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Full Length Article

Evaluation of different lipase biocatalysts in the production of biodiesel from used cooking oil: Critical role of the immobilization support

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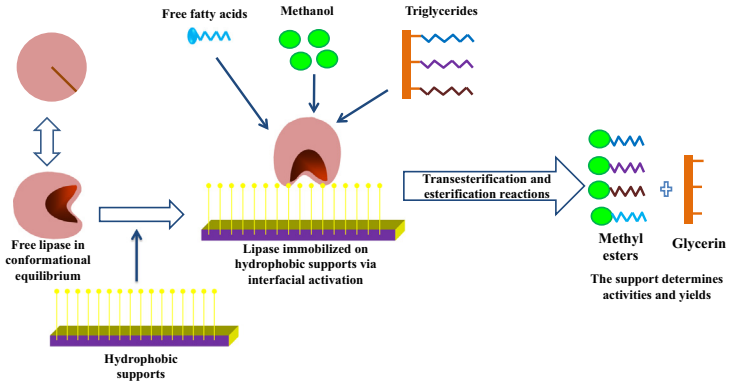
HIGHLIGHTS

- Different lipases were physically immobilized on hydrophobic supports via interfacial activation.
- These biocatalyst were utilized in the production of biodiesel from used cooking oil.
- The properties of the lipase was very depended on the immobilization support.
- Some of the new biocatalyst enhanced the results obtained with the commercial immobilized biocatalyst.
- TLL immobilized in the new supports showed to be the best biocatalyst, with more than 80% yield in 2 h.

GRAPHICAL ABSTRACT



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ABSTRACT

A new battery of biocatalyst was evaluated in the synthesis of biodiesel using a mix of used cooking oil and fats and methanol as substrates. Biocatalysts were prepared using five different commercial supports (Lifetech™ ECR1061M (styrene/methacrylic polymer), Lifetech™ ECR8804M (octadecyl methacrylate), Lifetech™ ECR8806M (octadecyl methacylate), Lifetech™ ECR1090M (styrene) and Lifetech™ ECR1030M (DVB/methacrylic polymer)) for the immobilization of four different lipases (from *Rhizomucor miehie* (RML), from *Thermomyces lanuginosus* (TLL) and the A and B forms from *Candida antarctica*, (CALA and CALB)) and of the phospholipase Lecitase Ultra™ (LU), and their performance were compared with that from commercial biocatalysts (when available: TL-IM, RM-IM and Novozyme 435). Results clearly showed that the methyl ester yields and specific activities greatly depend on the support. The addition of organic solvents usually had positive effects on all preparations activities but not on the yields, and the results depend on the solvent used, enzyme and media. In all cases, at least one of the new preparations was better than the commercial one in solvent free conditions, and in general supports having a layer of acyl groups gave better activities (octadecyl) that when the enzyme was directly immobilized on the support surface. TLL immobilized the new supports (except Lifetech™ ECR1061M) seemed to be very promising in solvent free medium, and yields near to 80% could be achieved in direct addition of

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3:1 methanol to triglyceride molar ratio. The results show that is not possible to discard one couple enzyme/support using other couple because the strong dependence.

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1. Introduction

The increasing production of used frying oils from household and industrial sources is a growing problem worldwide [1–4]. Huge quantities of used cooking oils and animal fats are available throughout the world, especially in the developed countries. Management of such oils and fats is a significant challenge due to disposal problems and possible contamination of water and land resources [5]. A likely solution is oil recycling by transformation into a valuable product, such as biodiesel (methyl or ethyl esters of the fatty carboxylic acids). Hence, we significantly enhance the economic viability of biodiesel production and solve two environmental problems, the uncontrolled disposal of used oil in the environment and the production of a combustible that has no CO_2 print [6,7]. Biodiesel is produced by transforming triglycerides into fatty acid alkyl esters in the presence of an alcohol, mainly methanol, and an acid, alkali or enzymatic (lipases) catalyst [8,9] each with some advantages and drawbacks.

Waste vegetable oils have different properties compared to refined and crude oils, since they undergo degradation by hydrolytic and oxidative reactions, and their properties are dependent on the type of treatment to which they have been subjected [2,10,11]. It has been reported that the high temperatures of typical cooking processes and the water from foods accelerates the hydrolysis of triglycerides and increases the free fatty acid (FFA) content [1,12]. High FFA content of used cooking oils affects negatively the most frequently employed technology for biodiesel production, alkaline catalyzed transesterification [13]. Therefore, these waste oils can hardly be used in this conventional process [14]. In addition, the chemical-catalyzed transesterification of vegetable oils to biodiesel suffers from several inherent drawbacks related to energy-intensive and environmentally unfriendly processing steps such as catalyst and product recovery, and waste water treatment [15]. In this regard, the use of lipases to transform used oils into biodiesel may be a very suitable alternative [16–19].

Particularly, enzyme catalyzed processes for biodiesel production is characterized by certain environmental and economic advantages over the conventional chemical method. These include room-temperature reaction conditions, elimination of treatment costs associated with recovery of chemical catalysts, enzyme reuse, high substrate specificity, the ability to convert both free fatty acids and triglycerides to biodiesel in one step, lower alcohol to oil ratio, avoidance of side reactions and minimized impurities, easier product separation and recovery; biodegradability and environmental acceptance [9,15,20–25].

Lipases offer a green route for this transformation, although their use is limited due to several facts such as moderate activity in the reaction (compared to alkaline catalysis), not good enough reusability, high cost, *etc.* [26,27]. Some work has been conducted showing how biodiesel production may be improved by using different strategies, such as combination of different lipases (oils are heterogeneous substrates) [13,28,29], optimal reactor configuration [18,30–34], and the way the lipases are immobilized on a support [18,35–43].

Frequently, the use of lipases 1,3 specific allows reaching 100% yields, this is due to the acyl migration that relocates the fatty acid in position 2 to position 1, making it a substrate of 1,3 selective enzymes [44–47]. It has been also shown that some diffusional problems may produce the moderate activity of immobilized enzymes observed in these reactions [48,49]. The accumulation in the support environment of reaction by-products (water and glycerin) is the main reason for lipase inactivation during operation, in addition to the negative effect of alcohols (mainly methanol) on the enzymes stability [20,50–52]. This situation has encouraged the use of free enzymes as an alternative to solve the problems generated by the support [53–56]. The authors show that the non-previously immobilized enzyme may be easily recovered from the reaction medium.

However, a proper immobilization may greatly improve enzyme features, from stability to activity and resistance to stirring, as well as decreasing inhibitions and the effect of chemical modifications, *etc.* [8,57–70]. Moreover, enzyme reuse is simpler when immobilized [71,72]. For these reasons, it seems a good strategy to look for supports where the problems generated in the biodiesel reaction may be decreased and simultaneously maintain the positive effects of immobilization on enzyme properties. It has been shown that the use of hydrophobic supports may prevent glycerin adsorption on the support leading to improved biocatalyst operational stability [39–43]. Hence, the use of hydrophobic supports may improve the enzyme performance in esterifications (using free fatty acids) by reducing the accumulation of water and in transesterifications (using the glycerides) by decreasing the concentration of glycerin in the enzyme environment.

Moreover, the negative accumulation of glycerol on supports on lipase activity and the diffusion problems generated using an immobilized enzyme may be reduced by using hydrophobic organic solvents such as hexane, n-heptane or cyclohexane as reaction media [48,49,71,73]. The hydrophilic *tert*-butanol is described to permit high transesterification yields and rates, due to its moderate hydrophobicity, is able to dissolve both glycerol and methanol, so the negative effects of short chain alcohols and glycerol on enzyme activity could be totally eliminated resulting in high reaction yields and high stability of lipases [23,74,75]. The use of solvent free medium or some solvent permits to go from biphasic systems to a homogenous reaction media [74]. These solvents also reduced the negative effects of methanol on the enzyme properties. This may be also reduced by a stepwise addition of the methanol, avoiding a high concentration of this solvent being reached [76–79].

Recently a new battery of biocatalysts of different lipases has been prepared using hydrophobic supports [80]. The supports utilized were always hydrophobic, but to different degrees and with different internal morphologies. Immobilization in these hydrophobic supports followed the same mechanism, interfacial activation of the enzyme versus the hydrophobic support (involving the open form of the lipase) [81]. However, the catalysts exhibited very different features, regarding substrate specificity in hydrolysis reactions and stability under different conditions, and always at least one of the new home-made lipase biocatalysts showed better features than the enzyme immobilized on octyl agarose or the commercial counterpart [80].

In this new research effort, we analyzed the possibilities of using this new battery of biocatalysts in the synthesis of biodiesel employing a mix of used cooking oil and fats and methanol as substrates. As enzymes, we have used some of the most frequently reported in literature: lipases A and B from *C. antarctica* [82–84], lipases from *T. lanuginosus* [85] and from *R. miehei* [86,87]. Lecitase Ultra, a commercial artificial chimeric phospholipase A1 [88,89]

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