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Enzymatic esterification of palm fatty-acid distillate for the production of polyol esters with biolubricant properties

Keysson Vieira Fernandes[a], Aikaterini Papadaki[b], José André Cavalcanti da Silva[c], Roberto Fernandez-Lafuente[d], Apostolis A. Koutinas[b,*], Denise Maria Guimarães Freire[a,*]

[a] Department of Biochemistry, Institute of Chemistry, Federal University of Rio de Janeiro, Cidade Universitária, Centro de Tecnologia, BL A, SL 549, Ilha do Fundão, 21949-900, Rio de Janeiro, Brazil
[b] Department of Food Science and Human Nutrition, Agricultural University of Athens, Iera Odos 75, 118 55, Athens, Greece
[c] Cenpes, Centro de Pesquisas Leopoldo Américo Miguez de Mello, Petrobras, Rio de Janeiro, Brazil
[d] Departamento de Biocatálisis, ICP-CSIC, C/Marie Curie 2, Campus UAM-CSIC, Cantoblanco, 28049, Madrid, Spain

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ABSTRACT

This contribution describes a sustainable, environmentally benign process for the production of biolubricants. The reaction was performed in a solvent-free system using a side stream from palm-oil refining (palm fatty-acid distillate, PFAD) and polyols as substrates for enzymatic catalysis. Biocatalysts consume less energy than chemical processes, and produce esters with good lubricant properties and environmentally friendly characteristics such as high biodegradability and low toxicity. The effects of different parameters (molar ratio, temperature and enzyme concentration) were evaluated during esterification of PFAD with neopentyl glycol (NPG) or trimethylolpropane (TMP) to produce polyol esters. The products obtained through esterification of PFAD with NPG and TMP in the stoichiometric molar ratio at 45 °C, using 4% (w/w) of *Candida rugosa* lipase, attained a modification of around 90% of hydroxyl groups (OH) at 10 and 8 h, respectively. These conditions were used to reach the maximum OH esterification for PFAD-TMP esters (94%) and PFAD-NPG esters (87%). NMR analysis of the final ester composition showed that the PFAD-TMP and PFAD-NPG esters were composed mostly of triesters and diesters, respectively. The properties of these esters were also characterized, including fusion and crystallization temperatures, viscosity, pour point and oxidative stability. The polyol esters showed promising lubricant properties, such as oxidative stability and viscosity within the acceptable range for many applications. This study demonstrated the potential of using PFAD for the production of environmentally benign polyol esters through non-conventional catalysis.

1. Introduction

The use of more-aggressive petroleum extraction techniques, impelled by the decrease in fossil fuel sources, transportation, and industrial processes for oil refining has resulted in many environmental problems such as oil leakage, low degradability of wastes and toxic effluents, contamination of water with gasoline and additives, and accumulation of carbon dioxide in the atmosphere (Kvemdokk, 1996). Currently, industries are searching for new, less costly and renewable raw materials in order to produce oleochemicals with high biodegradability, low toxicity and low environmental impact (McNutt and He, 2016). Bio-based oleochemicals are derived mainly from plant oils, and are used in the production of personal-care products, cosmetics, paints, bioplastics and lubricants (Pfleger et al., 2015).

Lubricants are usually liquid or semi-liquid oils and greases, which have industrial applications in order to reduce friction, heat, and wear when introduced as a film between two solid surfaces in contact. Currently, lubricants are obtained mostly from petroleum, with the problems mentioned above, and alternative sources as vegetable oils have been studied (Salimon et al., 2010). The lubricants that are commercially available are produced mainly from mineral and synthetic oils. Approximately 1% of the total mineral-oil consumption is utilized for lubricant production (Salimon et al., 2010). The world market for finished lubricants is around 35 million t per year, with biolubricants accounting for about 1% of the total production capacity (Mobarak et al., 2014). While the market for mineral-based finished lubricants has been stagnant, the market for biolubricants has shown an average growth of 10% per year over the last 10 years (Singh et al., 2015).

Biolubricants, considered as “green” products due to their

* Corresponding authors.
E-mail addresses: akoutinas@aua.gr (A.A. Koutinas), freire@iq.ufrj.br (D.M.G. Freire).

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biodegradability (Metzger, 2009), are constituted mostly of fatty-acid esters, and are preferred because their use avoids environmental pollution caused by possible leakages and by disposal of the used product. Many raw materials that meet this need are suitable for biolubricant production. Plant-derived oils are good candidates because they are environmentally friendly and structurally similar to long-chain hydrocarbons in mineral oils (Sharma et al., 2006). However, the use of vegetable oils is limited by their high melting point and low oxidative stability, which are not desirable features for lubricants (Fox and Stachowiak, 2007). The esterification of free fatty acids could lead to the production of more suitable products (Meier et al., 2007; Saboya et al., 2017; Silva da et al., 2015). Industrial processing of vegetable oils for food purposes includes a step of oil refining, where the free fatty acids are removed from the crude oil. This is achieved using molecular distillation of the oils, where free fatty acids contained in the crude oils are separated from the refined vegetable oil. Although this fatty-acid distillate (FAD) may have some practical applications, a high percentage of this by-product is discarded to the environment (Chongkhong et al., 2007; Chu et al., 2004; Ng and Wang, 2004). Thus, FAD is a low-cost by-product that could be used as raw material for the production of biolubricants via esterification, employing either enzymatic synthesis or chemical catalysis.

The utilization of polyols such as trimethylolpropane (TMP) and neopentyl glycol (NPG) has been described for the production of lubricants (Greco-Duarte et al., 2016; Gren, 2009; Gunam Resul et al., 2012; Silva da et al., 2015). Polyol esters can have good viscosity levels and a satisfactory pour point, but the final characteristics of the product will depend on the polyol used, the chain sizes of the fatty acids, and the number of unsaturated bonds and their positions in the chain (Kamalakar et al., 2013). Enzymes can be advantageous catalysts due to their substrate selectivity and specificity, preventing undesired modifications of the substrates; and their low toxicity, environmental impact, and energy consumption. Lipases (triacylesterol ester hydrolases, E.C. 3.1.1.3–IUPAC) show high catalytic activity in esterification reactions, because they are very stable, have high activity and are suitable for a wide range of substrates (Anobom et al., 2014). Lipases can be used to catalyze several synthetic reactions such as transesterification and esterification, increasing their industrial importance (Aguieiras et al., 2015). Although these enzymes have been extensively studied as catalysts for biodiesel production using different fatty-acid sources (Aguieiras et al., 2016; Åkerman et al., 2011; Silva da et al., 2015), their application to biolubricant production using a low-cost by-product like fatty acids distillates has not yet been described. The previous studies about enzymatic biolubricants were most focused on utilization of crude oils (Dossat et al., 2002), or even manufactured products like biodiesel (Greco-Duarte et al., 2017; Koh et al., 2014) as raw material. This can lead to a competition with other industries like food and fuels.

In this contribution, we describe the use of the palm fatty-acid distillate (PFAD), which is composed mostly of palmitic and oleic acids (Chongkhong et al., 2007), to produce biolubricants. For this purpose, PFAD was esterified with TMP and NPG in order to obtain mono-, di- and tri-polyol esters. The reactions were carried out using a commercial extract containing lipase activity from *Candida rugosa* (Lipomod™ 34MDP) as the biocatalyst. The lipase responsible for the formation of polyol esters is a 38 kDa enzyme (Greco-Duarte et al., 2016), and this lipase have been used in enzyme-catalyzed reactions to produce biodiesel (Fjerbaek et al., 2009) and biolubricant (Greco-Duarte et al., 2017; Silva da et al., 2015) using other sources of fatty-acids as feedstocks. This study also evaluated the reaction conditions in polyol-ester production, the composition of the polyol esters based on an NMR analysis, and the properties of the biolubricants produced.

2. Materials and methods

2.1. Materials

The lipase Lipomod 34MDP (free enzymes), derived from *Candida rugosa*, was purchased from Biocatalysts Ltd. The palm fatty-acid distillate (PFAD) was generously donated by Agropalma (Brazil). Since different batches of PFAD were used in this study some small variation could be found concerning the results. The trimethylolpropane and the neopentyl glycol (2,2-dimethyl-1,3-propanediol) were purchased from Sigma-Aldrich.

2.2. Analysis of fatty-acid composition

PFAD samples (8 μL) were transferred to tubes containing 3 mL of methanol/hexane solution (4:1 v/v) with subsequent addition of 300 μL of acetyl chloride (catalyst). The tubes were sealed under N_2 atmosphere and shaken in a water bath at 100 °C for 1 h. Then, the tubes were cooled to room temperature and 3 mL of $KHCO_3$ (10% w/v) was slowly added in order to stop the reaction and neutralize the catalyst, followed by vortexing for 30 s and centrifugation at 470 × *g* for 10 min. The organic phase was carefully transferred to storage flasks and the samples were analyzed by gas chromatography (Lepage and Roy, 1986).

2.3. Esterification reactions

The reactions between the PFAD and the polyols were carried out in jacketed glass reactors, connected to a pump-circulated water bath and continuously stirred using a magnetic stirrer. The substrate molar ratio, temperature, and enzyme concentration were initially analyzed in order to determine the best reaction conditions. For each reaction, 10 g of PFAD (269 g/mol) was used, and the amount of alcohol was calculated based on the desired PFAD:alcohol molar ratio. Different temperatures (40 °C, 45 °C and 50 °C) and enzyme concentrations (0.5%, 1%, 2%, 3%, 4% w/w of the reaction medium) were also evaluated for each reaction. The course of the reaction was followed for 72 h, then the samples were centrifuged for 5 min at 8000 *g* and the product separated from the pellet containing the enzymes was collected. The best conditions found for the PFAD-TMP esters and PFAD-NPG esters were used to produce 400 g of each product, for further characterization of the biolubricant properties.

The conversion of fatty acids to esters for each reaction was measured based on the difference in acidity between the substrate and the product solution. Specifically, 100 μL of the product was diluted in 40 mL of acetone/ethanol solution (1:1 v/v), followed by titration with 0.04 M NaOH. The acidity was calculated using the equation:

$$Acidity\ (\%) = \frac{V*M*FA}{w}$$

Where *V* is the volume of NaOH used for titration, *M* is the NaOH molarity, *FA* is the molecular weight of the fatty acids, and *w* is the weight of the sample used for titration.

The conversion of the free fatty acids to a non-acidic product was measured using the equation:

$$Conversion\ yield\ (\%) = \frac{(Ai - Af)}{Ai}*100$$

Where *Ai* is the initial acidity and *Af* is the final acidity.

Yields and conversions are given using the estimated modification of hydroxyl groups, calculated from the decrease in acidity.

2.4. Hydrolytic activity assay

The activity of Lipomod 34MDP was measured using 25 mM p-nitrophenyl laureate in acetonitrile/DMSO (1:1 v/v) as substrate,