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Comprehensive near infrared study of Jatropha oil esterification with ethanol for biodiesel production

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ABSTRACT

This work presents a comprehensive near infrared study for in-line monitoring of the esterification reaction of high acid oils, such as *Jatropha curcas* oil, using ethanol. Parallel reactions involved in the process were carried out to select a spectral region that characterizes the evolution of the esterification reaction. Using absorbance intensities at 5176 cm^{-1}, the conversion and kinetic behaviors of the esterification reaction were estimated. This method was applied to evaluate the influence of temperature and catalyst concentration on the estimates of initial reaction rate and ester conversion as responses to a 2^2 factorial experimental design. Employment of an alcohol/oil ratio of 16:1, catalyst concentration of 1.5% w/w, and temperatures at 65 °C or 75 °C, made it possible to reduce the initial acidity from 18% to 1.3% w/w, which is suitable for transesterification of high free fatty acid oils for biodiesel production. Using the proposed analytical method in the esterification reaction of raw materials with high free fatty acid content for biodiesel makes the monitoring process inexpensive, fast, simple, and practical.

1. Introduction

During the production of biodiesel via the transesterification of triglycerides with short chain alcohols in the presence of a basic catalyst, using raw materials with high free fatty acid (FFA) content, such as *Jatropha curcas* oil (JCO), large quantities of soap may be produced. Therefore, prior to the transesterification reaction, highly acidic vegetable oils require a preliminary acid esterification step in order to convert FFAs into esters, in the presence of both alcohol and acid catalysts [1].

Raw vegetable oils are complex mixtures, composed mainly of triglycerides and FFA [2]. Due to the presence of these two compounds in a single system, the esterification step becomes more complicated. Kinetic studies by Pisarello et al. [2] showed that, with highly acid raw oils, secondary reactions can occur with the triglycerides present in the oil, such as hydrolysis and transesterification. To evaluate these secondary reactions, the authors used sunflower oil, coconut oil and concentrated FFA and two types of homogeneous acid catalysts (sulphuric and methanesulfonic acids) with the following alcohols: anhydrous ethanol and methanol, and ethanol 96%. In addition, this kinetic study also included the reaction of sulphuric acid alkylation with ethanol. The same group [3] studied the secondary reactions (together with the autocalysis reaction) during FFA esterification of Butia Yatay coconut oil with ethanol, through kinetic studies. Two-step esterification was taken to develop the process and determine the kinetic constants, using sulphuric acid as the catalyst in both steps. The amount of ethanol in the first and second steps was 60% v/v and 40% v/v, respectively. The acid value was reduced from 15% w/w to 1.8 w/w in the second step, at 70 °C, using 0.75% v/v of sulphuric acid.

The main factors that may influence the esterification reaction are the alcohol/oil (A/O) molar ratio, the type of alcohol (methanol or ethanol), acid catalyst (homogeneous or heterogeneous), the temperature and time of reaction, among others. The literature reports several studies on the influence of these variables during the esterification of *Jatropha curcas* oil in order to reduce the amount of FFA present in the oil [4–10]. Tiwari et al. [4] optimized the JCO esterification reaction with methanol using the response surface methodology (RSM). The best experimental condition was achieved using a temperature of 60 °C, 1.43% v/v of H_2SO_4 and methanol/oil molar ratio of 6.5:1, after 88 min of reaction. Under these conditions, the amount of FFA present in the oil was reduced from 14% to less than 1%. Azhari et al. [5] obtained a reduction of the initial FFA concentration from 25.3% to less than 1% using 1% w/w H_2SO_4, with a methanol/oil molar ratio of 16.3:1, at a temperature of 60 °C after 180 min of reaction. Patil and Deng [6] achieved 95% ester conversion during the esterification of JCO using a methanol/oil molar ratio of 6:1, 0.5% w/w H_2SO_4, at 40 °C after 120 min of reaction.

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Lu et al. [7] reduced the acid value in JCO from 14 mg KOH/g oil to less than 1 mg KOH/g oil, using a methanol/oil molar ratio of 3.3:1, 1% w/w H_2SO_4, at a temperature of 70 °C and reaction time of 2 h. Bouaid et al. [8] performed a full two-level factorial design 2^2 and response surface methodology to evaluate the alcohol/oil ratio and catalyst concentration effects in the esterification of JCO with methanol at 60 °C after 60 min. The best results were acquired using a 20:1 methanol/oil molar ratio and 5% w/w of sulphuric acid. Huerga et al. [9] studied two different samples of JCO for biodiesel production, using two types of catalysts, sulphuric and p-toluene sulfonic acid, during the esterification step. Using a 20:1 methanol/oil molar ratio, sulphuric acid concentration of 0.25% v/v and temperature of 60 °C after 60 min, they obtained an acidity of 1.5% w/w. Sanchez et al. [10] reported a comparative study of the JCO transesterification with different alcohols (methanol, ethanol, n-butanol and 2-propanol). The 60-min FFA esterification step was carried out using a 20:1 methanol/oil molar ratio and an H_2SO_4 concentration of 1% w/w at 60 °C. Under these conditions, the acidity in the JCO was reduced from 12.5% to 0.13% w/w.

In the works cited above, the acid value reduction during the esterification step was evaluated by titration. This classic analytical method is time-consuming, uses a significant amount of reagents and requires off-line reaction monitoring. In-line monitoring using near infrared (NIR) has the advantage of performing the analysis in real time. Recently, our group reported the use of Near Infrared (NIR) spectroscopy for in-line monitoring of transesterification reactions employing soil bean oil and methanol for biodiesel production [11]. Multivariate calibration models were developed using Partial Least Squares Regression to predict the concentration of methyl ester (ME), monoglycerides (MG), diglycerides (DG) and triglycerides (TG). Blanco et al. [12] employed in-line monitoring of the esterification reaction of a pure fatty acid (myristic acid), using NIR combined with multivariate curve resolution (MCR). To our best knowledge, there is no work reported in the literature using NIR for in-line monitoring of the esterification reaction of acid raw material for biodiesel production. Therefore, the present work reports a simple NIR analytical method for in-line monitoring the esterification reaction of high acidic oils, such as *Jatropha curcas* oil (JCO), as the first step for the production of ethylic biodiesel. For this, a comprehensive spectral study of parallel reactions involved in the process was carried out to select the spectral region which best characterizes the evolution of the esterification reaction. This method was applied to evaluate the influence of temperature and catalyst concentration on the estimates of the initial reaction rate and ester conversion, as the responses to a 2^2 factorial experimental design.

2. Experimental

2.1. Materials

Jatropha curcas crude oil (JCO) samples were supplied by the Bioauto company, Brazil, and submitted to a degumming process adjusted from Moretto and Fett [13], by adding 8% w/w of water to heated oil at 80 °C and stirring the mixture constantly for 30 min, followed by decantation and separation of the gum fraction from the oil.

Ethanol (purity 99.5%, Dinâmica), phenolphthalein (Dinâmica) and sodium hydroxide pellets (purity 99%, Merck) were used to determine the free fatty acid content of the JCO samples. For the esterification reaction, sulphuric acid (purity 95–98%, Merck) and ethanol (purity 99.5%, Dinâmica) were employed.

2.2. Esterification experiments

Table 1 shows the experimental conditions used for all experiments described in this study. The first four experiments were designed to study these reactions one by one in order to select a suitable spectral region for monitoring the JCO esterification reaction in presence of the ethanol and acid catalysts. In addition, each of the secondary reactions was carried out separately, simulating the same conditions as the main reaction experiment to be monitored. The reagent concentrations and the reactor conditions, temperature and stirring, were kept the same for the reaction systems (experiments: 1 to 4). Experiment 4 was conducted, under the same conditions, using pure soybean oil that had only triglycerides, unlike the JCO, which had both triglycerides and free fatty acids.

Table 1
Summary of experiments.

N°	S	Alcohol/S (mol/mol)	Catalyst (% w/w)	Temperature (°C)
1	Jatropha oil (16)	16:1	1	75
2	Oleic acid	16:1	1	75
3[a]	–	16	1	75
4	Soy oil	16:1	1	75
5	Jatropha oil (15)	4:1	0.5	45
6	Jatropha oil (15)	4:1	1.5	45
7	Jatropha oil (15)	4:1	0.5	75
8	Jatropha oil (15)	4:1	1.5	75
9	Jatropha oil (15)	8:1	0.5	45
10	Jatropha oil (15)	8:1	1.5	45
11	Jatropha oil (15)	8:1	0.5	75
12	Jatropha oil (15)	8:1	1.5	75
13	Repetition exp. 1 (16)	16:1	1	75
14	Jatropha oil	16:1	0.5	65
15	Jatropha oil	16:1	1.5	65
16	Jatropha oil	16:1	0.5	75
17	Jatropha oil	16:1	1.5	75
18	Jatropha oil	16:1	1	70
19	Jatropha oil	16:1	1	70
20	Repetition exp. 17	16:1	1.5	75

In each parenthesis, the number of samples collected during the reaction to determine the FFA percentage using the reference method.
[a] Sulphuric acid alkylation carried out using the same amount of alcohol and catalyst as in experiments 1 without adding the oil.

Considering the results obtained with experiments 1 to 4, experiments 5 to 12 were designed with the purpose of analyzing the relationship between the absorbance values variation (at the spectral region found to be characteristic of ester production) and the trend of the acidity data gathered during the esterification reaction, representing the conversion of FFA into ethyl ester. The data of experiment 13 was employed as an external validation for a univariate model built using the data set of experiment 1. The last set of experiments (14 to 20) was carried out to investigate the effects of temperature and catalyst concentration on ester formation, using the characteristic band selected previously (Table 1).

2.3. Set-up, procedure and spectra

The experiments were carried out in an OptiMaxTM 1001 glass reactor. Fig. 1 shows the experimental set up. It comprises a temperature sensor (a), mechanical stirrer (b), samples input (c) and the Mettler Toledo OptiMaxTM 1001 – glass reactor (d). In addition, a NIR transflectance probe (e) was immersed in the reaction mixture for in-line monitoring of the reactions.

For each experiment, the sample S (*Jatropha curcas* oil, Soybean oil or Oleic acid) was first introduced into the reactor to reach the reaction at which the reaction will occur. Then, a mixture of H_2SO_4 and ethanol, at room temperature (22 ± 2 °C), was inserted into the reactor initiating the reactions.

During reactions, the NIR spectra (between 4933 cm^{-1} and 9315 cm^{-1}) were in-line acquired using an ABB Bomen FTIR (FTLA 2000–160) spectrometer (Fig. 1f) and a 1.0 mm optical path length transflectance probe (Solvias). Each spectrum was acquired using the equipment in kinetic mode (every 60 s) with a spectral resolution of 8 cm^{-1} and as an average of 100 scans.