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Enzymatic synthesis of dioctyl sebacate

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ABSTRACT

Pollution and environmental conservation have increased visibility in the global context over past decades. Specifically, regarding lubricants market, concern has been raised due to the large amount of this material released to the environment. In this scenario, development of biodegradable lubricants was investigated. One of the most important class of biodegradable lubricants includes esters of dicarboxylic acids, as sebacic esters. The aim of this work was to study the enzymatic synthesis of diesters derived from sebacic acid in solvent-free system. The effects of commercial immobilized lipase (Novozym 435, Lipozyme RM IM, Lipozyme TL IM), lipase amount (3, 5, 7, 9, 11, 13 wt.%), reaction temperature (90, 100, 110 °C) and molar ratio of reactants (sebacic acid/octanol molar ratio of 1:4, 1:5, 1:6, 1:7) were studied. Experiments using sulphuric acid as catalyst were carried out for the purpose of comparison. Sebacic acid conversion close to 100% and diester molar percentage higher than 90% were obtained at 100 °C, using 5 wt.% of Novozym and sebacic acid/octanol molar ratio of 1:5. Removal of water produced in the reaction (using molecular sieves, vacuum and free evaporation of water), and reuse of biocatalyst were also investigated. The product obtained was characterized (viscosity, viscosity index, flash point, pour point and acid number) and compared with commercial mineral lubricants. Synthesized esters showed suitable physico-chemical properties similar to naphthenic oil.

1. Introduction

The increase of the automotive fleet around the world has led to a huge demand of lubricants. To supply this demand, most lubricants are produced with mineral base oils. It's estimated that only 10% of lubricants used in the world are synthetic [1]. Lubricants derived from petroleum are poorly biodegradable and contain toxic aromatic hydrocarbons and sulfur compounds [2]. Not to mention that petroleum is a non-renewable resource, and any lack of this raw material can impact negatively in the automotive market [3].

Synthetic esters can be used as lubricants because of their specific properties, i.e. low volatility, high flash point, good thermal stability, low toxicity and good biodegradability [3,4]. These excellent properties enable them to meet all requirements and challenges imposed by modern motors and machines, both technically and environmentally concerned [1,5,6]. The great majority of ester oils are physiologically harmless and easily biodegradable in the environment [1]. However, these compounds have a higher cost compared to oils derived from petroleum [6].

One of the most important class of synthetic lubricants includes esters of dicarboxylic acids, as sebacic and adipic acids [4,7]. Dioctyl sebacate is an ester of particular interest due to its high oxidative and thermal stability, excellent lubricity, good biodegradability and moderate production costs and can be used as a synthetic lubricant [1,3,7]. Dioctyl sebacate can be synthetized by esterification of sebacic acid and octanol, using acid or enzyme catalyst. The method using homogeneous acid catalysts has many drawbacks like undesirable polymerizations reactions, corrosion processes, besides being harmful to manipulation. Its usage does not allow recuperation of catalyst to reuse. Another inconvenient related to the use of acid catalyst is the need for downstream processes to separate ester from catalyst and unreacted carboxylic acid [5,8].

On the other hand, the use of enzyme as catalyst can lead to higher specificity and mild reaction conditions. Lipases (triacylglycerol acylhydrolase, EC 3.1.1.3) are enzymes that act on carboxylic ester bonds. Their role is to hydrolyze triglycerides to diglycerides, monoglycerides, fatty acids and glycerol [9]. They also catalyze esterification, interesterification, acidolysis, alcoholysis and aminolysis. Lipases are one of the most important classes

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of industrial enzymes with various applications. New methods for synthesizing ester oils using lipases are being studied [1,4,7,10–14].

The main objective of this study was to investigate the synthesis of dioctyl sebacate via esterification reaction between sebacic acid and octanol (1-octanol and 2-octanol), using biocatalysts and conventional chemical catalyst (sulphuric acid). The source of commercial immobilized lipase, as well as temperature, sebacic acid/octanol molar ratio, lipase concentration and methods of water removal from the reaction medium were studied. The reuse of lipase Novozym 435 was also evaluated.

2. Experimental

2.1. Materials

Sebacic acid (decanedioic acid) 99%, 1-octanol (octan-1-ol) 99%, 2-octanol (octan-2-ol) 97%, sulphuric acid 98% and molecular sieves 3 Å were supplied by Sigma-Aldrich. The commercial immobilized lipases used were Lipozyme RM-IM (1,3-specific lipase from *Rhizomucor miehei* immobilized on an anionic resin), Lipozyme TL-IM (1,3-specific lipase from *Termomyces lanuginosus* immobilized on a gel of granulated silica) and Novozym 435 (non-specific lipase from *Candida antarctica* immobilized on a macroporous acrylic resin), all kindly donated by Novozymes Latin America Ltda. (Brazil).

2.2. Enzyme activity determination

Esterification activity was determined by consumption of oleic acid during esterification with butanol (oleic acid:butanol molar ratio of 1), using 3 wt.% of biocatalyst, at 45 °C. One esterification unit (U) was defined as the enzyme amount that consumes 1 μmol of oleic acid per minute under the experimental conditions [15]. The esterification activities of commercial immobilized lipases Novozym 435, Lipozyme RM IM and Lipozyme TL IM were 3688; 1816 and 702 (μmol of oleic acid min^{-1} g^{-1}), respectively.

2.3. Ester synthesis

Dioctyl sebacate (dioctyl decanedioate) was synthetized by esterification of sebacic acid and octanol (1-octanol and 2-octanol). The synthesis was carried out in a closed 15 mL batch reactor magnetically stirred, and coupled to a condenser in order to avoid alcohol loss. Temperature was kept constant by circulation of ethylene glycol in the reactor jacket. The reaction progress was monitored by gas chromatography. Several reaction parameters were investigated in order to reach higher conversion: source of commercial immobilized lipase (Novozym 435, Lipozyme RM IM and Lipozyme TL IM), reagent molar ratio (sebacic acid/octanol molar ratio equal to 1:4, 1:5, 1:6 and 1:7), enzyme concentration (3, 5, 7, 9, 11 and 13 wt.% of lipase as the sebacic acid mass), temperature (90, 100 and 110 °C). All experiments were carried out at atmospheric pressure.

2.4. Water removal method

The removal of water, a byproduct, was attempted by three techniques: adding 3 Å molecular sieves (adsorbent) to the reaction mixture, using vacuum (304 mmHg), and using an open batch reactor to favor free evaporation of water.

2.5. Lipase reuse

After reaction, lipase was separated by filtration and washed with 50 mL of solvent (hexane or octanol), filtered again and placed in a desiccator for 24 h. After this treatment, the enzyme was reused in a new batch.

2.6. Acid catalyzed esterification

Sulphuric acid was used as a homogeneous catalyst in different concentrations (0.1, 1 and 2 wt.% as sebacic acid mass) for the esterification, using sebacic acid/octanol molar ratio of 1:5 at 100 °C.

2.7. Gas chromatography analysis

The GC analysis of esters and sebacic acid was made in a VARIAN CP 3380 equipment with a capillary column VARIAN Factor Four (VF–1 ms de 15 m × 0,25 mm × 0,25 μm) and flame ionization detector (FID). Hydrogen was used as carrier gas. The column temperature was set to 80 °C during 30 s and then heated at 20 °C/min until 300 °C. Injector and detector temperatures were kept at 250 and 280 °C, respectively. Prior to analysis, samples were diluted with ethanol (1:25, v/v). Concentrations were calculated based on peak areas using calibration curves.

Conversion was defined as the number of mols of fatty acids reacted per mol of fatty acids fed to the system. Dioctyl sebacate mole fraction was defined as the number of mol of dioctyl sebacate produced per mol of species present on product that is not considering the alcohol employed.

2.8. Physico-chemical properties of esters

Physico-chemical properties of esters were determined according to the following standard test methods: viscosity at 40 and 100 °C [ASTM D445], viscosity index [ASTM D2270], pour point [ASTM D97], flash point [ASTM D92] and acid number [ASTM D974].

3. Results and discussion

3.1. Effects of source of commercial immobilized lipases

Novozym 435, Lipozyme RM IM and Lipozyme TL IM were tested to determine their activity towards dioctyl sebacate synthesis. Reactions were carried out with sebacic acid/octanol molar ratio of 1:5, 5 wt.% of lipase, at 100 °C. The results are presented in Table 1.

The highest sebacic acid conversion with 1-octanol was observed in reactions using Novozym 435 (100%), followed by Lipozyme RM IM (68.6%) and Lipozyme TL IM (7.8%). For reactions employing 2-octanol, the best performance of Novozym 435 was also verified. Conversions of 100%, 8% and 2.3% were obtained in reactions catalyzed by Novozym 435, Lipozyme RM IM and Lipozyme TL IM, respectively.

Different catalytic performance can be explained in terms of activity, selectivity and the support of these three immobilized lipases. The esterification activity of Novozym 435, Lipozyme RM IM and Lipozyme TL IM were 3688 U; 1816 U; and 702 U, respectively. The good performance of Novozym 435 and Lipozyme RM IM towards esterification reactions has been observed by several authors [16,17]. However, dioctyl sebacate molar percentage was less than 6% in reaction with 1-octanol using Lipozyme RM IM. Bruno et al. [18] observed that the sum of the number of carbon atoms of the reagents' molecule may exert an influence on the lipase activity. The size of carbon chain can restrict reactants access to the active site of the enzyme. According to them, the ideal number of carbon atoms of substrates was 15, for reactions employing Lipozyme RM IM. Therefore, only the production of mono-octyl sebacate (carbon number equal to 16) was improved for the reaction with lipase Lipozyme RM IM.

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