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Two-step enzymatic production of environmentally friendly biolubricants using castor oil: Enzyme selection and product characterization

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HIGHLIGHTS

- Castor oil hydrolysis using castor-seed lipases gives a high yield of unmodified COFFA.
- Molecules with good lubricant characteristics are produced by the esterification of COFFA.
- Estolides from COFFA esterification by CRL are the main reaction product.
- CRL prefers ricinoleic acid as a nucleophile compared to polyols.
- Estolide biolubricant properties are outstanding except for high acidity.

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ABSTRACT

We performed two-step enzymatic biolubricant production: castor oil hydrolysis and esterification of castor oil free fatty acids (COFFA) rich in ricinoleic acid. The hydrolysis step utilized castor seeds as catalyst yielding 93.13 ± 5.9% COFFA in only 1 h. In the esterification step, *C. rugosa* lipase (CRL) decreased the acidity by over 80% after 96 h, utilizing as polyols neopenthylglicol (NPG), trimethylolpropane (TMP) and pentaerytritol (PE) and showed about 70% acidity decrease without polyols, indicating the production of COFFA polymers (estolides). Nuclear magnetic resonance (NMR) confirmed estolides as the main product, reaching a polymerization degree of 6/7 without polyols, 4 in the presence of PE and ricinoleic acid dimers in the presence of NPG and TMP. Analyses of biolubricant properties showed that the best product was the estolide with a polymerization degree of 6/7: viscosity index of 162, oxidation stability of 51 min and pour point of −42 °C.

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1. Introduction

The 21st century is marked by environmental degradation and grave changes in the natural functioning of the biosphere [1]. It is essential to develop green technologies that allow economic growth without environmental disturbance [2]. Environmentally friendly processes that are comparably efficient to those already in use are being studied in order to develop technologies that allow gradual replacement of conventional chemical processes by biological processes [3].

Currently used mineral lubricants derived from petroleum sources are clear examples of useful but environmentally dangerous products [4]. The current legislative environmental standards have led to the replacement of mineral oils with more ecologically benign synthetic oils, usually based on esters of long-chain fatty acids from vegetable oils and polyols [5].

Vegetable oils are the mainly raw material for this purpose due to its renewable character and the quality of the final product. Biolubricants may be produced from chemical modification of vegetable oils that spare the structural problems of vegetable oils making them able for the application as lubricant [4] and this process can be made by chemical [6] or enzymatic catalysis [7–10]. Also vegetable oils present good viscosity index, good pour point and good evaporation loss, but their wider application is limited by the thermal and oxidative instabilities [11].

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Moreover the production by green enzymatic routes together with their biodegradability constitutes a clear example of green chemistry, to be considered biodegradable, biolubricants must decompose within one year through natural degradation [12]. Vegetable oils are known as typically 99% biodegradable, usually falling to 90–98% after mixing with additives, while mineral oils are only 20% biodegradable [13]. This is more one between the factors described here that make vegetable oils a promising substrate for biolubricant production.

One of the ways to produce biolubricants is through the esterification of the free fatty acids [9,10] that can be obtained by the vegetable oil hydrolysis. Ricinoleic acid esters have been suggested as potential biolubricants, due to their structure. Ricinoleic acid is the main component of the castor oil plant *Ricinus communis* L., reaching 70–90% of the total FFA content [14]. Castor-oil plant seeds, in addition to their high oil content [15,16], contain certain enzymes [17] of which lipases were used in this study [18,19].

Currently, the industrial hydrolysis of this oil to produce free fatty acids is performed by thermal or chemical hydrolysis (usually using alkaline catalysts) [20], which can cause oxidation of the final product (see below). Ricinoleic acid can also be produced by saponification followed by acidification [21]. This procedure, besides the mild temperatures compared to thermal hydrolysis, gives a product with color and odor degradations and a large quantity of an acid sludge and hard water in the downstream process [22], making it desirable to hydrolyze the oil using lipases [23] to obtain ricinoleic acid.

Ricinoleic acid, formally known as 12-hydroxy-9-cis-octadecenoic acid [24], is a fatty acid with specific physical properties due to the hydroxyl group in carbon 12 and the double bond between carbons 9 and 10. This rigid configuration offers several advantages, making this compound interesting for different applications such as cosmetics (emulsifiers), paper (as anti-foam), food (as an additive), etc. [25]. However, the oxidative stability of ricinoleic acid is questioned due to the hydroxyl group in its structure [26]. The preservation of this hydroxyl group makes it unsuitable to use chemical catalysis to produce the esters, and reinforces interest in enzymatic catalysis for the modification of this acid, which can be produced under milder conditions. However, the very rigid structure of the acid may make it difficult to find a lipase that can recognize it as a substrate. On the other hand, considering that lubricants may be used at high temperatures, this instability of ricinoleic acid could be a problem for their applications. One likely solution for this is esterification of the hydroxyl group [27].

Enzymatic catalysis, mainly using lipases (triacylglycerol ester hydrolases, E.C. 3.1.1.3 - IUPAC), has been used to successfully produce a variety of fuels like biodiesel and biolubricants [7–10,23]. In vivo, lipases generally act at a substrate/ aqueous interface, catalyzing the hydrolysis of triacylglycerol ester linkages, producing free fatty acids and glycerol [28,29]. To fulfill this function, lipases have a peculiar catalytic mechanism, called interfacial activation, which involves the movement of an oligopeptide that blocks the active center and the lipase adsorption on the hydrophobic surface of the oil drop [30,31]. In vitro, lipases can be used to catalyze several synthetic reactions such as esterification and transesterification [32,33], which increases their industrial importance.

According to [34], the thermal stability of the esters of ricinoleic acid is directly related to the presence or absence of the hydrogen in the β-carbon for the alcohol function. The presence of the hydroxyl group could cause decomposition of the ester molecule, producing an acid and an alkene with little energy input. Thus, the selected alcohols for this study were neopenthylglicol (NPG), trimethylolpropane for (TMP) and pentaerytrithol (PE); the absence of the β-hydrogen confers steric protection of the ester linkage and improved thermal and oxidative stability.

An esterification reaction is a thermodynamically controlled process [35–37] Thus, the thermodynamic constant of the process and therefore the water activity (product of the reaction), concentrations and molar ratios of the substrates, pH, temperature, etc. will determine the yield of the process, whereas the catalyst only determines the reaction rate [35–37]. However, using this hydroxy fatty acid, it is possible that, depending on the conditions and enzyme employed, some estolide (where the hydroxyl groups of one ricinoleic molecule can be esterified with the carboxylic group of another molecule) can be produced [38], and this could depend on the enzyme employed, affecting the overall ester yield. In addition to being a complication in the reaction design, the presence of this estolide may be considered as merely a problem, or on the contrary, may be interesting as a biolubricant (e.g., hydroxyl group oxidation is no longer a problem).

We analyzed the properties of the several biolubricants produced: oxidation stability, pour point, viscosity at 40 and 100 °C, viscosity index (VI), total acidity index (TAI) and water index. As catalysts, we utilized some of the most frequently used enzymes: lipase B from *Candida antarctica* (Novozym® 435) [39,40], lipases from *Rhizomucor miehei* [41,42] and commercial extracts from *Candida rugosa* lipases [43]. This last has been shown by zymography to produce some esterification using castor oil biodiesel [44].

Here we present a new strategy to produce biolubricant molecules based on ricinoleic acid, using castor oil as the raw material in a solvent-free reaction medium, to avoid the use of any solvent that could be considered a contaminant. The purpose is to obtain ricinoleic acid esters through hydroesterification [45,46,33] in a two-step enzymatic process: enzymatic hydrolysis of vegetable oils and subsequent esterification of the free fatty acids obtained by the previous step with the alcohol selected. Direct use of castor oil as a substrate would eliminate the chemical or thermal catalysis stage, making the process more ecologically benign and avoiding undesired modifications.

2. Materials and methods

2.1. Materials

Castor oil was purchased from Campestre (São Bernardo do Campo, Brazil); Castor seeds and ricinoleic acid were kindly donated by Bioóleo Bahia (Feira de Santana, Brazil) and Miracema-Nuodex (Jardim São José, Brazil) respectively. The polyols neopentylglycol (NPG), trimethylolpropane (TMP) and pentaerythritol (PE) were purchased from Sigma-Aldrich (Jurubatuba, Brazil). The lyophilized commercial lipase from *Candida rugosa,* Lipomod™ 34 MDP, was obtained from Biocatalysts Inc. (USA). The immobilized enzymes from *Rhizomucor miehei*, Lipozyme® RM-IM, and *Candida antarctica*, Novozym® 435, were obtained from Novozymes (Araucária, Brazil).

2.2. Methods

2.2.1. Determination of enzymatic activity

2.2.1.1. Activity determination of lipases from beans from castor-oil plant. The hydrolytic activity of the lipases present in the dormant castor beans was quantified by titration of butyric acid released in the hydrolysis of tributyrin (5% w/v) in Triton X-100 (25% w/v) in 0.1 M sodium acetate buffer pH 4.0 at 30 °C using the fat-free acetone preparation of lipases from the castor beans. This preparation was made as described in [47]. One unit (U) of hydrolytic activity was defined as the amount of enzyme that releases 1 μmole of butyric acid per minute under the assay conditions.

2.2.1.2. Hydrolytic activity determination of commercial enzymes. The hydrolytic activity of the commercial lipases was measured

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