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A cleaner approach for biolubricant production using biodiesel as a starting material

Edita Kleinaitė [a], Vaidas Jaška [b], Bronius Tvaska [b], Inga Matijošytė [a,*]

[a] Vilnius University, Institute of Biotechnology, Sector of Applied Biocatalysis, V.A. Graičiūno str. 8, Vilnius LT-02241, Lithuania
[b] JSC Biocentras, V.A. Graičiūno str. 10, Vilnius LT-02241, Lithuania

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ABSTRACT

By this study we aimed to develop a green and cleaner alternative to the existing oil-derived lubricant production by providing the market biolubricant synthesis catalyzed by enzymes. Moreover, the use of biodiesel to develop a higher added-value product is a very attractive solution for biodiesel production manufacturers in extending their production supply and the potential sales markets, especially in the East Europe region. The synthesis of 2-ethyl-1-hexyl oleate (biolubricant) was studied using commercially available immobilized lipase Lipozyme TL IM, biodiesel as a source of fatty acids and relatively cheap 2-ethyl-1-hexanol. The transesterification reaction was performed in solvent-free and water-free system. 2-Ethyl-1-hexyl oleate was successfully synthesized in 50 L scale with 100 % conversion in 10 h of reaction time at 60 °C temperature. The physico-chemical properties of 2-ethyl-1-hexyl oleate were estimated.

1. Introduction

Production of eco-friendly bio-based products using natural substances as starting raw material is a subject of scientific and industrial interest. It is also in this interest to explore natural raw materials to formulate biolubricants. Both enzymatic and chemical catalysts have been found to be effective for biolubricant production (Avisha et al., 2013; Linko et al., 1995, 1994). Nevertheless, chemical synthesis using acid or alkaline catalysts have several drawbacks: i) acid catalysis is hundreds of times slower than the alkaline, so it is not efficient to use in practice; ii) a lot of effort is needed to clean the end product from catalyst and the formed by-products, for example glycerol and remained fatty acids; iii) these chemical methods require more energy, in consequence raising the costs.

Fatty acid alkyl esters can serve as biolubricant components. So far, the investigation of biolubricant preparation have been conducted using a number of vegetable oils (sunflower, castor, soya-bean, palm, etc.) and use of various lower and higher alcohols (methanol, ethanol, n-propanol, n-octanol, etc.) for the synthesis of methyl, ethyl, propyl and octyl esters by transesterification reaction (Akerman et al., 2011). Uosukainen et al. (1998) studied transesterification of trimethylolpropane and rapeseed oil methyl ester to environmentally acceptable lubricants both by enzymatic and chemical methods, both in bench and pilot scales. They demonstrated that lipase-catalyzed transesterification of trimethylolpropane with methyl ester of rapeseed oil fatty acids to biodegradable trimethylolpropane tri-ester is possible in a relatively high yield: 64% of the trimethylolpropane was converted to the tri-ester in 24 h with *Candida rugosa* lipase, at a reduced pressure of 5.3 kPa, at 47 °C and 15% of added water (the added water quantity was a critical issue in biocatalytic reaction). In chemical transesterification using sodium methylate as the catalyst, up to 99% total conversion to trimethylolpropane esters was obtained in about 10 h, but the temperature required was as high as 120 °C. Afterwards, additional purification of final product was needed: neutralization with acidic water, washing with warm (50 °C) water, drying over anhydrous sodium sulphate. Similarly, the synthesis of methyl butyrate and octyl acetate through immobilized *Rhizopus oryzae* NRRL 3562 lipase mediated transesterification was studied under solvent-free conditions (Garlapati and Banerjee, 2013). The enzymatic synthesis of n-octyl oleate by direct esterification of oleic acid and octanol in solvent-free medium was shown to be efficiently catalyzed by a lipase from *Rhizopus miehei* covalently linked to a graft polymer (Rocha et al., 1999). Also, waste cooking oil showed high potential for lubricant production (Avisha et al., 2013; Trani et al., 1991). 2-Ethyl-1-hexyl oleate (EHOL) is a potential derivative for lubricant production and also as a non-toxic and biodegradable plasticizer in plastics production. Several attempts have been made to create

* Corresponding author. Tel.: +370 85 240 4679; fax: +370 85 2602116.
E-mail address: inga.matijosyte@bti.vu.lt (I. Matijošytė).

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biocatalytical routes by using lipases for the synthesis of 2-ethyl-1-hexyl oleate from various vegetable oils (Linko et al., 1995, 1994) and waste fats (Brenneis et al., 2004; Avisha et al., 2013).

Therefore, enzymatic synthesis has a lot of advantages over the conventional (chemical) synthesis methods such as reduced energy demand, less expensive waste treatment, "mild" conditions, no need of harmful reagents, ability to use cheap bio-based raw materials. The aim of the present work was to enzymatically synthesize 2-ethyl-1-hexyl oleate using biodiesel as a starting material. Moreover, the use of biodiesel to develop a higher added-value product is a very attractive solution for biodiesel production manufacturers in extending their production supply and the potential sales markets, especially in the East Europe region.

2. Methods

2.1. Materials

Ethyl-2-hexanol-1 and sodium phosphate dibasic dodecahydrate were purchased from Merck. Sodium phosphate dibasic and gum arabic were purchased from Fluka. Biodiesel, originated from rapeseed oil, was purchased from JSC Rapsoila. Isopropanol and p-nitrophenyl palmitate were obtained from Sigma–Aldrich. Lipozyme TL IM was purchased from Novozymes, sodiumdesoxycholate from Fisher Scientific, p-nitrophenol from Alfa Aesar. All reagents used in this study were of analytical grade and used as received. EIA09 software is disposed by Biocentras.

2.2. Analytical methods (GC)

GC spectra were recorded using GC-2010 (Shimadzu, Kyoto, Japan) which was equipped with a flame ionization detector and Stabilwax®-DA capillary column (30 m × 0.25 mm internal diameter) with a film thickness (0.25 μm) of stationary phase (polyethylene glycol). Helium was used as a carrier gas. Oven temperature was programmed as follows: from 100 to 260 °C at 10 °C/min, and then held at the final temperature of 260 °C for 30 min. The other chromatographic conditions were as follows: injector temperature 265 °C and detector temperature 270 °C; sample injection volume: 1 μL. The conversion was calculated using the following formula:

$$\text{Conversion} = \frac{A_{\text{EHO}}}{A_{\text{EHO}} + A_{\text{MetOle}}} \times 100\%$$

whereas, A_{EHO} – peak area of 2-ethyl-1-hexyl oleate at retention time of 21 min

A_{MetOle} – peak area of methyl oleate at retention time of 15.6 min

2.3. Enzyme activity test

Enzyme activity test for commercially available Lipozyme TL IM (Novozymes) was performed as described by Winkler and Stuckmann, 1979. 1 U is defined as 1 nmol of p-nitrophenol ($\lambda = 400$ nm) formed per 1 min at 40 °C temperature and pH = 8.0.

2.4. Influence of temperature for transesterification reaction

For reaction 89 g (0.3 mol) of biodiesel and 47 g (0.36 mol) of 2-ethyl-1-hexanol (EHOH) were taken to keep the molar ratio of 1:1.2. The reaction mixture was placed in a temperature-controlled 500 mL volume 3-neck round-bottomed flask and incubated for 10–15 min to stabilize the chosen reaction temperature. The mixing was performed by using mechanical stirrer. The reaction was initiated by slowly adding 13.6 g (913 kU or 10% w/w) of biocatalyst Lipozyme TL IM to the reaction mixture. Transesterification reaction was performed at four different temperatures: 30 °C, 40 °C, 50 °C and 60 °C. The formation of EHOL was followed on time by GC.

2.5. Influence of component ratio for transesterification reaction

The reaction was performed at 50 °C temperature in a temperature-controlled 500 mL volume 3-neck round-bottomed flask with mechanical stirring. The investigation was carried out at molar ratios of and the use of enzyme: 1:1.5; 1:1.2; 1:0.9; and 1:0.8. The amount of biodiesel was kept the same – 89 g. The amount of alcohol was used respectively to the defined molar ratio and the amount of enzyme was kept to be 13.6 g (913 kU or 10% w/w of total reaction mixture).

2.6. Reusability of biocatalyst

Biodiesel of 90 g and 2-ethyl-1-hexanol of 37.6 g were placed in a temperature-controlled 500 mL volume 3-neck round-bottomed flask and incubated for 10–15 min to stabilize reaction temperature at 60 °C. The reaction was initiated by adding 12.76 g (856 kU or 10% w/w) of Lipozyme TL IM to the reaction mixture. The reaction was followed on time by taking samples and analyzing by GC. After one reaction cycle, enzyme was filtered through glass filter (grade 160) from the reaction mixture and was applied again to perform another reaction cycle. Ten reaction cycles were investigated.

2.7. Up-scale of transesterification reaction

The reaction was performed in a temperature-controlled 70 L volume reactor with mechanical stirring. Initial reaction mixture consisted of 28.08 kg (28.5 L) biodiesel and 18.17 kg (21.9 L) 2-ethyl-1-hexanol was incubated for 1 h to reach the constant temperature of 55 °C. Afterwards, the reaction was initiated by adding 4.3 kg of Lipozyme TL IM. The stirring rate was kept to be 90 rpm and the vacuum was kept to be 100–150 mm Hg for removal of formed methanol. Reaction profile was analyzed by GC by taking samples from reaction mixture each 2 h. Afterwards, the reaction mixture was filtered from enzyme and reaction product was evaporated from the formed side products and characterized.

3. Results and discussion

Biodiesel is a mixture of alkyl (methyl or ethyl) esters of fatty acids (Al-Zuhair, 2007). In our study the synthesis of 2-ethyl-1-hexyl oleate was performed by transesterification reaction using biodiesel and 2-ethyl-1-hexanol as initial substrates and catalyzed by commercially available lipase (1).