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Computer simulation of biodiesel production by hydro-esterification

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ABSTRACT

The conventional production method of biodiesel by transesterification in two stages, chemical reaction and product separation, has several disadvantages. Compared to it, biodiesel production by hydro-esterification from fatty matter has many advantages but available technology still requires distinct steps for reaction and separation. This work presents computational simulations of a multi-step process of soybean oil biodiesel production by hydro-esterification. The hydrolysis step uses a packed bed reactor and the esterification step utilizes a reactive distillation column. Reactive distillation combines the reaction and separation steps in the same piece of equipment. Several chemical processes employ this intensification technique but its application to esterification processes is recent. The simulation results show that the methodology used is consistent and sensitivity analyses suggest that conversions close to 99% are possible.

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1. Introduction

The main route for the industrial production of biodiesel uses the transesterification of refined oils by alkaline catalysts, such as sodium and potassium alkoxides, because the process is relatively simple and achieves conversions above 95% [27,24]. However, this route has problems, mainly in the purification step, that cause income losses and waste generation. To tackle this problem, several research groups worldwide have proposed the use of heterogeneous catalysis, mainly in methanolic reactions [26]. Significant attention has been devoted to the development of efficient catalysts that result in better conversion rates and reduced saponification problems. In this context, it is worth mentioning the use of inorganic heterogeneous catalysts, insoluble in the reaction medium and easily recyclable [4].

The use of heterogeneous catalysts can potentially reduce the cost of biodiesel production, making it competitive against fossil diesel. They facilitate the purification of monoesters, reuse of the solid catalyst, minimize waste generation, decrease reaction time, yield higher conversions, and allow the use of low quality raw materials, thereby reducing costs. On the other hand, heterogeneous catalysis processes require more severe reaction conditions, such as high temperatures, so that the reaction rate is competitive with that of homogeneous processes [13,6,34].

Hydro-esterification consists of a step of vegetable oil hydrolysis, followed by esterification of the fatty acids produced. It has several advantages, such as the ability to function with materials of high acidity and humidity. In the first stage, all triacylglycerides are converted to fatty acids on the action of water. In the second stage, the formed fatty acids are esterified using methanol or ethanol. Both steps can be accelerated by acid catalysts and become more attractive when coupled to the use of heterogeneous catalysts, eliminating soap formation, reducing the number of separation units, enabling catalyst reuse, and producing high purity, salt-free glycerin [3].

The great advantage of hydro-esterification compared to transesterification is that the free fatty acid is reactant in the same reaction, thus not being a limitation in terms of specification of raw material [25,27,12]. This makes it possible to use raw materials of high acidity, such as macaúba (*acrocomia aculeata*) oil, with difficulties associated to harvesting and fruit processing, and of very high acidity (above 30 mg KOH/g), without the need for pretreatment of the feeding oil via a neutralization reaction. Similar constraints of algal biodiesel include humidity and high acidity of algae oil [9].

On the other hand, hydrolysis processes of raw materials are known and well established, with current operation on industrial scale. Moreover, the esterification step of fatty acids still has a number of technical challenges regarding the operation mode

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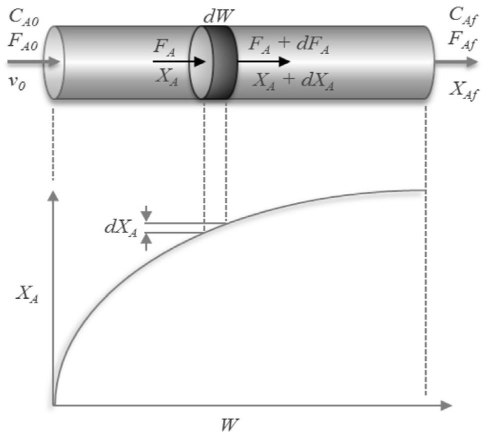

Fig. 1. Schematic of a differential mass element dW in a PBR. (adapted from [14].

(batch or continuous). Thus, it opens up opportunity to use reactive distillation column (RDC) technology in the esterification step. Reactive distillation is a hybrid operation that combines physical separation and chemical reaction in the same piece of equipment [30]. Thus, the use of RDCs increases productivity and selectivity, reduces energy use, eliminates the need for solvents; in other words, it leads to process intensification [32]. Some publications, such as those of [20],[16], and [29], show the use of this technology for the esterification of fatty acids to esters as biodiesel.

Several process simulation studies about fatty acid esterification in reactive distillation columns have appeared in the literature. However, none of them considers a hydro-esterification process that uses a PBR reactor combined with a RDC to perform the hydrolysis and esterification reactions, respectively. In those studies, the fatty material contains different types of fatty acids; however, few studies take this variety into account [10]. Most of them consider only a single fatty acid [28,32,5,23,21,18,19,22] due to the difficulty in obtaining experimental data, kinetic parameters, and thermodynamic properties for the different fatty acids found in raw materials. Only one simulation work that involves a mixture of fatty acids can be found in the literature [10]. However, the authors assumed a homogeneous catalyzed system where chemical equilibrium is attained on each reactive tray.

This work presents computer simulations of a continuous multi-stage process for the production of biodiesel by hydro-esterification from fatty organic acids (a mixture similar to soybean oil) and ethanol. The hydrolysis reaction is performed in a packed bed reactor (PBR), while the esterification step is conducted in a RDC; a pseudo-homogenous kinetic model had been used in these steps. In both cases, sensitivity analyses of design parameters and operating conditions are performed in order to optimize the operation of each step.

2. Methodology

2.1. Hydrolysis

The choice of the tubular reactor for the hydrolysis step is based on the fact that this reaction is conducted at high pressure and temperature, which can cause thermal degradation of the components if the residence time in the reactor is large. A mass balance is performed in a differential catalyst mass element dW, for component A, involved in one single reaction over the total mass of catalyst, W. Isothermal conditions and constant pressure along the PBR reactor are considered in this work. The tubular reactor can be described as in Fig. 1.

Based on Fig. 1, a mass balance for component A can be performed by the following equation:

$$F_A - (F_A + dF_A) = r_A{}'dW \quad (1)$$

where F_A is the input molar stream of A, $F_A + dF_A$ is output molar stream of A and $r'_A dW$ is the consumption/generation rate of A by reaction.

The mass balance can be rewritten in terms of the conversion of component A, X_A, leading to:

$$F_A = F_{A0}(1 - X_A) \quad (2)$$

where F_{A0} is the molar inlet stream of compound A in the PBR reactor and X_A is the conversion of component A. Written in terms of conversion, the differential mass balance for component A is:

$$\frac{dX_A}{d\left(\frac{W}{F_{A0}}\right)} = r'_A \quad (3)$$

Its integrated form is the design equation of a tubular reactor:

$$\frac{W}{F_{A0}} = \int_0^{X_A} \frac{dX_A}{r_A{}'} \quad (4)$$

In this work, a pseudo-homogeneous model is used to express the chemical reaction rate as a function of reactants concentrations. Eq. (5) shows this model, which considers a chemical reaction between two reactants forming two products ($aA + bB \Leftrightarrow cC + dD$).

$$r'_A = k_1 C_A C_B - k_{-1} C_C C_D \quad (5)$$

where C_A and C_B are the molar concentrations of components A and B, respectively, C_C and C_D are the molar concentrations of components C and D, respectively, k_1 and k_{-1} are reaction constants of the direct and reverse reactions, given by the Arrhenius Eq. (6):

$$k_i = k_{0i} \exp\left(\frac{-E_{ai}}{RT}\right) \quad (6)$$

where T is the temperature, R is the universal gas constant, k_{0i} is the pre-exponential factor and E_{ai} is the activation energy of reaction i.

The concentration of all species in the reaction can be written as a function of volumetric flow rate (V_0), molar stream of the species (F_{i0}), conversion of component A (X_A) and their stoichiometric coefficients as follows:

$$C_A = \frac{F_{A0}}{v_0}(1 - X_A); C_B = \frac{F_{A0}}{v_0}\left(\theta_b - \frac{b}{a}X_A\right); C_C = \frac{F_{A0}}{v_0}\left(\theta_c - \frac{c}{a}X_A\right); C_D = \frac{F_{A0}}{v_0}\left(\theta_d - \frac{d}{a}X_A\right) \quad (7)$$

where $\theta_i = \frac{F_{A0}}{F_{i0}}$.

The design equation of PBR, for the particular reaction considered, is obtained by combining Eq. (5)–(7) into Eq. (4):

$$W = \frac{v_0{}^2}{F_{A0}} \int_0^{X_A} \frac{dX_A}{k_{01}\exp\left(\frac{-E_{a1}}{RT}\right)(1 - X_A)\left(\theta_B - \frac{b}{a}X_A\right) - k_{0-1}\exp\left(\frac{-E_{a-1}}{RT}\right)\left(\theta_C - \frac{c}{a}X_A\right)\left(\theta_D - \frac{d}{a}X_A\right)} \quad (8)$$

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