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Fish oil acidity reduction by enzymatic esterification

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Abstract

This work studies the enzymatic esterification for fish oil acidity reduction. Lipozyme TL 100L showed greater acidity reduction (75 %) for esterification at 40 °C, with ethanol 96 %, with enzyme/oil and alcohol/FFA mass ratios of respectively 0.01 and 3.24 w/w, reaching 3.13 mg KOH/g oil of final acid value or 1.57 % FFA content. Lipozyme CALB L showed greater acidity reduction (76 %) for esterification at 45 °C, with ethanol 99.8 %, with enzyme/oil and alcohol/ FFA mass ratios of respectively 0.0045 and 4.92 w/w, reaching 3.33 mg KOH/g oil of final acid value or 1.67 % FFA content.

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Keywords: Acidity reduction; Enzymatic esterification; Fish oil; FFA; Lipozyme TL 100L; Lipozyme CALB L

1. Introduction

The food industry generates a significant amount of by-products at different stages of food production [1-3]. In particular, by-products from meat, poultry and fish processing factories that constitute a source of hazardous waste [4]. For this reason there has been a great pressure to provide a suitable destination for these type of by-products, avoiding excessive discharges of polluting residues into the environment, reducing their environmental impact [5]. Currently, these by-products are mainly used for animal feed production, although it is also possible to use them for

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fertilizers and biodiesel production [6]. This work focuses its attention on the fish oil obtained from fish by-products and studies a process for reducing its acidity. Fish oil has been receiving particular attention and it has an important market value, because it contains long-chain polyunsaturated fatty acids, especially eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) that are part of the omega-3 series, in addition to some important minerals and several compounds with applications in nutraceuticals, cosmetics and pharmaceuticals [7].

For animal feed production the fish oil needs to have a low acidity (preferably < 6 %). A high amount of free fatty acids (FFA) present in the fish oil is an indication that the oil has been exposed to water, acids or enzymes, or has been stored for a long period of time, which affects its quality, reducing their energy and nutritional value [8]. Also, the existence of FFA in the oil increases the possibility of hydrolysis in the presence of moisture, during storage and processing. Thus, the high acidity represents the main problem associated with the fish oil processing, being extremely important to evaluate and implement economically and environmentally viable solutions to reduce it. One possible solution for the reduction of oil acidity that is studied in this work is the enzymatic esterification of the FFA present in the oil, in which carboxylic acids reacts with an alcohol to give an ester and water. At room temperature this reaction is slow, so it is necessary to use catalysts and/or heat to accelerate it. In addition to enzymes, other possible catalysts that are frequently used are strong acids such as sulfuric acid [9]. Although the chemically catalysed process is simple and rapid it has some disadvantages, such as the difficulty in completely separate the catalyst that may remain in the final product, preventing its use for food purposes. On the other hand, the enzymatic catalysts are non-toxic, act in wide pH ranges and the reaction can take place at lower temperatures, with a low probability for secondary reactions to occur, reducing the energy costs of the process and the corrosion of the equipment, in comparison with the acid or alkalis catalysed reaction [10,11]. The main disadvantages associated with the enzymatic catalysis are the high cost of enzymes and the increase in reaction time [12,13].

The biological catalysts commonly used in esterification are the lipase group of enzymes, which present high concentrations of hydrophobic amino acids that occupy strategic positions in the molecule, allowing the interaction of the enzyme with hydrophobic substrates. For industrial applications it is essential to check the properties of lipases. They are known for several characteristics such as substrate selectivity, optimum range of temperatures, pH, thermal stability and stability to organic solvents [8]. In the oils and fats industry, lipases allow reducing energy consumption and the thermal degradation of the compounds [11-13]. Hence, in this work the enzymatic catalysed esterification was selected as the preferred method for the acidity reduction of oils and fats. This method proved to be effective and environmentally sustainable, to increase the commercial value of the product and its implementation at industrial level.

2. Methods

2.1. Fish oil samples characterization

The fish oil samples were collected in a Portuguese company that converts by-products from animal processing industries into stable, value-added materials, such as fat or oil and meal that are used for producing animal feed. At the laboratory the fish oil samples were first characterized for the following parameters: density (kg/m^3), kinematic viscosity (mm^2/s), acid value (mg KOH/g oil), iodine value (g iodine/100 g oil) and moisture content (%). These properties were determined by applying the standard methods described in Mata et al. [13].

Table 1 shows the properties evaluated in the characterization of three fish oil samples used in this work for the enzymatic esterification reaction assays. The main difference between the three oil samples characterized for this work is their composition in terms of the types of fish present in the mixture. The three fish oils samples have high acid values (between 10.0 and 12.5 mg KOH/g oil) and iodine values (between 146 and 200 g iodine/100 g oil) meaning that a high amount of free fatty acids is present in the oil. The acid value also depends on the nature of the oil sample, its FFA content and degree of unsaturation measured by the iodine value. The iodine value is related to the halogenation reactions, which assumes that each double bond present in the unsaturated fatty acids can easily react with two halogen atoms, in this case iodine. Thus, the higher the iodine content the higher the amount of unsaturated fatty acids. A slight modification of the acid value of the samples occurred in time, during storage in the laboratory, which may be associated to several factors, such as temperature, humidity and exposure to light and atmospheric air. The fish oil moisture content is relatively low since during the extraction of the fish oil from the