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Homogeneous catalysis of soybean oil transesterification via methylic and ethylic routes: Multivariate comparison

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ABSTRACT

An experiment to establish the best reaction conditions for the transesterification of soybean oil is described. We conducted the ethylic and methylic routes using two different protocols, and evaluated how the variables time, stirring, alcohol/oil molar ratio, catalyst (%), catalyst type, and temperature affected the process. The highest yield of biodiesel was obtained using the following conditions: ethylic route – $t = 60$ min, stirring: 100 rpm, ethanol/oil molar ratio = 12:1, catalyst relative to oil (%) = 0.2%, catalyst = potassium ethoxide, temperature = 35 °C; methylic route – $t = 30$ min, stirring: 100 rpm, methanol/oil molar ratio = 6:1, catalyst (%) = 0.2%, catalyst = KOH, temperature = 55 °C. We analyzed the acidity, moisture content, density at 20 °C, kinematic viscosity at 40 °C, oxidative stability, and carbon residue at the biodiesels obtained under optimal conditions. The results were consistent with the values allowed by the Brazilian ANP (Resolution 07/2008). We also conducted the physicochemical analysis of the soybean oil used as feedstock to produce biodiesel.

1. Introduction

The oil crisis seen in recent decades together with growing demand for fuel and increasing concern about the environment has prompted the search for alternative energy sources both in Brazil and worldwide [1,2]. Research has focused on developing new basic inputs of renewable character, to produce fuels that can replace petroleum products. In this context, biomass plays a leading role. It is renewable, widely available, biodegradable, and inexpensive [1,2]. Indeed, plant oils had already been tested and used as fuel in diesel engines before the advent of petroleum diesel. However, for both economic and technical reasons, they gave way to diesel oil [3,4]. Currently, biodiesel is a well established example of the use of biomass to produce energy and offers advantages over petroleum diesel [5–7]. It is non-toxic, originates from renewable sources, and leads to better quality of emissions during the combustion process [8]. Although biodiesel provides about 10% less energy than diesel fuel, motor performance is essentially the same with respect to power and torque [6]. Additionally, biodiesel is highly viscous, enhancing lubricity and reducing wear of the moving parts of the engine. Several processes exist to produce biodiesel, but transesterification is the method that is often employed most worldwide [9–11]. It involves reacting a lipid (known as triglycerides or triacylglycerols) with a mono-short chain alcohol (methyl or ethyl) in the presence of a catalyst (acid or base), which produces a mixture of alkyl esters of fatty acids (known as biodiesel) and glycerol [9–11].

The transesterification reaction has been conduced employing different catalytic routes. The catalysts used for the transesterification can be classified into: homogeneous and heterogeneous (basic and acid), or biological (enzymes) [9,12,13]. Among all catalytic routes, the basic homogeneous catalysts, typically sodium and potassium hydroxide, in fact have been most often used industrially, by various as reasons, such as [9,12–14]: low cost catalyst, high catalytic activity with maximum conversion achieved

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in a minimal time, simple operational due to the mild conditions, and minor problem with the corrosive effects.

Many factors affect the transesterification of oils and fats; for example, the presence of free fatty acids, humidity, alcohol type, molar alcohol/oil ratio, catalyst type and concentration, reaction time, and temperature [15,16]. Therefore, studies involving transesterification of vegetable oil must be performed considering the effect of the various factors during the optimization, and simultaneously, because the experimental parameters are interrelated. This necessity/approach can be achieved from the use factorial design, where from a small number of experiments diverse variables are studies simultaneously at different levels and taking into account its interactions with the others variables [17,18]. Thus, the recent literature reports the application of factorial design for the optimization of the homogeneous catalysis transesterification from different feedstocks, such as lard [17], castor oil [19], sunflower oil [20], beef tallow [21], Muskmelon (*Cucumis melo*) seed oil [22], waste vegetable oil [23], among others. In regard the biodiesel production from soybean oil the traditional univariate methodology for optimization of the process has been adopted [24]. However, Oliveira et al. [25] presented the optimization of alkaline transesterification of soybean oil using a Taguchi experimental design, and from this experimental design the effect of the variables temperature, reaction time, catalyst concentration and oil-to-ethanol molar ratio were available. The influence of other very important factor were not considered in this reported work, as type of alcohol and basic catalyst [25].

In this work a novel approach for the homogeneous catalysis optimization of soybean oil transesterification via methylic and ethylic routes is presented, which all experimental parameters were systematically evaluated using a factorial design. Thus we investigated which of the variables reaction time, reaction rate, molar alcohol/oil ratio, catalyst type, catalyst concentration, and temperature significantly influence the yield of the transesterification reaction using a fractional factorial design 2^{6-2} in duplicate, which resulted in 32 experiments conducted for each design.

2. Experimental

2.1. Characterization of the soybean oil and biodiesel

Soybean oil was analyzed for the following parameters: refractive index (40 °C), saponification index, acidity, moisture content, density at 20.0 °C, kinematic viscosity at 40 °C; oxidative stability, and carbon residue.

The same analyses were also conducted for the biodiesel obtained in the optimum experimental conditions, except for the refractive index and saponification number. The parameters refractive index (40 °C), saponification number, and acidity were determined according to the official procedures recommended by the American Oil Chemists Society [26]. The moisture content was analyzed according to the norm ASTM D-6304 using a Karl Fischer colorimetric titrator model 831 KF. The density was determined according to the norm ASTM D-4052, which corresponds to the Brazilian norm ABNT NBR 14065, using a DA-500-Kyoto densimeter. Kinematic viscosity at 40 °C was obtained according to the norms ASTM D-445 and ASTM 446. The oxidative stability was analyzed by the method EN 14112, on a Rancimat equipment model 743 from Metrohm.

2.2. Transesterification of the soybean oil

Refined commercial soybean oil, household, packaging 900 mL, model Liza, industrially processed by Cargill Agricultural SA was used. Table 1 shows the fatty acid composition of the oil.

For the transesterification reaction, the catalyst was added to the solvent; the mixture was stirred until complete dissolution and transferred to a 250 mL Erlenmeyer flask. Next, the oil was added, and transesterification was performed by following the experimental conditions described in the experimental design ethyl 1 and 2 and methyl 1 and 2 (Table 2). After transesterification, two phases were noted: upper and lower crude biodiesel glycerin. Then, biodiesel was removed from the mixture and washed five times with water at 80 °C at a water/biodiesel ratio 1:3 (v/v), to remove impurities. The biodiesel was then dried in a rotary evaporator. The wash water containing the residue catalyst was properly neutralized with 0.1 mol L^{-1} HCl solution before being discarded.

2.3. Experimental design

To establish the experimental conditions that improved the efficiency of transesterification, the reaction was carried out using a fractional factorial experimental design, in duplicate. The option used in the experiment was 2^{6-2}, which is interesting for investigative purposes, because it reduces the number of tests. This design is not completely saturated and no main effects mix with first order, which ensures that the effects of the variables analyzed in the response are reliably calculated, without statistical information quality. Table 2 lists the values employed at each level of the variables, chosen on the basis of literature studies [27,28].

3. Results and discussion

3.1. Experimental design

3.1.1. Optimization of the ethylic route using KOH or NaOH as catalyst

Tables 3–6 present the corresponding values of mass production regarding the methylic and ethylic transesterification of soybean oil conducted according to the experimental design 2^{6-2}. We compared the performance of the catalysts KOH, NaOH, and potassium ethoxide in the ethylic route of soybean oil transesterification. We also compared the use of KOH, NaOH, and potassium methoxide as catalysts in the methylic route. We calculated the mass yield of the process on the basis of the transesterification reaction stoichiometry: 1 mol of oil affords 3 mol of ester (Table 7).

Fig. 1 represents the Pareto chart obtained from the data summarized in Tables 3–6 using the fractional factorial design; we evaluated the effects of each variable and their interactions on the yield of soybean oil transesterification.

The Pareto chart corresponding to the design shown in Table 3 (Fig. 1a) revealed that the interactions between factors (1) and (4), (1) and (3), (2) and (5), (1) and (5) affected transesterification less than the variables disregarded then in subsequent statistical analyses.

Table 1
Composition of fatty acids in soybean.

Fatty acids	Structure	Reference values (%)
–	C<14	<0.1
Myristic	C14:0	<0.5
Palmitic	C16:0	7.0–14.0
Palmitoleic	C16:1	<0.5
Estearic	C18:0	1.4–5.5
Oleic (Omega 9)	C18:1	19.0–30.0
Linoleic (Omega 6)	C18:2	44.0–62.0
Linolenic (Omega 3)	C18:3	4.0–11.0
Araquidic	C20:0	<1.0
Eicosenoic	C20:1	<1.0
Behenic	C22:0	<0.5