



Enzymatic conversion of sunflower oil to biodiesel in a solvent-free system: Process optimization and the immobilized system stability

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ABSTRACT

The feasibility of using the commercial immobilized lipase from *Candida antarctica* (Novozyme 435) to synthesize biodiesel from sunflower oil in a solvent-free system has been proved. Using methanol as an acyl acceptor and the response surface methodology as an optimization technique, the optimal conditions for the transesterification has been found to be: 45 °C, 3% of enzyme based on oil weight, 3:1 methanol to oil molar ratio and with no added water in the system. Under these conditions, >99% of oil conversion to fatty acid methyl ester (FAME) has been achieved after 50 h of reaction, but the activity of the immobilized lipase decreased markedly over the course of repeated runs. In order to improve the enzyme stability, several alternative acyl acceptors have been tested for biodiesel production under solvent-free conditions. The use of methyl acetate seems to be of great interest, resulting in high FAME yield (95.65%) and increasing the half-life of the immobilized lipase by about 20.1 times as compared to methanol. The reaction has also been verified in the industrially feasible reaction system including both a batch stirred tank reactor and a packed bed reactor. Although satisfactory performance in the batch stirred tank reactor has been achieved, the kinetics in a packed bed reactor system seems to have a slightly better profile ($93.6 \pm 3.75\%$ FAME yield after 8–10 h), corresponding to the volumetric productivity of 48.5 g/(dm³ h). The packed bed reactor has operated for up to 72 h with almost no loss in productivity, implying that the proposed process and the immobilized system could provide a promising solution for the biodiesel synthesis at the industrial scale.

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1. Introduction

Biodiesel (monoalkyl esters of long-chain fatty acids) has shown promise as an alternative diesel fuel because of its favorable properties, environmental benefits and the fact that it is derived from the renewable biological resources (Ma and Hanna, 1999). It contains no sulfur or aromatics, and the use of biodiesel in a conventional diesel engine results in a substantial reduction of unburned hydrocarbons, carbon monoxide and particulate matter. The most common method for producing biodiesel is the chemically catalyzed process consisting of the transesterification of vegetable oils with short chain alcohols, such as methanol, in the presence of non-selective inorganic base or acid catalysts (Marchetti et al., 2007). This chemical approach to the synthesis of biodiesel has been used at industrial scale for decades, but there are several associated problems such as removal of catalysts, excessive energy requirements, recovery of glycerol, undesirable side reactions, and the cost of the refined feedstocks. To overcome the drawbacks of the chemical process, there have been several attempts to develop the alternative methodologies for producing biodiesel including the usage

of solid heterogeneous catalysts insoluble in alcohol (Arzamendi et al., 2008), the transesterification processes in supercritical fluids (Rathore and Madras, 2007) or the enzymatic processes (Al-Zuhair, 2007).

Nowadays, the biotechnological production of biodiesel with lipases has received great consideration and is undergoing a rapid development (Ranganathan et al., 2008; Shimada et al., 2002). This is understandable since the trend towards ecologically acceptable processes is steadily growing. The employment of lipases as biocatalysts in the transesterification of triglycerides allows mild reaction conditions and easy recovery of glycerol without purification or chemical waste production. In addition, the enzymatic process tolerates the water content of oil and increases the biodiesel yield by avoiding the soap formation. Moreover, the immobilization of lipase in/on a support combines these advantages with those of the heterogeneous catalysis (Dizge et al., 2009; Nouredini et al., 2005).

There have been a number of studies investigating the use of lipases as catalysts for the biodiesel synthesis from different sources of oil and fats in the non-aqueous, the organic solvent or the solvent-free reaction systems (Al-Zuhair et al., 2007; Iso et al., 2001; Lu et al., 2008; Shieh et al., 2003). It has been shown that there are many benefits in using the solvent-free system in

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comparison with the organic solvent system, including the costs reductions and the improvement in the process control (Kose et al., 2002; Selmi and Thomas, 1998). However, although the yields obtained in the organic solvent system were high, the design of the efficient solvent-free reaction system with immobilized lipase possessing high activity and improved stability for the biodiesel synthesis still has many unresolved issues.

The major problem in implementing the enzymes into the biodiesel synthesis in the solvent-free systems is rather low enzyme stability in the presence of excess methanol, occurring as drops in oil, during the reaction. In a typical methanolysis reaction, the reaction mixture exists in two phases due to the low solubility of methanol in oil, leading to the inactivation of the enzyme and the decreased fatty acid methyl ester (FAME) yield. Among the tested lipases, Novozym 435, *C. antarctica* lipase supported on a macroporous acrylic resin (CAL-B), has been reported to be an effective catalyst for the transesterification reaction carried out in these systems and it has been selected in this study (Kose et al., 2002). To minimize the enzyme inactivation, the solvent-free reaction systems have been proposed to operate with the stepwise addition of methanol and the high conversion of 98.4% has been achieved after 48 h (Shimada et al., 1999). Several other studies have shown that the three-step addition of methanol is superior to the one-step addition (Shimada et al., 2002; Watanabe et al., 2001, 2002). Another approach of improving the performance of the lipase in the media with a high polarity as those constituted by methanol is the biocatalyst regeneration by washing its solid particles with C3–C5 alcohols. For instance, the completely deactivated *C. antarctica* lipase has restored 56% and 75% of its original activity when washed with 2-butanol and *tert*-butanol, respectively (Chen and Wu, 2003). It is apparent that extensive work has been concentrated on the use of methanol to transesterify oil and fats to methyl esters; however, no significant work has been done on the use of other acyl acceptors in the solvent-free system and these researches are still in progress (Modi et al., 2007; Xu et al., 2003). This type of reaction system was of specific interest for the research in this study.

Although we can find several examples in the literature of the biodiesel production by using other acyl acceptors including methyl acetate, these reports often present the preliminary process feasibility studies focused on the selection of acyl acceptors types and on the use of lipases and triacylglycerols of different origin. For example, Du et al. (2004) reported the transesterification of the refined and crude soybean oil with different acyl acceptors by using the immobilized CAL-B (Novozyme 435) in the solvent-free system. This study has shown that synthesis of biodiesel using methyl acetate is feasible without loss of the enzyme activity even after being continuously used for 100 batches, which is usually associated with the use of methanol. Huang and Yan (2008) have also dealt with the lipase-catalyzed interesterification of five different oils with methyl acetate using Novozyme 435, and two types of Lipozyme lipase, indicating that the Novozyme 435 was the best biocatalyst for any of the studied oils. They have explored the effect of the reaction temperature, the substrate molar ratio and the enzyme amount on the methyl esters yield and investigated the operation stability of the lipase under optimal conditions. The contribution of Kose et al. (2002) has dealt with the alcoholysis of the refined cotton seed oil with primary and secondary alcohols by using the Novozyme 435 lipase. They explored the effect of alcohol types on the alcoholysis of cotton seed oil indicating that the highest ester yield was obtained with isoamylalcohol. Generally, these works provide preliminary results on the use of methyl acetate or some alcohols as the acyl acceptors for transesterification of various oils and some principal process parameters have been investigated on the methyl ester yields on the scale of flasks. An analysis of the effect of reactor configuration and hydro-

dynamic conditions on the reaction rate and the enzyme stability was not included in these contributions. This work represents an extension of these studies involving the interesterification of sunflower oil with methyl acetate in both the batch stirred tank reactor and the packed bed reactor. The mass transfer of triglycerides to the biocatalyst sites could be a critical step limiting the rate of the transesterification reaction because the reaction mixture is heterogenous, consisting of two immiscible phase. Thus, the hydrodynamic conditions appear to be of a particular importance for this heterogenous solvent-free system. We explored the effect of the mode and intensity of stirring, reactor configuration, and the flow conditions on the activity and stability of the immobilized lipase. This knowledge will be a useful tool for further kinetic studies and design purposes.

Out of the possible raw materials with a potential to obtain biodiesel, sunflower oil is a desirable substrate for the transesterification because of the increased stability of its alkyl esters when stored and the improved fuel properties (Akoh et al., 2007). The esters of sunflower oil actually cause less injector tip fouling than diesel fuel and yield higher brake thermal efficiencies and lower smoke values (Antolin et al., 2002). Although widely used in chemical processes, reports are relatively scarce in the literature regarding the production of biodiesel from sunflower oil by lipase-catalyzed reactions, particularly in a solvent-free system (Mittelbach, 1990). A few studies have reported the enzymatic alcoholysis of sunflower oil in solvent and solvent-free systems to compare the activity of various biocatalysts and to optimize the process conditions in terms of the organic solvent, the reaction temperature, the initial water content and the methanol/oil molar ratio. It was shown that the porcine pancreatic lipase (PPL) and *Candida rugosa* lipase (CRL) immobilized on Celit 545 have been able to catalyze the transesterification of sunflower oil with short chain alcohols to simple alkyl esters in the organic solvent system effectively (Sagiroglu, 2008). In the solvent-free system, lipase from *Pseudomonas fluorescens* seems to show the greatest methanol resistance among the tested lipases, even in the solvent-free system the FAME yield has reached >90% at 4.5 M equivalents of methanol (Soumanou and Bornscheuer, 2003). However, commercially available lipases (Lipozyme, Novozyme) appear to be more suitable catalysts for the large-scale application, since the use of *Pseudomonas* lipase requires the additional immobilization step. In general, yields obtained in organic solvent were high, but enzyme consumption was relatively high in solvent-free system, which would increase production costs (Dossat et al., 2002; Selmi and Thomas, 1998). In addition, most of the studies have been based on the conventional one-at-a-time variation of parameters, which often does not demonstrate the interactive effects of the parameters.

This study has been aimed to explore the feasibility of producing biodiesel from sunflower oil using the immobilized *Candida antarctica* lipase as the catalyst in the solvent-free system. In the first part of study, the response surface methodology (RSM) and the 5-level-4-factor central composite design (CCD) have been used to identify the factors that influence the methanolysis of sunflower oil and to verify whether any changes should be made in their settings to improve the reaction. To the best of our knowledge, this report represents the first comprehensive study of the parameters affecting the biodiesel synthesis from sunflower oil in the solvent-free system. The second part of the study deals with the optimization of the operational stability of the immobilized lipase. Since the excess of methanol has been reported several times to inactivate the lipase, the alternative acyl acceptors (2-propanol, *n*-butanol and methyl acetate) have been tested for biodiesel production with respect to their effects on the enzyme activity and stability. Once the most efficient acyl acceptor had been identified, the experiments were conducted in both batch stirred tank reactor and packed bed reactor systems. The bioreactor characteristics and

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