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Studies on reaction parameters influence on ethanolic production of coconut oil biodiesel using immobilized lipase as a catalyst

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ABSTRACT

Biodiesel production by enzymatic catalysis has been the subject of much research for developing processes that can potentially compete with other types of catalysis. The objective of this paper was to study the variables that affect the transesterification of coconut oil in biodiesel production using immobilized enzymes as catalysts and ethanol. The transesterification reactions were carried out in closed glass reactors kept under agitation at 200 rpm and catalyzed by the commercial immobilized lipase Novozym 435. An experimental design with the variables: temperature (40–60 °C), enzyme concentration (3–7%) and oil:-ethanol ratio (1:6–1:10) was carried out. The best result – 80.5% conversion – was achieved with the highest temperature, molar ratio and enzyme concentration.

1. Introduction

Growing concerns over the economy and the environment, coupled with predictions that non-renewable energy reserves will be exhausted in the next 50 years, have spurred research into alternative sources of energy, such as solar and wind power, and biofuels.

In recent years, the search for renewable fuels has grown rapidly. Biodiesel has emerged as an alternative to oil and its derivatives, as its production is less costly and generates less pollution, in addition to being a source of renewable energy. Although biodiesel has similar physicochemical properties to those of conventional diesel, they are both distinct classes of compounds, and the former has the advantage of being biodegradable, renewable and generates less pollution [1]. Biodiesel and conventional diesel blends, known as BX, are used in Brazil. In these blends, X refers to the quantity of biodiesel (%v/v) added to the diesel. For example, in the B2 blend, 2%v/v of biodiesel is present [2].

Animal and vegetable oils and fats, both pure and residual, are the raw materials used for biodiesel production. Vegetable oils and fats are essentially compounds of triglycerides, glycerol esters and fatty acids. The transesterification of vegetable oils is currently the method of choice among the various methodologies described in the literature for biodiesel production, mainly because the physical properties of fatty acid esters are very similar to those of diesel [3]. Many vegetable oils have been studied for their potential as biodiesel

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material, always taking into account the technical and economic factors that affect different regions within producing countries. Recent studies include: "castanhola" oil (*Terminalia catappa* L.) [4]; "moringa" oil (*Moringa oleifera*) [5]; castor oil [6]; and "ouricuri" oil (*Syagrus coronate*) [7]. Coconut oil is widely produced in Brazil and is the main source of lauric acid used in the food, cosmetic, soap and alcohol industries [8].

The most common method for producing biodiesel is transesterification, which is a process of converting triglycerides into fatty acid esters and glycerine through alcoholic reaction. This process can include the presence of an acid, a base or an enzyme as catalysts. In the case of biodiesel, the triglycerides used are generally animal or vegetable oils or fats. Ethyl or methyl is used as alcohol, while the base is sodium or potassium hydroxide. The acid used is sulfuric, and the enzyme is lipase. The final product consists of methyl or ethyl esters (biodiesel) and glycerine [9].

The commercial methodology for biodiesel production often uses alkaline means to transesterify oil or fat in the presence of an alcohol, producing fatty acid methyl esters and glycerol. However, this methodology is somewhat inconvenient, considering the difficulty in recovering glycerol, the use of an alkaline catalyst that remains in the medium, the post-production treatment of alkaline effluent, the strong energetic nature of the process, the interference of free fatty acids and the presence of water in the reaction [10]. It has recently been observed that enzymatic catalysis specifically synthesizes alkyl esters, and allows for the simple recovery of glycerol, the transesterification of glycerides with a high content of fatty acids, the complete transesterification of free fatty acids, the reuse of the catalyst when an immobilized lipase is used, and mild conditions during the process, making it a considerably attractive alternative [11]. The major limitations of using lipase (e.g. Novozym 435) in biodiesel production include: longer reaction time, deactivation of the lipase by the alcohols and glycerol inhibition due to its adsorption on the lipase. Several studies have used diverse types of lipases to analyze the transesterification of various types of oils: soybean oil [12,13]; sunflower oil [14,15]; cottonseed oil [16]; and animal fat [17]. These studies have shown that the main factors affecting the yields produced by these reactions are: oil:-alcohol molar ratio, type of alcohol, temperature, quantity of water, oil or fat purity, and enzymes. In order to enhance Novozym 435-catalyzed transesterification and minimize the enzymatic process limitations, various methods, including the use of a second solvent [16], a step-wise reaction scheme where alcohol is added in portions [18] and ultrasound irradiation [19] have been employed. All the methods achieved yields of up to 80%.

The aim of this paper was to the study the variables that interfere in the transesterification of coconut oil catalyzed by immobilized lipase in the production of biodiesel. Transesterification was carried out in closed glass reactors agitated at 200 rpm and catalyzed by the commercial immobilized lipase Novozym 435, using ethanol as an alcohol. An experimental design with the variables: temperature (40–60 °C), enzyme concentration (3–7%); and oil:ethanol ratio (1:6–1:10) was carried out.

2. Materials & methods

2.1. Materials

The samples of raw coconut oil were kindly donated by SOCOCO Coconut Food Industry, Brazil. According to the company, the extraction of coconut oil was done by mechanical pressing of the dehydrated pulp.

The enzymes used in the study were supplied by Novozymes Latin America Limited (Brazil). Other reagents used were of analytical grade.

2.2. Characterization of transesterification products

To determine biodiesel yield (%), the characterization of ethyl esters was done by gas chromatography (GC). The parameters used for chromatography are shown in Table 1.

The analyzed sample was prepared by mixing 0.15 mL of biodiesel previously purified with 1 mL of standard solution (tricaprylin + hexane in a desiccator). A 1 μL aliquot of the sample was then injected into the chromatograph with a 10 μL glass needle.

The yield calculation in esters was carried out based on the mass and areas under the peaks corresponding to the ethyl and methyl esters, and on the internal standard, using equation (1):

$$\text{Yield}(\%) = \frac{m_p A_b f}{m_b A_p} \times 100 \quad (1)$$

where: m_p = internal standard weight (0.08 g); A_b = sum of the peak areas corresponding to the esters in the sample (peaks detected between 8 min and 13 min); f = response factor (0.78); A_p = peak area corresponding to the internal standard (tricaprylin + hexane − peak detected between 15 min and 18 min); m_b = sample weight (0.15 g).

Conversion analyses were performed in duplicate. The average conversion of each experiment was also calculated.

3. Experiment

3.1. Enzymatic transesterification

The laboratory-scale reactions were carried out in 250 mL closed glass reactors. The commercial lipase, in predetermined concentrations, was added to the ethanol–oil mixture and the flasks were incubated in a rotating chamber

Table 1 – Parameters used in the chromatography.

Chromatograph used	VARIAN CP-3800 instrument
Detector	FID (Flame Ionization Detector)
Column	2.3 m short capillary column
Temperature of the detector	250 °C
Oven temperature	150–260 °C
Heating rate	10 °C/min
Carrier gas	Hydrogen