). After optimization by an artificial neural network, a methyl ester yield of approximately 98% was achieved using a molar ratio of 1:6 (oil/alcohol) and 5% of the biocatalyst under 42 °C after 39 h of reaction (Hajar and Vahabzadeh, 2014a). The enzymatic transesterification of castor oil with methanol decreased its viscosity (> 18-fold) (Hajar and Vahabzadeh, 2014a). The inhibition of Novozym 435 caused by methanol was higher than that promoted by castor oil in this process ($K_{i,methanol} < K_{i,oil}$) (Hajar and Vahabzadeh, 2014b). In another research, palm stearin was transesterified with methanol by Novozym 435 (Afifah et al., 2019). The enzymatic modification of palm stearin with methanol resulted in higher viscosity index (195.3 *versus* 172.4) and oxidative stability (267.3 min *versus* 214.9 min) than the corresponding feedstock (Afifah et al., 2019).

Vegetable oils have also been transesterified utilizing polyols. For example, the transesterification of castor oil with glycerol catalyzed by immobilized CALB, RML and TLL has been performed in solvent free system, with the objective of producing monoricinolein and diricinolein (Sun et al., 2018). Among the tested lipases, Novozym 435 yielded the highest conversion (> 92%) under optimized reaction conditions (1:6 (castor oil/glycerol), 5% of biocatalyst, 90 °C and 3h) (Sun et al., 2018). Magnetic cross-linked enzyme aggregates (mCLEAs) is a suitable strategy to produce home-made magnetic immobilized biocatalyst (Del Arco et al., 2021) to be employed in the transesterification of vegetable oils aiming to produce biolubricants. As such, ETL-mCLEAs were employed in the transesterification of WCO with different alcohols (methanol, ethanol, octanol and isoamyl alcohol) (Guimarães et al., 2021). Among

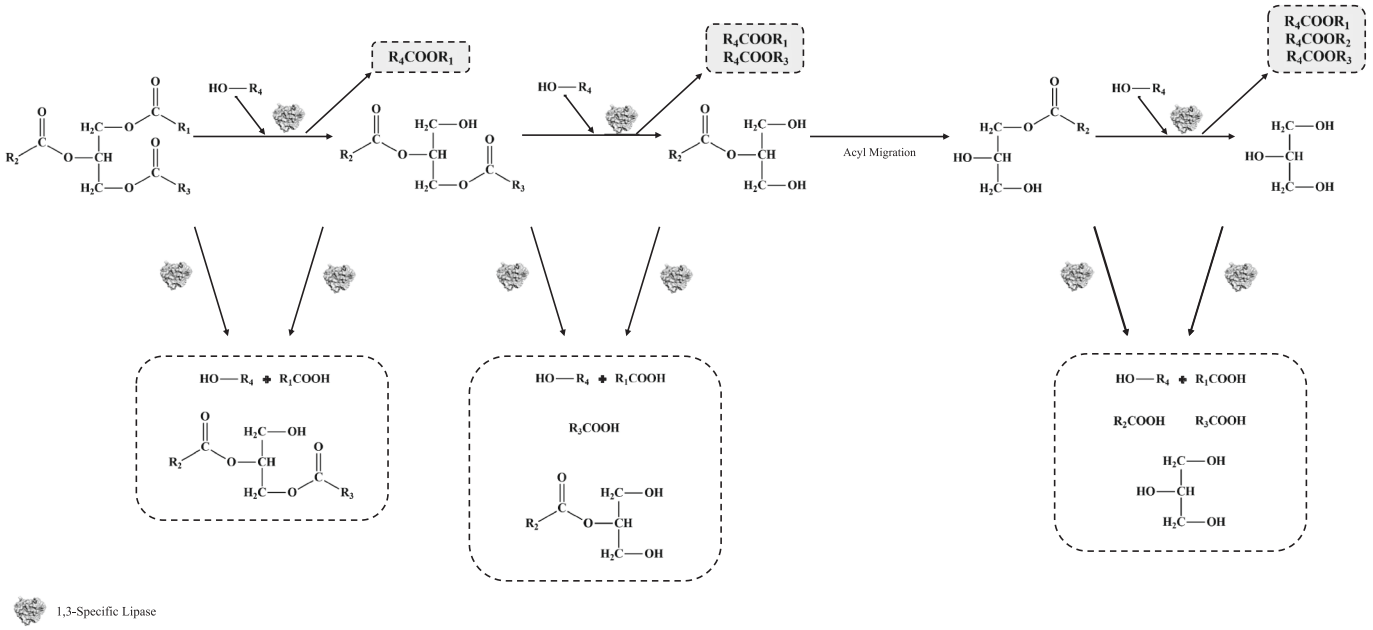

Fig. 10. Kinetically controlled synthesis catalyzed by a 1,3-specific lipase using a triacylglycerol as activated acyl donor: the role of acyl migration.

the tested alcohols, magnetic ETL-CLEAs were more active towards isoamyl alcohol, reaching a conversion of approximately 90% (against 34% for free ETL) (Guimarães et al., 2021). In another paper, the lipase from *Burkholderia cepacia* (BCLt) was immobilized onto an epoxy matrix silica-hydroxyethyl cellulose; then, the immobilized biocatalyst was employed in the transesterification of palm kernel oil with fusel oil (Guimarães et al., 2021). The authors also compared the batch and continuous processes; as a result, a conversion into esters of 99 wt.% was achieved for the batch process after 48 of transesterification while this yield was reached in only 8 h for the continuous process (Cerón et al., 2018).

In another quite interesting example, microalgae oil was transesterified with fusel oil, using BLC immobilized on Nb_2O_5 particles (Da Silva et al., 2020), which can be used itself as catalyst to produce biolubricants (García-Sancho et al., 2017).

Feedstocks with high FFAs content have been also used in the production of biolubricants (Fig. 9). These are the conditions where is clearer a mixture between kinetically and thermodynamically controlled synthesis (transesterification and esterification). For example, soybean oil deodorizer distillate (SODD) with a high FFAs content (18.52 wt.%)

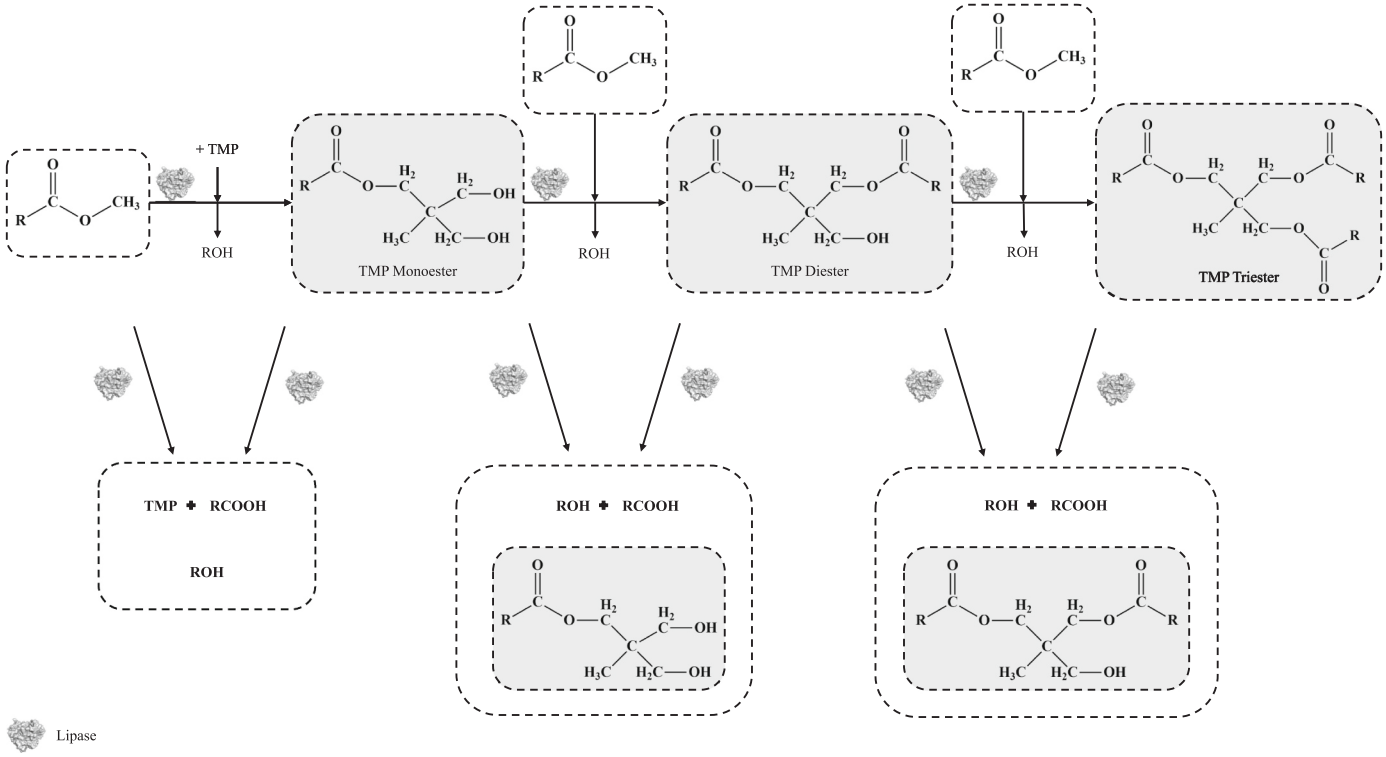

Fig. 11. Transesterification of methyl esters (e.g., from biodiesel) with trimethylolpropane (TMP) catalyzed by a lipase.

was transesterified/esterified with isoamyl alcohol by ETL; as a result, a biolubricant with interesting properties was obtained, especially the high viscosity index (>160) can be remarked (de Araujo-Silva et al., 2022).

Another feedstock to produce biolubricant via transesterification is biodiesel (Fig. 11) (esters of short alcohols), due to the difference in prices of biodiesel and biolubricants. Glycerin production is avoided, but methanol or ethanol may be produced (in some instances may be eliminated by evaporation). One example of this strategy is the transesterification of commercial biodiesel produced from rapeseed oil with 2-ethyl-1-hexanol by immobilized TLL (Kleinaitė et al., 2014). In another research, commercial biodiesels produced from castor oil, soybean oil and jatropha oils were transesterified with TMP by immobilized CALB, immobilized RML and lyophilized CRL (da Silva et al., 2015). The transesterification of castor oil biodiesel with TMP catalyzed by lyophilized CRL resulted in the highest conversion (95%), under optimized reaction conditions (3.915:1 (castor oil biodiesel/TMP, 4.0% of biocatalyst content, 1.0% of water content, 40 °C and 24h) (da Silva et al., 2015). In this system, in order to enhance the conversion of biodiesel into biolubricant, the released methanol was removed by decreasing the pressure by vacuum (0.01 bar) to facilitate its evaporation (da Silva et al., 2015). Similarly, a vacuum system was employed to remove the released methanol in the transesterification of palm oil biodiesel with TMP catalyzed by Novozym 435 (Wafti et al., 2021). In this paper, the conversion of biodiesel into biolubricant increased as the pressure decreased (1.0-0.1 mbar) once methanol may inhibit CALB and compete with TMP in the transesterification reaction (Wafti et al., 2021). The same strategy was employed to remove the released methanol during the transesterification of palm oil biodiesel with TMP catalyzed by Novozym 435 (Abd Wafti et al., 2022). In a similar approach, lyophilized CRL was used to catalyze the transesterification of biodiesel from castor oil and TMP, removing the methanol by a pervaporation system, thereby enhancing the biolubricant production in 115% (Diaz et al., 2017).

NPG is another example of polyol employed in the transesterification of biodiesel to produce high-performance biolubricant. For example, biodiesel from soybean oil or castor oil was transesterified with NPG, in a reaction catalyzed by immobilized CALB and RML (Aguieiras et al., 2020). Conversions up to 95% were obtained for both biodiesels using both lipases; however, the reaction time using soybean oil biodiesel was shorter (24 h) than that employing castor oil biodiesel (48 h) (Aguieiras et al., 2020). The enzymatic transesterification of biodiesel with polyols enhanced the lubricant properties of the product, so that it may be used as a high-performance biolubricant. In the enzymatic transesterification of castor oil biodiesel with NPG, for example, the viscosity index increased (from 59 for the biodiesel to 84 for the biolubricant) as well as the pour point (from – 21 °C of the biodiesel to – 27 °C of the biolubricant) and the oxidative stability (from 22 min of the biodiesel to 35 min of the biolubricant) (Aguieiras et al., 2020). In another study, CRL was immobilized onto 3-aminopropyltriethoxysilane-functionalized and glutaraldehyde-activated Fe_3O_4 via covalent bonding (not confirmed by the authors) (Hajar and Vahabzadeh, 2016). The home-made immobilized biocatalyst was employed in the transesterification of castor oil with methanol in a magnetically stabilized fluidized bed reactor, reaching approximately 97% of conversion under optimized reaction conditions (40 °C, 10 mT, 24h, 15mL/min, 5:1 (methanol/castor oil)) (Hajar and Vahabzadeh, 2016).

One of the papers compared the enzymatically and the chemically catalyzed transesterification of biodiesel with TMP (Angulo et al., 2018). In this study, methyl oleate was transesterified with TMP by Novozym 435 or sodium ethoxide, with the chemical transesterification reaching a conversion approximately 2-fold higher than that of the biological transesterification but using a much higher temperature (140 °C against 100 °C) (Angulo et al., 2018).

3.4. Oligomerization

The oligomerization of FFAs is another strategy employed to produce high-performance biolubricants (Hayes and Kleiman, 1995), even though it is not as widely used as the other strategies. To perform this strategy, using a hydroxy-fatty acid is required, and the goal is to promote the esterification between the hydroxyl group of one molecule with the carboxylic group of other molecule, these polymers are called estolides. Estolides may be found in many natural oils, as the result of some indigenous reactions (Hayes et al., 1995). Very recently, it has been shown that the culture of *Pseudomonas* sp 4252 in oleic acid produces (*E*)-10-hydroxy-8-octadecenoic acid and (*E*)-7,10-dihydroxy-8-octadecenoic acid molecule (Peláez et al., 2003). These molecules are later esterified to form estolides. The authors proposed that a lipase from this strain is involved in this oligomerization, obtaining from FAAs dimers to hexamers in the final culture medium (Peláez et al., 2003).

In this review, we will focus on the specific production *in vitro* of estolides. One problem, not mentioned in most papers, is that when using the free fatty acids (that is, a thermodynamically controlled strategy) there will be a free fatty acid in the initial FFA, and this acid may generate an acid index that is not recommendable for final application (Fig. 12). This may be solved by adding (initially or at the end of the process) some standard alcohol, which after reaction can block the carboxylic group, but we have not found any paper showing this possibility (Fig. 13). The problems will not exist if fatty esters are utilized (that means to use a kinetically controlled strategy) (Fig. 14). All strategies described above may be used to produce these estolides (esterification, transesterification, hydroesterification) (Figs. 4, 6 and 7).

Castor oil is rich in ricinoleic acid (12-hydroxy-9-*cis*-octadecenoic acid) (>80 wt.%), an unsaturated hydroxy fatty acid; and, depending on the lipase specificity and reaction conditions, the hydroxyl moiety of one molecule of ricinoleic acid can react with the carboxy moiety of another molecule of ricinoleic acid, and it is the oil where most researchers have focused their attention to produce estolides (Bódalo-Santoyo et al., 2005; Bódalo et al., 2009).

One example uses a hydroesterification strategy (Fig. 6). In this paper, castor oil was hydrolyzed, then, the produced FFAs were mixed with NPG, TMP, and PE, with the expectation of getting esters of these alcohol, using lyophilized CRL as catalyst (Greco-Duarte et al., 2017). However, the real product of the reaction was the production of estolides when using this enzyme. Utilizing other lipases, such as Novozym 435 or immobilized RML, the polyol esters were detected while no estolides were found (Greco-Duarte et al., 2017). This paper concluded that the estolides are a main reaction product when using CRL as catalyst even in the presence of polyols (Greco-Duarte et al., 2017). The estolides size increased exponentially from 8h to 14h, reaching a plateau after 16 h of reaction; however, the average oligomerization degree increased as the time increased, producing approximately half of pentamers (+) after 24 of reaction (Greco-Duarte et al., 2019). It must be mentioned that an increase in the estolide number corresponds to an increase in viscosity index and oxidative stability, as well as a decrease in pour point (Greco-Duarte et al., 2019).

3.5. Epoxidation and oxirane-ring opening

Use of some promiscuous activities of lipases have permitted the use of lipases to produce the epoxidation of unsaturated fatty acids, that followed by oxirane-ring opening may upgrade the properties (e.g., oxidative stability) of the product as biolubricants. Initially, the production of peracids by using hydrogen peroxide catalyzed by lipases was considered the starting point of this modification of fatty acids and other interesting processes (Hagström et al., 2011; Orellana-Coca et al., 2005; Törnvall et al., 2009; Tufvesson et al., 2011). However, the exact mechanism is unclear, a recent paper suggests that from the 5 different epoxidation routes, epoxidation could be formed by the previous formation of peracids, or by direct modification of the hydrogen peroxide

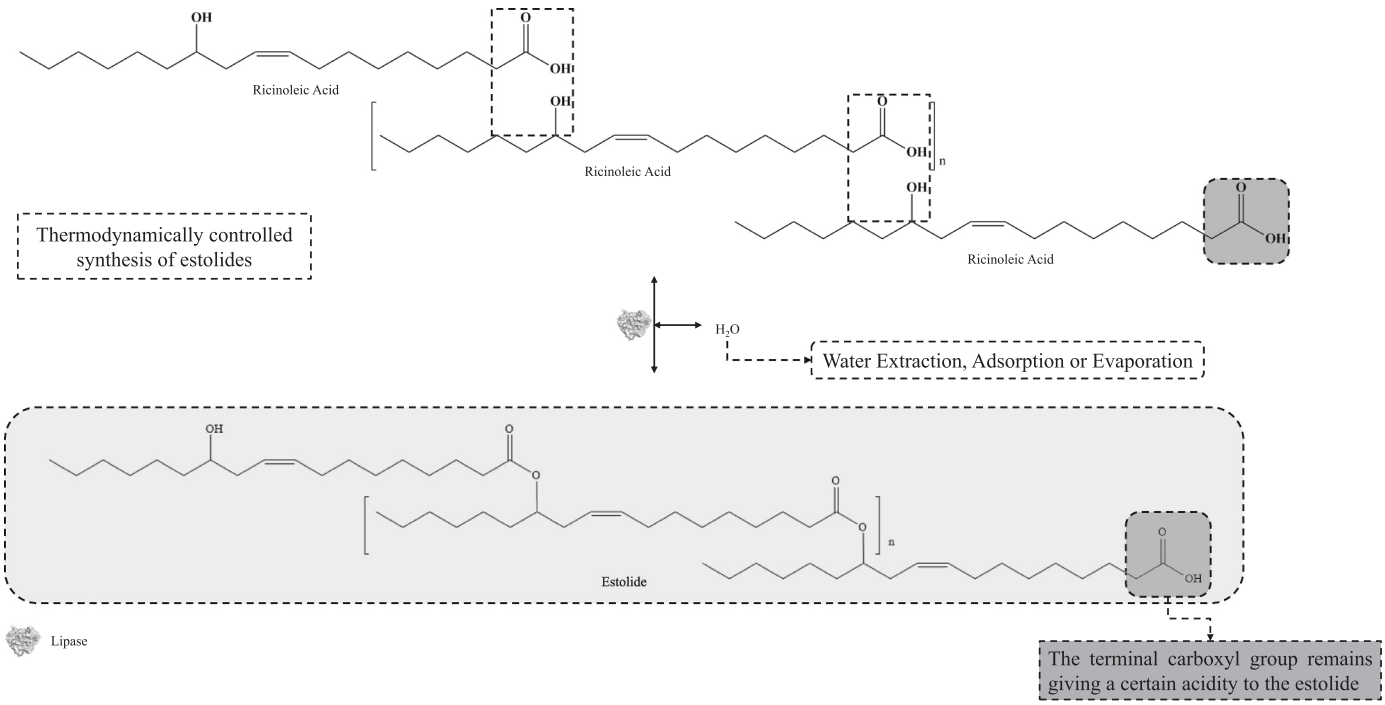

Fig. 12. Lipase-catalyzed oligomerization of ricinoleic acid into estolides via esterification.

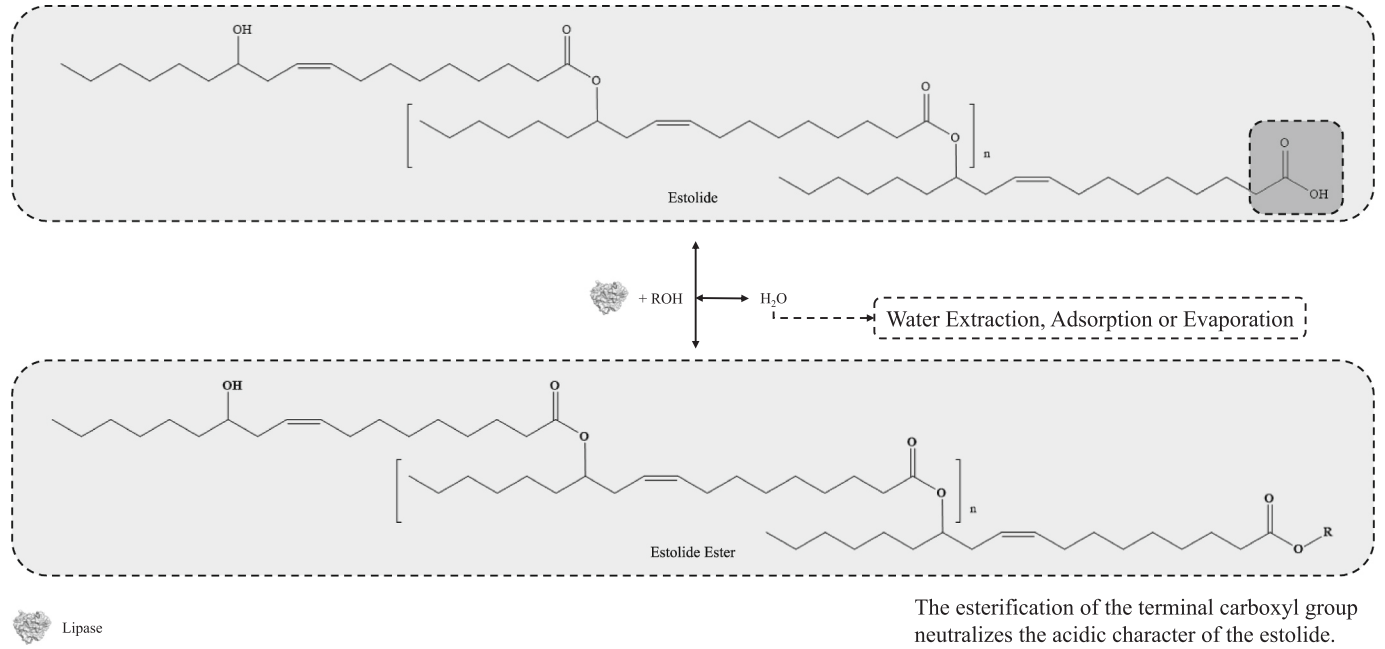

Fig. 13. Lipase- catalyzed esterification of the carboxylic group of ricinoleic estolides to decrease its acidity.

with the double bond, the model suggest that both can be true, although both will be catalyzed by the lipase (Salmi et al., 2022). Hydrogen peroxide is a strong oxidant agent that can produce many undesired effects on the enzymes (Hernandez et al., 2012), but many efforts have been performed to increase the stability of lipases in the presence of this enzyme inactivating agent (Hernandez and Fernandez-Lafuente, 2011; Irani et al., 2013; Törnvall et al., 2010; Törnvall et al., 2007).

For example, linoleic acid was epoxidized by immobilized-CALB using H_2O_2 as oxidant agent; then, the epoxidized linoleic acid was used as biolubricant (Salimon et al., 2012). The epoxidized linoleic acid presented increased pour point (– 41 °C against – 2 °C) and flash point (128 °C against 115 °C), but decreased viscosity index (130.8 against 224) and oxidative stability (168 °C against 189 °C) compared to linoleic acid (Salimon et al., 2012). In another research effort, WCO was hydrolyzed by lyophilized *Candida sp*. 99–125 to selectively release unsaturated free fatty acids, which were esterified with 2-ethyl-1-hexanol by Novozym 435 (Zhang et al., 2020). Then, the esters were epoxidized by immobilized CALB, using H_2O_2 as oxidant agent to form a peracid (Zhang et al., 2020). Finally, the oxirane ring of the epoxidized ester was open using octanoic acid as nucleophilic agent using as catalyst [HMIm][PF6] (an ionic liquid) (Zhang et al., 2020). Overall, the epoxidation and oxirane-ring opening of WCO resulted in an octylated branched

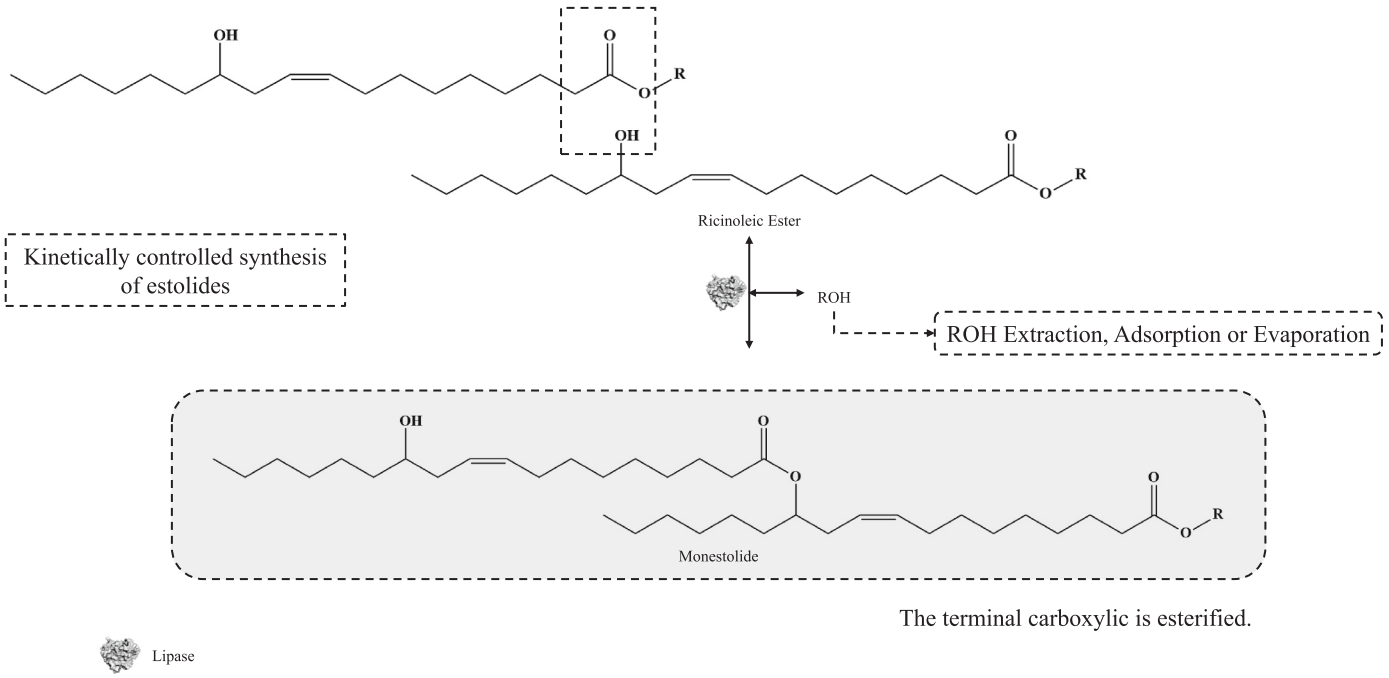

Fig. 14. Lipase-catalyzed oligomerization of ricinoleic methyl ester into estolides via transesterification.

biolubricant with excellent properties, such as low pour point (– 61 °C), high viscosity index (149) and high thermo-oxidative stability (oxidative onset temperature of 312.06 °C) (Zhang et al., 2020). Similarly, palm stearin methyl ester was epoxidized by Novozym 435, using H_2O_2 as oxidant agent and acetic acid (Afifah et al., 2021). After optimizing the reaction conditions by RSM, a conversion of ester into epoxide of approximately 99% was achieved, using a biocatalyst content of 6.416 wt.% for a H_2O_2/C=C molar ratio of 1.51 mol and for acetic acid/C=C molar ratio of 0.163 mol at 52 °C for 4.34 h (Afifah et al., 2021). The epoxidation of palm stearin methyl ester resulted in enhanced tribological properties (lower friction coefficients and wear scar diameter) (Afifah et al., 2021). A research concluded that the enzymatic epoxidation of oleic acid with hydrogen peroxide takes place by the adsorption of oleic acid and hydrogen peroxide onto the surface of the immobilized lipase, thus forming peroleic acid as the epoxidation agent; in addition, it was concluded that the adsorption of oleic acid on the immobilized lipase surface is predominant when compared to the adsorption of hydrogen peroxide, water, peroleic acid or the epoxidized oleic acid (Salmi et al., 2022).

In another interesting approach, linoleic acid was first hydrated, evaluating four different hydratase enzymes (from *Lactobacillus acidophilus, Elizabethkingia meningoseptica, Stenotrophomonas maltophilia, Lysinibacillus fusiformis*) for the process (Xu et al., 2021). Among the screened hydratases, the hydratase from *Lactobacillus acidophilus* (OleA) resulted in the highest yield (84.2 wt.%) of hydroxyl fatty acid (Xu et al., 2021). Then, the produced hydroxyl fatty acid was epoxidized by immobilized CALB, using H_2O_2 as oxidant agent (Xu et al., 2021). The epoxidized hydroxyl fatty acid was then esterified with ethanol catalyzed by immobilized CALB (Xu et al., 2021). Subsequently, the ester produced in the previous step was intramolecularly epoxidized using LiBr as catalyst (Xu et al., 2021). Finally, the product from the previous reaction was esterified with methyl laurate using [HMIm][PF6] as catalyst (Xu et al., 2021). Remarkably, the chemoenzymatic modification of linoleic acid resulted in a biolubricant with low pour point (– 64 °C) (Xu et al., 2021).

4. Conclusions

The production of biolubricants should maintain or even increase its steady growth in the future. The necessities to save energy make the utilization of lubricants fully necessary to avoid energy loses; the ecological danger of the petroleum-derived lubricants evidences the convenience of using biolubricants. The use of enzymes, which permits to use milder reaction conditions and greener processes seem to be an optimal alternative to their production, mainly when the utilized fatty acids are unstable (under drastic pH values or at high temperatures). The relatively high price of biolubricants (e.g., compared to biodiesel) has helped the use of these relative expensive biocatalysts to become feasible. However, there are significantly fewer of reports on enzymatic production of biolubricants than in the production of biodiesel, and some points remain fully unexplored, and they can be a further input in the enzymatic process intensification.

At first glance, the simplest strategy to produce esters with biolubricant properties is the direct esterification, as this is a one step process and the purification may be simpler. The use of biodiesel as feedstock is more problematic, as it is a two steps process, requiring the production and purification of biodiesel before the biolubricant production. However, a company that produce biodiesel may have some excess of this biodiesel and its transformation to a product with higher value may be a way to utilize it. On the other hand, the biolubricant strategies based on hydroesterification of the substrate, described in Section 3.2, requires a step of purification of the free fatty acids before their esterification with the selected alcohol. It has the advantage of eliminating the competition between glycerin and the new alcohol, but the final balance will be the results of the specificity of the used enzyme. Moreover, using this strategy the final purification of the product may be simpler, as glycerin has been previously eliminated (that is require two steps of purification, but may be a simpler one). The final selection of the strategy of enzymatic biolubricant production may be defined by the necessities and facilities of the specific company.

For example, the use of mixtures of lipases should permit, as in the case of biodiesel, to increase reaction rates and yields in many instances, and this strategy has not been applied in the area of biolubricants. Some specific problems for the different biolubricants remain unstudied. For example, the acidity of estolides final product may be a problem, but could be easily solved using an adequate alcohol (added to the initial mixture or at any point of the reaction course). However, we have not found just one paper on this regard. The epoxidation reactions require

the use of hydrogen peroxide, and this is an enzyme inactivating agent. Thus, a great effort to produce lipase biocatalysts with a high resistance to this reagent should be performed.

Moreover, the use of immobilized enzymes in these highly viscous mixtures should be considered as an additional difficulty, where the appropriate dispersion of the biocatalyst particles and its recovery may not be a simple task. Many authors use free enzymes, but this can promote some complications downstream, and the advantages of using heterogeneous biocatalysts are lost. For these reactions, these difficulties should be considered when selecting the immobilization material. In these instances, the use of monoliths, membranes and other biocatalysts configurations where it is not necessary to retain and recover the biocatalyst by using a filtration step and it is not necessary to disperse the biocatalysts in the biolubricant suspension may be a more adequate solution than the use of particulate biocatalyst. This viscosity problem will reach the maximum intensity when using solvent free reactions, where a large percentage of the reaction medium will be the biolubricant at the end of the reaction. However, solvent free systems have many advantages (e.g., high concentration of product, higher productivity of the reactor, saving of solvents (that means saving of contaminants). As main drawbacks may be the high viscosity of the medium point below, and if some inactivating agent is released (e.g., methanol), its concentration may be very high in this solvent free systems, and even higher in the immobilized enzyme environment, than using an appropriate solvent. This may be solved by extraction of the negative compound, mainly when it is more volatile that any of the products (again, as it is the case of methanol). Although some of the studies have used some solvents (Bassi et al., 2016; Da Silva et al., 2020; de Lima et al., 2022; Hajar and Vahabzadeh, 2014a, 2014b, 2016; Happe et al., 2014; Lage et al., 2016; Malhotra et al., 2015; Salimon et al., 2012; Vilas Bôas et al., 2021), most of the papers use solvent free systems, showing the interest of these systems for medium added products such as biolubricants. Ionic liquids may become a problem for the downstream and also too expensive for this reaction and supercritical fluids use to have a negative effect on enzyme stability, perhaps these reasons justify the lack of studies in these media.

Apparently, all these problems can be solved, researchers just need to focus their attention on these different topics. That way, we can be optimistic in the future of enzymatic production of biolubricants. Considering the wide range of possibilities to produce biolubricants (esters of polyols or long alcohols, estolides, modified fatty acids), each with different features and very likely adequate for specific applications, the use of enzyme produced biolubricants should greatly increase in the short time.

Credit author statement

Rodolpho R. C. Monteiro performed the initial literatures search and edited the final version of the paper and prepared the figures.

Angel Berenguer-Murcia edited the final version of the paper and Figures.

Javier Rocha-Martin, Rodrigo S. Vieira and Roberto Feranandez-Lafuente designed and wrote the initial draft of the paper, edited the figures and the final version of the manuscript.

Declaration of Competing Interest

None.

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