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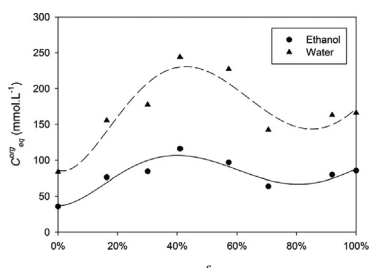
## Liquid–liquid phase equilibrium studies of organic–aqueous medium during biodiesel synthesis

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## HIGHLIGHTS

- LLE of biodiesel reaction mixtures were equilibrated with aqueous ethanol.
- Organic phase ethanol concentration peaked at moderate reaction extent (40–50%).
- Aqueous glycerol content profile has a maximum at 57% reaction extent.
- Distribution coefficient of water captured by a decaying sinusoidal model.
- Linear relationship between global and organic phase reactant molar ratio.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Article history:

Received 18 April 2013

Received in revised form

28 July 2013

Accepted 6 September 2013

Available online 5 October 2013

## Keywords:

Liquid–liquid phase equilibrium

Biodiesel

Vegetable oil

Ethanol

Lipase

## ABSTRACT

This work investigates the liquid–liquid phase equilibrium of reaction mixtures arising from the ethanolysis of vegetable oil. Knowledge of equilibrium phase distribution of key components in such biphasic systems is essential for guiding the design and optimisation of a counter-current extractive reactor for lipasic biodiesel production. Waste cottonseed frying oil was reacted with (to different conversion levels) in the presence of lipase B (Novozym 435). The reaction mixtures were then combined with aqueous solutions of ethanol (5, 15 and 25%v/v) at three different volume fractions (0.20, 0.35 and 0.50) and allowed to equilibrate at 318 K, followed by compositional analysis of the resultant organic phase (mainly composed of glycerides and fatty acid ethyl esters) and aqueous phase (largely water and ethanol). Distribution coefficients of ethanol and water peaked at moderate reaction extents (40–50%) and could be described by a decaying sinusoidal expression (with respect to extent of reaction) symptomatic of the dynamics for two interacting mixing tanks-in-series implicating species migration between the organic and aqueous phases. Equilibrium aqueous glycerol concentration profiles also exhibited double maxima at reaction extents of 57% and 95% with the magnitude increasing at higher organic phase volume fraction. Among the operating variables studied, reaction extent had the most significant influence on phase equilibrium possibly due to changes in the hydrophilicity of the reaction medium occasioned by compositional variation in the course of the reaction. In particular, a linear relationship was found between global and organic phase molar ratio of ethanol-to-fatty acid residues. Consequently, the findings of this study would permit a realistic determination of the rate-composition envelope as a function of the organic volume fraction along the extractive reactor column and hence, improved biodiesel recovery efficiency.

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## 1. Introduction

Immobilised lipase has several advantages over conventional homogeneous alkali catalysts in the alcoholysis of vegetable oil for biodiesel production. These include, exclusion of undesirable saponification of free fatty acids (FFA), enabling the use of cheap, low quality oil feedstocks in a single reaction step without pre-esterification or subsequent washing (Halim and Kamaruddin, 2008); simpler recovery of solid catalyst from the reaction mixture and its reuse (Leca et al., 2010); elimination of caustic and saline species thereby reducing downstream purification and wastewater treatment costs (Sotoft et al., 2010); lower alcohol to oil ratio requirement (Szcześnie Antczak et al., 2009); milder reaction temperature (20–60 °C versus 60–80 °C) thus reducing energy costs (Ghaly et al., 2010); and easier separation of a higher quality glycerol by-product (Fjerbaek et al., 2009). Despite these advantages, several key drawbacks have hampered commercial uptake of lipasic biodiesel production. Most notably, the high cost of lipase (Fukuda et al., 2001), comparatively low reaction rate and loss of activity (Fjerbaek et al., 2009) are current challenges.

Lipasic biodiesel production, and particularly the alcoholysis of vegetable oils using immobilised lipases, has been the subject of considerable research interest within the past decade with a view to optimise reaction conditions and improve the commercial viability of the process. A large proportion of previous studies have been carried out in stirred batch reactors, with some using packed bed reactors (Royon et al., 2007; Watanabe et al., 2000). A promising means of reducing both capital and production costs of the immobilised lipasic biodiesel process is the integration of the reaction and by-product separation steps into a stirred countercurrent liquid–liquid extractive reaction column (XRC). The authors have recently developed a steady-state computer model of such an XRC and run simulations with a triolein feed stream, dilute aqueous ethanol ( $\approx 15\%v/v$ ) solvent stream and employing reaction kinetics from the literature to demonstrate the potential of such a system (Chesterfield et al.). In principle, an XRC utilising aqueous ethanol as co-reactant and polar solvent would facilitate both ethanolysis of the fatty acid (FA) residues present in the oil while simultaneously stripping glycerol from the organic reactive phase into a secondary aqueous phase. There are several advantages to lipasic biodiesel production in an XRC, including increased equilibrium biodiesel yield, lower purification costs, generation of a glycerol by-product stream for conversion to value-added compounds, and higher production rate (Dussan et al., 2010).

Equilibrium distributions of ethanol and water in biphasic aqueous/organic systems are of particular importance in the case of an XRC applied to lipasic biodiesel production. Firstly, ethanol is co-reactant with oil in the esterification (carboxylic acids) and transesterification (triglycerides) reactions. As solubility of the triglycerides and FFA found in oil is very low in water (da Silva et al., 2009), interphase mass transport of ethanol into the organic phase and subsequent diffusion within the organic phase to an active lipasic site is necessary for reaction. Furthermore, the molar ratio of ethanol-to-oil affects lipase activity. Specifically, rate and yield tend to increase with feed ethanol:oil molar ratio up to a certain value, above which the onset of competitive ethanol inhibition and permanent ethanol-induced deactivation of lipase cause a downturn. The optimum molar ratio of ethanol-to-FA moieties depends upon factors such as type of oil feedstock, lipase species and loading, immobilisation technique, organic solvent if any, and support (Ghaly et al., 2010; Fjerbaek et al., 2009). It has variously been reported as 0.77–0.90 for pure triolein substrate (Calabrò et al., 2010), 3.7 for cod liver oil (Robles-Medina et al., 2009) up to as high as 6 for soybean oil as substrate (Hernández-Martín and Otero, 2008) (based on 1 mol of oil containing

approximately 3 mol of FA moieties). Solubility of ethanol in vegetable oil is approximately 33% of the stoichiometric amount, and the undissolved alcohol may form a hydrophilic film on the lipase surface, leading to competitive inhibition, increased mass transfer resistance for hydrophobic reactants and products and lipase deactivation (Robles-Medina et al., 2009; Shimada et al., 2002). From a thermodynamic standpoint, stepwise sub-stoichiometric additions of the alcohol to the reaction system have been proven to mitigate permanent lipase deactivation and the attainment of higher biodiesel yields (Shimada et al., 2002). In the case of a continuous counter-current XRC, a strategic approach may require setting the feed alcohol:oil molar ratio at sub-stoichiometric levels in a reactors-in-series arrangement or a product recycle stream for a single reactor (Chesterfield et al.; Shimada et al., 2002).

The presence of water in the transesterification reaction medium also has a significant effect on lipase activity and stability. As such the quantity of water affects both reaction rate and equilibrium yield (Fjerbaek et al., 2009). Lipases generally require a minimum amount of water for activation, but on the other hand water can flood the pores of the catalyst support, preventing or slowing diffusion of hydrophobic substrates to active lipase sites (Páez et al., 2003). The optimal water content depends on immobilisation technique, lipase species, oil feedstock, and alcohol and is typically in the range 0–30 wt% (Ghaly et al., 2010). We have previously reported the detrimental effect of water on the ethanolysis rate of waste cottonseed frying oil using Novozym 435 (immobilised *Candida antarctica*) when of 0.02 g water/g of oil was introduced into the reaction medium (Chesterfield et al., 2012). However Lu et al. (2009) observed an improvement in yield upon increasing water content from 5 to 20 wt% in the methanolysis of triolein in n-hexane catalysed by immobilised *Candida* sp. 99–125 while up to 50% increase was registered in the yield of fatty acid ethyl esters (FAEE) after replacing anhydrous ethanol with 96% ethanol in the ethanolysis of sunflower oil using immobilised lipases from a variety of genera (Deng et al., 2005). When water is present in quantities sufficient to form a distinct aqueous phase, it has been shown to enhance lipasic fatty acid esterification rate by stripping polar reaction products from the reactive organic phase thereby shifting equilibrium to the right (Foresti et al., 2007). This benefit may also be translatable to transesterification of vegetables oils, particularly due to the potential dissolution of glycerol in the secondary aqueous phase.

This study considered dilute aqueous ethanol solvents mixed with biodiesel reaction mixtures as would occur in a biphasic XRC and the effects of degree of reaction extent, ethanol concentration and phase volume fraction on phase equilibrium. Knowledge of equilibrium distribution of ethanol, water and glycerol between the organic and aqueous phases in the proposed biphasic reaction system provides thermodynamic compositional limits, allowing assessment of extraction efficiency, guiding optimisation of phase ratios and solvent composition.

## 2. Materials and methods

### 2.1. Chemicals

Novozym 435 (*Candida antarctica* lipase B) was supplied as an immobilised enzyme on macroporous acrylic resin (90–800  $\mu\text{m}$  particles) by Novozyme Pty. Ltd. Waste cottonseed frying oil was obtained from a UNSW campus café. Oil properties and fatty acid composition are detailed in Table 1. Ethyl oleate (> 98% purity) was purchased from Sigma Aldrich for GC calibration. Absolute ethanol (> 99%, 0.154 wt% water) and HPLC-grade n-heptane

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