



Steady-state simulation of a novel extractive reactor for enzymatic biodiesel production

Dean Chesterfield ^a, Peter L. Rogers ^b, Essam Al-Zaini ^a, Adesoji A. Adesina ^{a,*}

^a Reactor Engineering and Technology Group, School of Chemical Engineering, University of New South Wales, Sydney, New South Wales 2052, Australia

^b School of Biotechnology and Biomolecular Sciences, University of New South Wales, Sydney, New South Wales 2052, Australia

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ABSTRACT

Intensification of the biodiesel production process may offer significant capital and operating cost benefits due to fewer unit operations. In addition, the continuous removal of co-product glycerol from the reactive phase during transesterification promises higher biodiesel yield relative to conventional batch reactors. As a result, this paper investigates the application of a novel liquid-liquid extractive reactor with basket-like mixing impellers containing enzyme particles for biodiesel production. Steady-state modelling using commercial process simulation software coupled with an iterative method for estimation of holdup was carried out. Models considered countercurrent flow of vegetable oil and aqueous ethanol solution in a multistage, mixer-settler type extractive reaction column (XRC), catalysed by immobilised lipase. Simulation results revealed that the conversion was insensitive to solvent to feed ratios beyond stoichiometric ratio of ethanol-to-triglycerides, thus making the XRC superior to batch process which uses excess alcohol. Increasing number of stages, stirring speed and raffinate recycle ratio improved conversion over the respective ranges studied. Optimum ethanol content in the solvent (water) was located at 46%v/v. In all simulations, glycerol recovery in the extract stream exceeded 99.9%, while biodiesel was retained almost exclusively in the product raffinate stream, illustrating exceptional product quality associated with the novel XRC.

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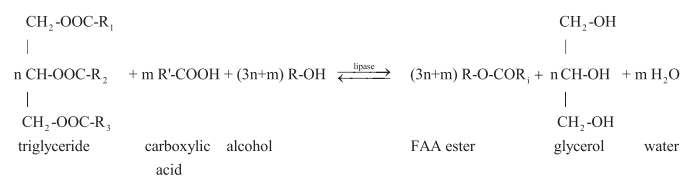
1. Introduction

Biodiesel offers several benefits as either a direct substitute for, or blended with petrodiesel. It is produced from the alcoholysis of plant oils and animal fat and hence offers closed carbon cycle with overall CO₂ emissions being about 80% less than those of fossil fuels [1]. Emissions of CO, volatile organic compounds (VOCs) and particulates from combustion of biodiesel are also lower [1]. Furthermore, biodiesel provides a market for used and excess vegetable oils and fats, and reduces dependence on oil imports [1,2].

Despite the benefits of biodiesel mentioned above, growth in its production is hampered largely by its high cost relative to petrodiesel. High production costs stem primarily from the cost of virgin oil feedstocks, which can contribute nearly 90% of production costs [3,4]. A much less expensive source of vegetable oil is waste cooking or non-edible oil. Unfortunately, waste cooking oil, in addition to triglycerides, tends to have high free fatty acid (FFA) content. When a conventional homogeneous alkaline catalyst such as sodium hydroxide is used for biodiesel production, the saponification side-reaction necessitates downstream purification steps for soap removal

and substantially lowers biodiesel yield [5]. Furthermore, wastewater treatment costs associated with homogeneous alkaline or acid-catalysed processes are high.

The use of immobilised lipase as a catalyst eliminates the problem of soap formation [6], since it also catalyses the esterification of the resident FFA to ethyl esters, thus enabling the utilisation of low quality waste oil and animal fats as feedstock. Effectively, the lipase-catalysed process has 100% biodiesel selectivity, and reduces purification and wastewater treatment costs [7]. Moreover, the reaction may be carried out at low temperature (<50 °C), and with lower alcohol to oil ratio, thereby providing savings in production costs [8]. As such, immobilised lipase-catalysed biodiesel production is the subject of intense research [6,9–11]. The alcoholysis of triglycerides and FFA present in waste oil may be catalysed by lipase and written as:



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* Corresponding author. Tel.: +61 2 9385 5268; fax: +61 2 9385 5966.
E-mail address: a.adesina@unsw.edu.au (A.A. Adesina).

Notation	
C_T	Parameter related to geometrical characteristics of column, dimensionless
D	Column diameter, m
D_i	Impeller diameter, m
e	Fractional free area of stator between stages
F	Feed (oil) volumetric flow rate, Lh^{-1}
Fr_i	Impeller Froude number, dimensionless
F_{TO}	Inlet molar flow rate of triolein to reactor, $mmolh^{-1}$
g	Acceleration due to gravity, $9.81 ms^{-2}$
H	Stage height, m
k	Rate constant, $mmol^{-1} h^{-1}$
K_i	Inhibition constant, $gmmol^{-1}$
K_m	Reaction equilibrium constant, $gmmol^{-1}$
n	Number of stages
N_p	Power number, dimensionless
N_s	Stirring speed, rpm
P	Impeller power input, W
r	Reaction rate per unit mass, $mmolg^{-1} h^{-1}$
Re_i	Impeller Reynolds number = $\frac{\rho_{mix} D_i^2 N_s}{\mu_{mix}}$, dimensionless
S	Solvent (aqueous ethanol) volumetric flow rate, Lh^{-1}
U	Superficial velocity, ms^{-1}
V_e, V_m	Lumped rate constants, $mmol^{-1} h^{-1}$
V_i	Volume of stage i , L
X	Triolein conversion
Y	Ethyl oleate yield
<i>Greek symbols</i>	
γ	Interfacial tension, Nm^{-1}
ϵ	Power input per unit mass, Wkg^{-1}
μ	Viscosity, Pas
π	3.1416
ρ	Density, kgm^{-3}
φ	Dispersed phase volume fraction (holdup), dimensionless
<i>Subscripts</i>	
c	Continuous phase
d	Dispersed phase
mix	Liquid–liquid mixture

However, the lipase-catalysed route has some demerits including the low reaction rate compared with alkali catalysts [12] and the high enzyme cost.

Currently, the only two feasible acyl acceptors in biodiesel production are the short-chain alcohols methanol or ethanol [8,12], due to their relatively low cost. While both alcohols have been found to cause inhibition and deactivation of immobilised lipase, methanol is more prone to deactivation than ethanol [13]. Further, ethanolysis of sunflower oil using a common commercial immobilised lipase (Novozym 435) has been found to progress at higher reaction rate than methanolysis [9]. Ethanol has the added advantage that it can be readily produced via fermentation of renewable plant feedstocks.

The presence and quantity of water in the reaction mixture have also been studied. Water is thought to facilitate the opening of hydrophilic “lids” covering the lipase active sites, thus permitting acyl groups of the glycerides (or free fatty acids) to bind to form lipase complexes [11]. The optimal water content for activity enhancement varies dramatically depending on lipase species, immobilisation technique, oil feedstock, and alcohol and is typically in the range 0–

30 wt.% [8]. Interestingly, Mahmud et al. [14] have recently reported the decaying oscillatory effect of water on oleic acid esterification by ethanol in the presence of immobilised lipase. The crests of the sinusoid coincided with the reaction yield maxima reported by other authors [15]. Glycerol is soluble in water and hence may be removed from the lipasic sites in the separate aqueous phase, leading to improved reaction rate and product yield.

Many of the previous investigations on enzymatic biodiesel production have been carried out in stirred batch reactors, with some using packed bed reactors [16,17]. At the end of the reaction, the biphasic mixture is allowed to settle before decanting the glycerol-rich polar phase. A potential means of reducing both capital and production costs of a lipase-catalysed biodiesel plant is the integration of the reaction and separation steps into a stirred extractive reaction column (XRC). The justification for this derives from both the characteristics of the reaction system as discussed below, and process intensification principles [18], viz.: the reduction of interphase mass transfer resistance between immiscible oil and alcohol; the possibility of achieving conversion in excess of thermodynamic equilibrium; and continuous rather than batch reactor operation. Ideally, such a reactor would allow simultaneous biodiesel production and separation of by-product glycerol. There are several advantages to such a scheme, including increased biodiesel yield, lower purification costs, generation of a glycerol by-product stream for conversion to value-added compounds, and higher production rate [19].

Agitation by enzyme-filled basket impellers within each stage of the XRC is expected to provide benefits in two areas: firstly, containment of enzyme within the highly-mixed regions of the reactor; and secondly, centrifugal motion imparted by the impellers increases dispersed phase holdup and interfacial area. Kumar and Hartland have developed correlations for prediction of dispersed phase holdup [20] and drop size [21] (and consequently interfacial area) as a function of impeller power number for a variety of agitated liquid–liquid extractors. In this study, since the organic phase is considered dispersed and reaction takes place exclusively in this phase, an increase in dispersed phase holdup increases effective reactive volume of the XRC. Increased interfacial area enhances interphase mass transfer rates of reactants and products, improving reaction rate in the case that the reaction is mass transfer limited. Hence, manipulation of stirring speed may offer control of conversion within the XRC. The present simulation work assumes negligible interphase mass transfer resistance [22] and hence, the influence of stirring speed on interfacial area was not investigated.

Based on this brief review, the beneficial effects of a multistage, stirred, countercurrent, liquid–liquid XRC for enzymatic biodiesel production has been investigated via process simulation. The conceptual reactor utilises a 15%v/v aqueous ethanol solution as the solvent. The cost benefit analysis of utilising crude bioethanol with this concentration in biodiesel synthesis has been discussed by Boudreau and Hill [22].

2. Reactor simulation

2.1. Conceptual process description

Steady-state modelling of the XRC was carried out with Aspen Plus (v12.1) process simulation software. Numerical runs were conducted for XRC's containing 2 to 16 stages. Fig. 1(a) illustrates a schematic of the XRC with two stages. Since the XRC is a mixer-settler type column, it was comprised of alternating reactive mixing regions (in the vicinity of impellers) and inert phase settling regions (near stage boundaries). Each mixing region is divided into upper and lower circulation zones of equal size, one above and one below the midpoint of the impeller, based on the approach of Barnea et al. [23]. For modeling purpose, the XRC was conceptually divided into subunits, representing the constituent reaction, phase equilibration and separation

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