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Evaluating the kinetics of the esterification of oleic acid with homo and heterogeneous catalysts using in-line real-time infrared spectroscopy and partial least squares calibration

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ABSTRACT

Biodiesel is a mixture of fatty acid alkyl esters with properties similar to petroleum-based diesel. Thus, biodiesel can be used as either a substitute for diesel fuel or, more commonly, in a fuel blend. Biodiesel production can be catalyzed with mineral acids or bases or enzymes. The use of real-time techniques for monitoring the reaction and evaluating the efficiency of the catalyst can be of great use for optimizing the reaction and monitoring the process. In the present work, an in-line real-time methodology was used to evaluate and compare the kinetics of a reaction catalyzed with homo (hydrochloric acid) and heterogeneous (the enzymes Novozym 435, Lipozyme RM, and Lipozyme TL) catalysts. The esterification of oleic acid with ethanol was used as the reaction model. The study used attenuated total reflexion/Fourier transform infrared (ATR/FT-IR) and a single partial least squares (PLS) regression model to evaluate the kinetics of the various catalysts, without multiple calibrations, with validation by GC–MS. Novozym 435, which showed complete conversion after 165 min, was the best catalyst for this reaction. Lipozyme RM and Lipozyme TL had inferior conversion after the same amount of time, in agreement with the literature. All enzymatic catalysts showed higher conversion than hydrochloric acid at the same reaction conditions.

1. Introduction

Biodiesel is a fuel comprised of fatty acid alkyl esters and may reduce soot discharge by one third compared to petroleum-based diesel. Furthermore, biodiesel may reduce CO, SOx, particulate matter, and organic compounds [1–4]. The properties of this renewable biofuel are similar to those of petroleum-based diesel; thus, biodiesel can be used as either a substitute for diesel fuel or, more commonly, in a fuel blend. Several strategies for producing biodiesel have been published in the literature [2,5]. However, the transesterification of triacylglycerides and the esterification of free fatty acids (FFAs) with low molecular weight alcohols are the most important processes [6]. These reactions can be catalyzed by using mineral acids or bases, or by using enzymes. Producing biodiesel using a mineral catalyst has several drawbacks such as difficulty removing the catalyst from the product, high energy requirements for faster kinetics, difficulty recovering the catalyst for reuse, and potential pollution in the environment [7,8]. Today, enzyme-catalyzed biodiesel production has received more attention because of advantages such as nontoxicity, environment-friendly processes, low energy costs, and soft operating conditions compared with chemical-catalyzed methods [9,10]. However, this method is still not favored for industrial use because high costs and low stability of lipases limit potential applications [11,12].

The biodiesel reaction has been monitored with several chromatographic and spectroscopic techniques [13–15]. Among these methods, the use of spectroscopy exhibits great differentiation due to the increase in technology, the advance of real-time analysis, and easy-to-use application. This technique can be applied in- or on-line, eliminating the systematic error of sampling and facilitating data acquisition [16,17]. One of the most frequently used real-time analyses is the attenuated total reflexion–Fourier transform infrared (ATR/FT-IR) spectroscopy, which uses an internal reflection of the radiation beam inside a crystal. The intensity of the signal is attenuated due to multiple reflections along the length of the crystal in contact with the sample [18]. This technique automates the analysis, and the spectra can be acquired in a time resolution, which make the dynamic study of a chemical system possible. ATR/FT-IR

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can rapidly analyze the vibrational bands of the molecules present in the system, which may change during a reaction. Thus, tracking and monitoring of reactions are possible [19].

The reaction system can be more clearly understood by transforming the spectroscopic data into concentration information about the species in the system [15]. This transformation arises from the fact that there is linearity between the spectroscopic quantity (i.e., absorbance) and the concentration, as stated by the Beer–Lambert law. Numerous chemometric strategies can be used for this transformation, from a simple univariate linear regression to a more complicated non-linear multivariate regression, when linearity does not exist [20]. In the case of the infrared spectra of a reaction mixture, there can be much juxtaposition between vibrational bands of different compounds. Therefore, multivariate regressions must be used to quantify the concentrations. The most common regression used in these cases is partial least squares (PLS) [21,22].

In the present work, an in-line real-time methodology was used to evaluate and compare the kinetics of an esterification reaction catalyzed with homo (mineral acid) and heterogeneous (supported enzymes) catalysts. As a model for the reaction, oleic acid was reacted with ethanol and catalyzed with hydrochloric acid, Novozym 435, Lipozyme RM, and Lipozyme TL. ATR/FT-IR and PLS regression modeling were used to easily evaluate the kinetics of the different catalysts without multiple calibrations. Coupled gas chromatography–mass spectrometry (GC–MS) was also used to confirm the final conversion for the best catalyst.

2. Experimental

2.1. Equipment

ReactIR 45 m (Mettler Toledo) equipment was used for monitoring the reactions; it was equipped with an AgX 9.5 mm × 2 m Fiber (Silver Halide), with a 6.35 mm diamond crystal with 6 internal reflections as an ATR element, ZnSe as a support/focusing element and an MCT detector using Happ–Genzel apodization. The spectra were acquired in the range of 2000–650 cm^{-1} with a wavenumber resolution of 8 cm^{-1} in a 15-s interval between each spectrum (average of 25 scans).

The calibration and reactions were carried out in a 100 mL reactor controlled with a EasyMax Workstation (Mettler Toledo). The temperature was regulated by the equipment with a Pt 100 temperature sensor and a Peltier cooling system. The reaction was stirred at 200 rpm by using a propeller stirrer, also controlled by the equipment. The reactor was coupled with a condenser, to prevent loss of ethanol by evaporation, since the reaction temperature was close to its boiling point.

2.2. Multivariate calibration

Thirty-five standard mixtures of oleic acid, ethanol, water, and ethyl oleate were prepared, simulating different conversion times of the reaction. Table 1 shows the concentration of the components in each standard mixture.

The standard mixtures were maintained in the reactor with a stirring rate of 200 rpm and at 57 °C, and the spectra were acquired as an average of 250 scans. Once the spectra were collected, a PLS model was built using the software iCQuanti (Mettler Toledo). The responses of the model were the concentrations of the reaction components (oleic acid, ethanol, and ethyl oleate/water), where each one was calculated in an individual model. A spectral region between 1800 and 1540 cm^{-1} and 1400–1000 cm^{-1} of the first derivative of the spectra with mean centering for the model has used.

2.3. Reaction settings

The reactions started with 0.206 mol L^{-1} of oleic acid, 0.712 mol L^{-1} of ethanol, and the corresponding amount of cyclohexane as solvent. The temperature was set to 57 °C, and after it was stabilized, the catalyst was added. The concentration of the catalyst was 10% w/w in relation to oleic acid. The reactions were monitored by using the ATR/FT-IR probe for 165 min. As the reaction progressed, the PLS model was used for real-time quantification of each component. Reactions were performed in triplicate in order to estimate the experimental variance.

2.4. GC–MS analysis

The reaction conversion was determined by gas chromatography–mass spectrometry (GC/MS) using an internal standard (IS) calibration curve for the quantification of ethyl oleate. Pentadecanoyl propanoate was used as IS [23,24].

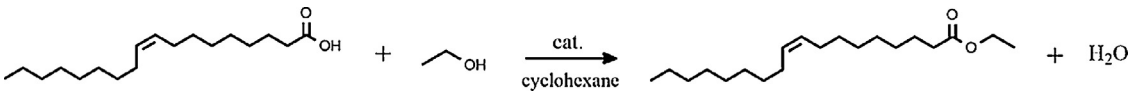
GC/MS analyzes were performed on a Shimadzu GC-QP2010 gas chromatography coupled to a Shimadzu GC–MS-QP2010 mass spectrometer. Electron ionization at 70 eV ionization energy was used. An RXi-1MS (100% methylpolysiloxane) capillary column with 30 m, 0.25 mm i.d., and 0.25 μm df was used. The carrier gas was helium at a flow rate of 2.4 mL min^{-1}. The temperature program was an isothermal period of 3 min at 210 °C, then increased at 20 °C min^{-1} to 290 °C, and final isothermal period of 3 min. Injection volume was 1.0 μL in split mode and with 1:30 split ratio. The injector temperature was 290 °C. The transfer line and ion source were held at 290 °C and 250 °C, respectively. Samples from the reactional media in the reaction catalyzed by Novozym 435 were taken at times: 0, 5, 30, 55, 80, 105, 130 and 155 min. The injection samples were prepared by mixing 500 μL of the 100× diluted reaction medium solution, 50 μL of the IS solution and 450 μL of cyclohexane. Analyses were performed in triplicates.

3. Results and discussion

Scheme 1 shows the esterification of oleic acid with ethanol, which was used in this work as a model reaction for biodiesel production.

The esterification reaction was monitored for 165 min, and an IR spectrum was taken every 15 s (as an average of 25 scans). The 3D infrared surface of the time-dependent spectra throughout the entire course of the reaction was obtained, as shown in Fig. 1 for the reaction catalyzed with Novozym 435. Fig. 1a and b shows the regions with the main variations in the spectra.

In Fig. 1, significant changes are shown in the region around 1750 cm^{-1} (a), which correspond to the carbonyl absorption bands of oleic acid and ethyl oleate, and in the region from 1200 to 1000 cm^{-1} (b), which correspond to the C—O-related vibrations from ethanol and ethyl oleate. As the reaction progresses, the concentrations of the reagents (oleic acid and ethanol) decrease, and



Scheme 1. Esterification of oleic acid with ethanol.