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Modeling of biodiesel production in Liquid-Liquid Film Reactors including mass transfer effects

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ABSTRACT

Biodiesel production in Liquid-Liquid Film Reactors (LLFR) has been investigated to increase mass transfer without dispersion between the oil and alcohol phases. The use of this type of reactor reduces separation time and increases process productivity. In this work, a model to predict continuous production of biodiesel in a co-current operated LLFR was developed and experimentally validated. This model includes the prediction of the methanol mass transfer from the alcohol phase to the interface. Experimental validation also assessed the effect of the packing surface area to reaction volume ratio (444 to 5333 m^{-1}), vegetable oil (VO) flow rate (5 to 40 g min^{-1}), and reactor length (0.25 to 1 m) on conversion and yield to fatty acid methyl esters (FAME), at constant temperature (55 °C), catalyst concentration (1 wt%) and molar ratio methanol to oil (6:1). The mathematical model accurately describes the reactor behavior. Conversion, yield and reactor productivity increase with packing quantity and VO flow rate. The highest conversion and yield obtained experimentally were 99.9% and 97.5% respectively with a productivity of 2.5 m^3 Biodiesel m^{-3} h^{-1}. This value resulted 8 times higher than the typical BSTR operation.

1. Introduction

Biodiesel has been extensively produced and commercialized as biofuel because its properties are close to those from diesel. Thus, its use in current internal combustion engines is possible without engine modifications. Besides, raw materials required for its production, vegetable oils (VO), are renewable and available in many regions around the World. Many countries have implemented policies to promote the use of biodiesel, usually in blends with diesel. These policies justify the investment of public resources through subsidies and tax exemptions based on prolongation of oil availability, reduction of the negative environmental effect of gas emissions from fossil fuels and generation of employment in rural sectors [1–3].

Biodiesel is mainly produced by the transesterification of VO and methanol using homogeneous basic catalyst, mainly sodium or potassium methoxide. Most of the industrial processes use stirred tank reactors either batch (BSTR) or continuous (CSTR) [4]. Kinetics and thermodynamic characteristics of this reaction, where chemical equilibrium is a key factor, imply residence times of about 1 h for the BSTR [5]. The stoichiometric ratio for transesterification requires three moles of alcohol for one mole of triacylglycerol to obtain three moles of fatty acid ester and one mole of glycerol. In practice, the ratio needs to be higher to drive the equilibrium to a maximum ester yield. The practical range of molar ratio was proposed as 3.3:1 to 5.25:1 methanol to VO [6].

Some studies have reported kinetic models for vegetable oil alcoholysis. Most of these studies refer specifically to methanolysis [1,7–10] or ethanolysis [11–14], they studied the influence of time, alcohol content, catalyst content, and temperature on the kinetic behavior. The reaction rate is maximal at the reaction beginning and it is highest for high alcohol content, catalyst content and temperature.

Additionally, low miscibility between raw materials (VO and methanol) generates mass transfer resistance, mainly when the reaction starts, reducing the overall reaction rate [15–17]. In stirred tank reactors, mixing generates dispersion between phases, which increases the interfacial area and reaction rate [18]. The higher the mixing rate, the smaller the size of the drops, and the mass transfer rate increases as well as the residence time in the downstream two-phase separator [19]. As a consequence, there is a reduction in the productivity of the process, especially if emulsions are formed.

In order to reduce residence time and increase process productivity, some intensification strategies have been investigated. A continuous

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Nomenclature

k_i	Kinetic constant $\left(\frac{L}{gmol \cdot \mathrm{min}}\right)$
L	Reactor length (m)
k_C	Global mass transfer coefficient (m/min)
α_C	Packing surface area to reaction volume ratio (m^2/m^3)
C_1, C_2, C_3	Parameters of the mass transfer coefficient (Dimensionless)
n_{Pack}	Number of threads
D_{Pack}	Thread diameter (m)
D_{rxn}	Reactor diameter (m)
k_{eff}	Effective transport coefficient
AAF	Area available for flow
δ^I	Ester film thickness (m)
δ^{II}	Alcoholic film thickness (m)
V_z	Average flow velocity over the packing (m/min)
V_0	Average flow velocity in the reactor (m/min)
D_{12}	Methanol diffusivity in the ester-rich phase (m^2/s)
${Q_{Pack}}^I$	Volumetric flow rates ester-rich phase around each thread (m^3/min)
${Q_{Pack}}^{II}$	Volumetric flow rates alcoholic phase around each thread (m^3/min)
Q^I	Volumetric flow rates of the ester-rich phase (m^3/min)
Q^{II}	Volumetric flow rates of the alcoholic phase (m^3/min)
Re	Reynolds number
Sc	Schmidt number
D_H	Hydraulic diameter
α	Ratio between the ester film diameter and the thread diameter
b	Ratio between the alcoholic film diameter and the thread diameter

oscillatory flow reactor was studied [20], achieving the equilibrium condition of rapeseed methanolysis after 30 min reaction time. Soybean oil ethanolysis with reactive distillation was evaluated [21]. The system was semi-continuous and used a stirred tank pre-reactor where a conversion of 98.18% after 6 min reaction time was obtained. Reactive distillation using different configurations was simulated [22] obtaining 97.5% yield with a reflux ratio of 0.1 and 6 reactive stages. Biodiesel production using static mixers also was studied and their behavior was compared to the traditional mechanical mixers [23]. It was found that the static mixer can significantly accelerate the transesterification reaction.

Biodiesel production using micro tube reactors shows increments in conversion and FAME yield with the reduction of tubes internal diameter [24]. This behavior is attributed to an improvement in the mass transfer between the oil-rich and methanol-rich phases. Pontes et al. [25] reported higher triglyceride conversions for smaller microreactor heights, due to the augment in the surface area to volume ratio. Santacesaria et al. [26–29] studied the role of the liquid-liquid interface area in the biodiesel production, they studied microreactor, static mixers, and microchannel devices in order to increase the reaction rate and also they proposed a mathematical model able to describe the effect of the mass transfer resistance in the reaction behavior.

Palm oil biodiesel production in a Liquid-Liquid Film Reactor (LLFR) operated in co-current was evaluated by Narvaez et al. [30]. This reactor is a device in which interfacial area is created without dispersing the oil and the alcohol phases one into the other, by using a semi-structured packing. Conversion and biodiesel yield were 97.5% and 92.2% respectively, whereas the residence time in the two-phase separator was only 5 min. As chemical and phase equilibrium limit the yield, two reaction stages are necessary to achieve the concentration of glycerides required to meet the quality standards in the biodiesel industry. Process productivity reported in the LLFR operated in co-current was 1.2 m^3 Biodiesel m^{-3} h^{-1} [31], 4 times higher than the reported in a batch stirred tank reactors (BSTR).

To overcome yield limitation of LLFR operated in co-current, palm oil biodiesel was produced in an LLFR operated in counter-current flow pattern. Palm oil conversion of 97.7% and biodiesel yield of 99.5% were obtained in only one reaction stage. The process productivity was 1.8 m^3 Biodiesel m^{-3} h^{-1} [32], 6 times higher than the reported in BSTR.

Current development of biodiesel industry around the world makes necessary to improve process productivity and product quality. Nowadays, several available technologies exist for the continuous biodiesel production. Their improvement is only possible if a deep understanding of the fundamentals involved in the entire production process is achieved. In the particular case of LLFR, a continuous biodiesel technology with high conversion, yield and productivity, it is necessary to understand the transport phenomena inside the reactor, especially mass transfer effects and hydrodynamics, in order to improve its performance.

This work presents a mathematical model for biodiesel production using an LLFR operated in co-current mode. The model includes mass transfer limitations and describes hydrodynamics inside the reactor. It was validated through experimental data obtained in a bench level reaction system. The effect of packing surface area to reaction volume ratio (444 to 5333 m^{-1}), VO flow rate (5 to 40 g min^{-1}) and reactor length (0.25 to 1 m) on conversion and FAME yield, at constant temperature (55 °C), catalyst concentration (1% w/w based on VO weight) and molar ratio methanol to oil (6:1), were studied.

2. Materials and methods

2.1. Physical background

A schematic diagram of the LLFR configuration including a differential element of volume is shown in Fig. 1. A tubular reactor with uniform diameter (D_{rxn}) is packed with a defined quantity of stainless steel threads (n_{Pack}) with uniform diameter (D_{Pack}).

This semi-structured packing makes possible to generate interfacial area between the liquid phases inside the reactor without dispersing one into the other. VO and methanol are fed at the top of the reactor. The ester-rich phase wet the packing surface, generating a film of thickness δ^I over it. The alcoholic phase flows over the ester-rich phase forming a film of thickness δ^{II} over the ester-rich phase. Biodiesel and glycerol produced are recovered at the bottom of the reactor. The hydrodynamics of the flow inside the reactor could be explained because ester-rich phase wettability over the stainless steel packing is higher than the alcoholic phase wettability. The reaction occurs in the two films created over the threads but principally in the ester-rich phase.

2.2. Experimental procedure

2.2.1. Materials

Refined, bleached and deodorized edible grade soybean oil was obtained from SIGRA S.A. (Bogotá, D.C. Colombia). Soybean oil fatty acid profile and some specifications are shown in Table 1. Analytical grade methanol and sodium hydroxide were obtained from Merck (Darmstadt, Germany). Reference standards, including methyl palmitate, methyl oleate, DL-α palmitin, dipalmitin, tripalmitin, glyceryl trioleate and the silylating agent *N,O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA) of > 99% purity, were purchased from Sigma-Aldrich Chemical Company (*St* Louis, MO). Tricaprine was obtained from Fluka (Buchs, Switzerland) and used as the internal standard. Pyridine, isopropanol, and toluene of ACS grade were obtained