



Evaluation of the use of degummed soybean oil and supercritical ethanol for non-catalytic biodiesel production



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ABSTRACT

In this work the production of fatty acid ethyl esters (FAEE) from degummed soybean oil in supercritical ethanol was investigated. The process parameters were defined as reaction temperature (250–340 °C), residence time (11–50 min) and ethanol:oil molar ratio (9:1–51:1). All experiments were performed in a continuous reactor at 20 MPa. The effect of each parameter and their interactions on the yield of fatty acid ethyl esters was studied using design of experiments (DOE). Results showed that all three single parameters were significant on the yield of FAEE and that reactions of degummed soybean oil with ethanol led to esters yields up to 65%, in these experimental conditions. These values are inferior when compared to the ones obtained with refined soybean oil probably due to the presence of several impurities in degummed soy bean oil such as pigments, antioxidants and phospholipids. Despite of this lower yield, the use of degummed soybean oil can still be a good alternative since this is a non-edible lower cost raw material.

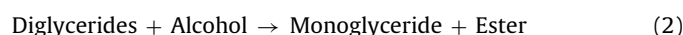
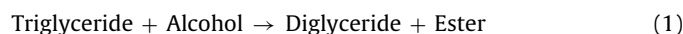
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1. Introduction

The majority of all energy consumed in the world, especially in the transportation sector, comes from fossil sources. However, the consumption of fossil fuels has a significant impact on the quality of the environment, because burning fossil fuels leads to emissions of carbon dioxide and other greenhouse gases. Besides that, the worldwide demand for energy is increasing continuously and the known reserves of these fuels are limited. Therefore, it is necessary to develop alternative energy sources for petroleum-based fuels, which are feasible, economically competitive, cheap and more environmental friendly.

Biodiesel is a fuel produced from vegetable oils or animal fats and it is a promising alternative to petroleum-based fuels because it has an energetic content close to diesel fuel [1]. Besides, it is renewable, non-toxic, biodegradable, and it has lower contaminants contents. Due to the high viscosity of the pure vegetable oils (11–17 times higher than conventional diesel), some methods are used to convert vegetable oils into a more appropriated form to be used as engine fuel. Among several techniques, chemical conversion of oil through transesterification is the most promis-

ing solution to the high-viscosity problem [1]. In this reaction, the alcohol in contact with the triglycerides removes esters from its molecular structure, forming a mixture of esters as a main product (biodiesel) and glycerin as a byproduct, as shown in Eqs. (1), (2) and (3).



Conventionally, biodiesel is produced from the transesterification of vegetable oils with short chain alcohol using a homogeneous catalyst. However, this process has some drawbacks: the catalysts are very sensitive to water and free fatty acids contents, the energy costs are high, the recovery of glycerol is difficult and the catalyst must be removed from the product, among other problems [2]. Therefore, some non-conventional methods can be an interesting alternative to obtain this fuel, such as the reaction without catalyst under alcohol in supercritical conditions. This route has the advantages of promoting a better contact between the reagents [3], decreasing mass-transfer limitations, leading to higher reaction rates, making the separation and purification steps of the products easier [4] and the ability of accepting lower quality oils, with higher water [5] and free fatty acids contents [5,6] by promoting simultaneously the esterification and transesterification reactions.

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The basic idea of supercritical treatment is a relationship between pressure and temperature upon thermophysical properties of the solvent such as dielectric constant, viscosity and polarity [1]. Liquid alcohols are polar solvents and they have strong electrostatic attractive interactions between hydrogen of one molecule and the oxygen of another molecule (hydrogen bondings). In a supercritical state, there is a reduction of hydrogen bondings with increasing temperature leaving to a decrease in alcohol polarity. This means that supercritical alcohols have a hydrophobic nature with lower dielectric constant. As a result, non-polar triglycerides can be solvated with supercritical alcohols to form a single phase of vegetable oil/alcohol mixture, which is likely to promote the transesterification reaction [3].

Despite the severe conditions of temperature and pressure required by the transesterification of biodiesel using supercritical alcohol, this route has been researched around the world. In order to reduce the operational costs, cheaper raw materials can be used, such as residual oils and crude oils. The degummed soybean oil is a great potential option for non-catalytic synthesis of biodiesel, because it has a low cost and it is non-edible. This oil is composed not only by the same main components of refined soybean oil but also contains some minor components such as antioxidants, pigments, phospholipids, etc [7].

Methanol is used in the most of studies since it presents lower cost. However, ethanol is more environmental friendly because it can be derived from agricultural products, renewable and is easily available in the market, especially in Brazil.

Based on these aspects, the objective of this study was to investigate the production of biodiesel from degummed soybean oil using ethanol in supercritical conditions. The experiments were performed in a continuous reactor and the process parameters investigated were temperature (250–340 °C), residence time (11–50 min.) and ethanol:oil molar ratio (9:1–51:1), at pressure of 20 MPa. The effect of each parameter, as well as, of their interactions in the conversion of fatty acid ethyl esters (FAEE) was evaluated using design of experiments (DOE).

2. Material and methods

2.1. Materials

Degummed soybean oil used in this study was provided by Cargill (Brazil). Absolute ethanol (JT Baker, 99.9%) was used for the synthesis of fatty acid ethyl esters. Table A1 shows the fatty acid composition of the degummed soybean oil used in this study. The acidity of this oil was 0.76%, humidity of 0.16% and phosphorus content of 77.86 ppm. The percentage of free fatty acid (acidity) was determined following the method used by Abdala et al. [8], based on the AOCS Official Method Ca 5a-40, which uses an acid–base titration. The titrant is an ethanol solution of potassium hydroxide (KOH) previously standardized. The phosphorus content in the oil was determined based on the AOCS Official Method Ca 12-55. This method starts with charring and ashing the oil sample with zinc oxide, followed by the colorimetric measurement of phosphorus as a blue phosphomolybdic acid complex. With this procedure, the equivalent phosphorus content in the oil could be calculated [9]. Solvents *n*-heptane (Química Moderna, 99.9%) and methanol (Vetec, 99.8%) were used for the gas chromatography analysis.

2.2. Apparatus and experimental procedure

A schematic diagram of the experimental apparatus used for the synthesis of fatty acid ethyl esters is illustrated in Fig. B1. All experiments were performed in continuous reactors, at conditions above the critical temperature and pressure of ethanol (243 °C and

6.38 MPa). The reactions were carried out using two reactors: a tubular (a pre-heating section that acted as a reactor) and a packed bed reactor. Both reactors were made from stainless steel and have volume of 81.74 mL and 14 mL, respectively.

In each experiment, the mixture of ethanol and degummed soybean oil in predetermined proportions was agitated by a mechanical stirring device (Ika, RW 20). The feeding of substrate in the system was controlled by a high pressure liquid pump (Lab Alliance, Series III) which was adjusted to the desired flow rate. After filling the reactors with the substrate, the process of heating the furnaces and pressurizing the system started. For the pressurization, the back pressure regulator (Swagelok, KPB1S0A415P20000) was adjusted to maintain the desirable pressure. The reactors were heated by two electric furnaces (heating power of 2000 W) connected to temperature controllers (Novus N1100), with a heating rate of 10 °C/min and precision of ± 2 °C. Finally, when the temperature and pressure were stabilized in the desired conditions, samples were collected in triplicate, after waiting at least 2 residence times. The residence time was calculated according to Eq. (4):

$$\tau = \frac{V}{fr} \quad (4)$$

where “V” is the volume of the reactors (mL) and “fr” is the flow rate (ml/min) of the substrate, which was set at the peristaltic pump. The volumes of the reactors were measured by pumping the substrate inside the reactors and measuring the volume with a burette, in triplicate.

2.3. Sample analysis

Samples were analyzed for esters content by gas chromatography (GC) and the analytical method is based on the method of Silva et al. [10]. To ensure the total evaporation of ethanol, samples were dried using an incubator at 80 °C. After this, to guarantee the separation of glycerol formed during the reaction, 2 mL of heptane and 2 mL of water were added to the samples and they were centrifuged for 10 min at 3000 rpm. The upper layer is biodiesel and the lower layer is glycerol. Finally, the organic phase was sent to be dried in an incubator at 80 °C, to ensure the complete elimination of heptane and water.

In order to determine the yield of fatty acid ethyl esters (FAEE), 300 mg of the sample was weighed in a 10 mL flask and this volume was completed with *n*-heptane. After this, 1 μ L of this solution was added in a 1 mL flask with 1 μ L of the internal standard at a concentration of 13000 mg/L and the volume was completed with *n*-heptane. The ethyl ester samples were directly analyzed by capillary GC, using a GC Shimadzu GC-2010, equipped with flame ionization detector (FID) and a capillary column RTX-Wax (Restek, 30 m, 0.32 mm i.d, 0.25 μ m d.f). Helium was used as the carrier gas, with a split ratio of 1:50. The injection and detector temperatures were 250 °C and the column temperature was 210 °C. The identification and quantification of the peaks of the ethyl esters were accomplished by comparing the retention time of each compound in the sample with the standard compound methyl heptadecanoate (Sigma–Aldrich).

2.4. FAEE decomposition

The method used to analyses the process of decomposition is similar to the one proposed by Vieitez et al. [11]. Samples were treated with KOH/MeOH to derivatize all the fatty acids (mono-, di-, and triglycerides, free fatty acids, and also ethyl esters) to the corresponding methyl esters, and then analyzed by GC. For the eval-

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