



Research paper

Effectiveness of using deep eutectic solvents as an alternative to conventional solvents in enzymatic biodiesel production from waste oils



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HIGHLIGHTS

- Enzymatic biodiesel production from waste oils in DES was considered.
- Use of ternary DESs at different water contents was investigated.
- Enzyme-DES system was regenerated for five consecutive cycles through washing with 1-butanol.

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ABSTRACT

Ionic liquids (ILs) have been proposed as a more benign replacement to toxic and volatile organic solvents in enzymatic biodiesel production, used to minimize methanol inhibition effect and enhance the stability of immobilized enzyme. Despite their several advantages, ILs are expensive, which renders the overall process unfeasible. In this work, the use of low-cost deep eutectic solvents (DESs) has been investigated as a new reaction medium for enzymatic biodiesel production from waste oils. A DES composed of chlorine-chloride and glycerol (ChCl:Gly) was tested and its effectiveness was compared to 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF₆], which has shown positive results. To decrease the viscosity of ChCl:Gly DES, ternary ChCl:Gly:water DESs with different water contents were prepared and tested. Despite lower cost compared to ILs, without successful repeated reuse of the DES-immobilized lipase system, their advantages remain theoretical. Therefore, the reusability of the DES-Novozym[®]435 system in consecutive cycles was examined. It was shown that 34% biodiesel production yield could be achieved in ChCl:Gly at 1:2 molar ratio, compared to 23% when [bmim][PF₆] was used. The yield increased further, when the ternary DES of ChCl:Gly:water (1:2) with 3 wt% water was used, reaching 44%. By removing the by-product glycerol, the reusability of the DES-immobilized system was improved, with better results achieved using 1-butanol compared to using ethylene glycol.

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1. Introduction

The interest in biodiesel production using immobilized lipase has increased in recent years, due to the several advantages that immobilized enzymes offer over conventional alkaline catalyzed process (Marchetti et al., 2007). Novozyme[®]435, which is lipase from *Candida antarctica* immobilized on acrylic resin, is the most commonly used enzyme in biodiesel production (Taher et al., 2014; Madras et al., 2004; Ha et al., 2007). Despite its advantageous features, the major obstacle facing the commercialization of

enzymatic process is the high cost of the enzyme and the methanol inhibition (Taher et al., 2014; Modi et al., 2007). Typically, the direct exposure of the lipase to excess methanol strips-off the hydration layer necessary for the enzyme to be active.

To overcome the high cost problem, the enzyme has to be used in immobilized form to allow its repeated reuse (Modi et al., 2007; Lu et al., 2007). In some cases, the enzyme was reported to be reused effectively for 50 cycles (Shimada and others., 1999). However, using immobilized enzyme has its own challenges, which are mainly the mass transfer limitations and the by-product glycerol accumulation in the pores of the porous matrix of the support preventing reaction substrates from reaching the enzyme active sites (Xu et al., 2011).

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Using an organic solvent, as a reaction medium, have been suggested to enhance the mass transfer diffusion, and to reduce the methanol inhibition and glycerol accumulation. In that regard, *n*-hexane and *tert*-butanol were used, the former is suggested to alter the substrates affinity (Yang et al., 2004) and the former was selected because of its high glycerol solubility on one hand, and low interference with the reaction on the other (Park et al., 2013). Nevertheless, from an environmental point of view the use of these volatile organic solvents is not recommended, as they are toxic and non-biodegradable. In addition, they require an additional separation unit to separate them from the final product. Therefore, the search for a more environmental benign solvent has been gaining more attention in recent years.

Ionic liquids (ILs) have been suggested as alternatives to volatile solvents (Ha et al., 2007). ILs are non-volatile compounds composed of organic cations and inorganic anions with properties that can be tailored easily by changing the anion or cation part. In addition to solubilizing the substrates and reducing the enzyme inhibition, being practically involatile, makes ILs more environmental friendly. Furthermore, the charged cations and anions in the ILs may interact electrostatically with the lipase in a favorable manner resulting in an enhanced activity and stability (Kim et al., 2014). 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF₆], and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [bmim][NTf₂], have been widely tested for biodiesel production (Taher et al., 2017; de Diego et al., 2014; Lai et al., 2012), with yields reaching 86% and 72% were achieved in [bmim][PF₆] from microalgae lipids (Lai et al., 2012) and waste oils (Taher et al., 2017), respectively. The main disadvantage of ILs is their high cost preventing their employment at large scales. For example, it was reported that the cost of [bmim][PF₆] is 10 times higher than that of *n*-hexane (Wasserscheid, 2002).

On the other hand, DESs are cheap and easily prepared by mixing an ammonium salt with a hydrogen bond donor and heating at moderate temperature for a couple of hours (Zhao et al., 2015). The DESs shares the same favorable properties of ILs, and at the same time have a low cost and their components can be chosen so that the DESs are biodegradable and non-toxic, making them more preferable than ILs for use in enzymatic biodiesel production. Choline chloride (ChCl) based DESs have been suggested in different applications (Zhao et al., 2015, 2011, 2013) because of the favorable characteristics of ChCl. For example, ChCl and glycerol (Gly) was tested, at different molar ratios, to extract the reaction by-product glycerol from biodiesel, produced by a chemical catalyst, namely potassium hydroxide (Abbott et al., 2007; Hayyan et al., 2010). The same DES was also used in the enzymatic biodiesel production using Novozym[®]435. High yields, reaching 97%, were obtained within 3 h from Miglyol[®] oil 812 (Zhao et al., 2011) and 81% from soybean oil after 24 h of reaction (Zhao et al., 2013).

Although the use of DESs with immobilized enzymes seems promising, the viscosity of such solvents is high, reaching 376 mPa s for ChCl:Gly (1:2) at 45 °C (Yadav et al., 2014; Smith et al., 2014), compared to 97.8 mPa s for [bmim][PF₆], at same temperature. This could be a problem at large-scale production and in continuous flow processes. To overcome this, the addition of a third component, such as water, to form a ternary DES, has been suggested to reduce the viscosity. Yadav et al. (2014) measured the viscosity of pure ChCl:Gly (1:2) and different ChCl:Gly:W mixtures and found that the viscosity decreased with the increase of water fraction in the mixture. The viscosity of pure ChCl:Gly decreased to 70 mPa s when 3% water was added. Reducing the viscosity enhances the mass transfer of the reaction substrates to the enzyme active sites, and therefore increases the reaction rate and yield.

In this work, the effectiveness of using DESs in enzymatic biodiesel production from waste oils was examined and compared

Table 1

Fatty acid composition of the waste cooking oil used in this work.

Fatty acids	Carbon chain	Composition (wt%)
Myristic	C14:0	0.27
Palmitic	C16:0	8.61
Stearic	C18:0	4.6
Oleic	C18:1	57.2
Linoleic	C18:2	27.1
Linolenic	C18:3	1.22
Arachidic	C20:0	0.6
Lignoceric	C24:0	0.4

to [bmim][PF₆]. Ternary ChCl:Gly:W mixtures containing different quantities of water were prepared and tested. The work tested the activity and reusability of Novozym[®]435 in selected ChCl:Gly (1:2) water ternary DESs.

2. Materials and methods

2.1. Chemicals and enzyme

n-Hexane (99% assay), methanol (99.9% assay), 1-butanol (99% assay), Choline-chloride (98% assay), glycerol (99.5% assay) and standards solution of high purity fatty acids methyl esters (FAMES) consisting of: 4% myristic acid (C14:0), 10% palmitic acid (C16:0), 6% stearic acid (C18:0), 35% oleic acid (C18:1), 36% linoleic acid (C18:2), 2% of arachidonic acid (C20:0) and behenic acid (C22:0) were purchased from Sigma-Aldrich, USA. 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]) with a purity ≥ 99% was obtained from io-li-tec, Germany. High purity helium was purchased from Air Product Company, UAE. Zero air and hydrogen were produced by gas generator (F-DGSI, France). Novozym[®]435 with an activity of 11,900 propyl laurate (PLU) g⁻¹ with an optimum operating temperature between 30 and 50 °C was a kind gift from Novozymes A/S, Denmark (Venter and Nieuwoudt, 1998).

Waste cooking oil was obtained from Lootah Biofuels Company, UAE. Fatty acid analysis of the oil was determined using Gas Chromatography (GC) according to procedure described in Section 2.6, and the results are shown in Table 1. As per supplier's information, the free fatty acids content does not exceed 2%–3%. Anyway however, the free fatty acids content does not affect the enzymes activity.

2.2. Preparation of DESs

The ChCl:Gly DES was prepared by mixing the choline ChCl with Gly at a 1:2 molar ratio, as described by Abbott et al. (2003). Ternary DESs, denoted in this work as ChCl:Gly:W were prepared by mixing the pure ChCl:Gly (1:2) with specific amounts of distilled water. It should be noted that the water percentages, reported in the manuscript, are not with respect to the reaction volume, but with respect to the ternary DES used. Adding the water during the preparation of the DES makes it part of the solvent through strong hydrogen bonding and not free or available for the enzyme. In all cases, the mixtures were heated and mixed at 80 °C until a homogeneous liquid was formed without any solid precipitation. The formed DES was then cooled to room temperature. The procedure for preparing the DESs was much easier and less expensive than that needed for ILs synthesis.

2.3. Enzymatic biodiesel production

Transesterification reactions were performed in 5 ml screw-capped vials incubated in an orbital shaker (Stuart SI 500, UK) at a constant temperature of 45 °C and a shaking speed of 150 r min⁻¹.

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