BIODIESEL PRODUCTION VIA ESTERIFICATION REACTIONS CATALYZED BY LIPASE

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***Abstract*— The synthesis of ethyl hexadecanoate was carried out by esterification of palmitic acid with ethanol in a solvent-free system. A commercial immobilized lipase (Lipozyme RM-IM) was mixed with the reagents, in a 15 mL closed batch reactor with constant stirring and coupled with a condenser. The effects of palmitic acid/ethanol molar ratio (0.16 to 1.84), reaction temperature (65 to 75°C) and enzyme concentration (0.48 to 5.52% w/w) on the initial reaction rate of ethyl hexadecanoate were determined using central composite design 2^3 with six central points. Statistical analysis indicated that the enzyme concentration and palmitic acid/ethanol molar ratio had been found to be the most significant variables affecting the initial reaction rate. The best result was obtained under the following experimental conditions: palmitic acid/ethanol molar ratio of 0.50, temperature of 67°C, and enzyme concentration of 4.50% (w/w).**

***Keywords*— Biodiesel, Esterification, Lipase.**

I. INTRODUCTION

Biodiesel has been defined as the monoalkyl esters of long-chain fatty acids, preferentially methyl and ethyl esters, derived from renewable feedstocks, such as vegetable oils or animal fats. Its properties are close to diesel fuels, and therefore biodiesel becomes a strong candidate to replace the diesel fuels (Srivastava and Prasad, 2000). Recently, because of increases in crude oil prices, limited resources of fossil oil, environmental concerns, population increase and hence, higher energy demand, biodiesel represents a promising alternative fuel for use in compression ignition (diesel) engines.

The biodiesel advantages over conventional fuels are its lower toxicity, high biodegradability, substantial reduction in SO_x emissions, considerable reduction in carbon monoxide (CO), polyaromatics hydrocarbons, smoke and particulate matter. It is obtained from renewable resources (vegetable oils) consuming more carbon dioxide from the atmosphere during the production than is added to it by their later combustion. Therefore, it reduces the carbon dioxide content of the atmosphere and hence, reduces the greenhouse effect. Furthermore, the sulphur contents of vegetal oils are close to zero and consequently, the environmental damage caused by sulphuric acid is reduced (Vicente *et al.*, 1998; Srivastava and Prasad, 2000; Fukuda *et al.*, 2001; Soumanou and Bornscheuer, 2003).

The industrial process of biodiesel production is usually carried out by heating an excess of alcohol usually methanol or ethanol with vegetable oils under different conditions in the presence of an inorganic catalyst (Mittelbach, 1990). This chemical process is called by transesterification or alcoholysis. The most commonly used catalysts are alkali hydroxides (NaOH, KOH), carbonates and corresponding sodium and potassium alkoxides. A disadvantage of alkali-catalyzed procedures is that the homogenous catalysts are removed with the glycerol layer after the reaction and cannot be reused. Furthermore, neutralization to prevent toxic wastes is necessary and the purification of glycerol is more difficult when large amounts of catalyst have to be removed. Another disadvantage is the partial saponification reaction, which produces soap. The soap lowers the yield of esters and makes the separation of ester and glycerol difficult (Ma and Hanna, 1999; Fukuda *et al.*, 2001; Köse *et al.*, 2002). Besides, the use of more expensive refined oils is necessary because oils should have low free fatty acids content (inferior to 1%). Thus, the cost associated to oils and fats is relatively high constituting about 80% of the total cost of the biodiesel production (Bender, 1999; Faria *et al.*, 2003).

So, the production of biodiesel by direct esterification of fatty acids and alcohols (methanol or ethanol) catalyzed by lipase is an interesting alternative to decrease the operating costs associated to the conventional process as well as to overcome the above mentioned problems. In addition, it is possible the use of fatty acid mixtures in this process, usually obtained from the vegetable oil refining with a lower cost than that of the triglycerides. Normally, methanol is used as it is the cheapest alcohol in most countries. However, in Brazil it is advantageous to use anhydrous ethanol, which is already produced in large quantities for blending with gasoline. Furthermore, the environmental concern should also be emphasized, since ethanol is obtained from biomass and hence, it is not contributing for the greenhouse effect; unlike methanol, which is mainly obtained from petroleum resources (Schuchardt *et al.*, 1998; Júnior *et al.*, 2003).

It is well established that the palmitic acid is the saturated fatty acid of long chain found in larger proportion in vegetables oils. In the same way, considering the possibility to use fatty acid mixtures as raw material for