



A novel response surface methodology optimization of base-catalyzed soybean oil methanolysis



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HIGHLIGHTS

- The yield of base-catalyzed soybean oil methanolysis was optimized to 87.09%.
- The time of base-catalyzed soybean oil methanolysis was optimized to 30 min.
- There is a strong interaction between temperature and catalyst concentration.

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ABSTRACT

The mass yield of a base-catalyzed soybean oil methanolysis was maximized to 87.09 (wt/wt%) through response surface methodology with five levels and four factors. An economy of 33% methanol, 33% sodium hydroxide, and 50% reaction time was achieved in relation to other optimization researches which were previously reported in the literature. The obtained biodiesel attends the ANP quality standards for the following items: ester amount wt%, free glycerol (wt/wt%), mono-, di-, and triacylglycerols (wt/wt%), and total glycerol (wt/wt%).

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1. Introduction

The biodiesel is a biofuel composed of alkyl esters originated from the transesterification of triacylglycerols (TAGs) with short-chain alcohols (usually methanol or ethanol) in the presence of a catalyst (homogeneous or heterogeneous), generating glycerol as coproduct [1]. If a transesterification reaction is not completed, monoacylglycerols (MAGs), diacylglycerols (DAGs), and triacylglycerols (TAGs) also will be present in the reactional medium among the produced methyl esters [2].

The remaining MAG, DAG, and TAG concentrations are employed as parameters to evaluate the conversion of reagents in alkyl esters and, therefore, obtain the reaction yield. The efficiency of a biodiesel purification process is evaluated through the concentration of alkyl esters in the final product [2].

In most of cases, the reaction products are analyzed through gas chromatography (GC) with flame ionization detector (FID) [3,4]. In order to achieve these results, a time of 01 h30 min is needed.

Vicente et al. [5] verified that the transesterification reaction yield can be obtained from a gravimetric method, which relates purified biodiesel mass with the employed raw material. This technique can be used in the control quality sector of a biodiesel industry aimed at the real time monitoring of its fabrication process in order to give a rapid response about possible abnormalities during the synthesis. These problems can be confirmed later with chromatographic analysis. The application of this method is even more facilitated because biodiesel industries always register the acquired raw material and produced biodiesel masses.

If a produced methyl ester mixture is destined for commercialization as biodiesel, then it must attend the quality standards determined by ASTM D6751 [6] and UNE-EN14214:2009+A1:2010 [7]. In Brazil, these specifications are established by Agência Nacional do Petróleo, Gás Natural e Biocombustíveis (ANP) through the number 7 resolution from 2008 [8] based on ASTM e EN specifications [9].

In the industrial scale production of biodiesel, alkaline homogeneous catalysts, such as sodium and potassium hydroxides, are widely employed due to the high product yields achieved with them in a short amount of time and low temperatures [10–12]. Other reasons for the use of the cited hydroxides are as follows: low price and easy storage [10]. Although alkoxides such as sodium

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methoxide are more efficient in terms of catalytic activity, because low molar concentrations of them (about 0.5 mol%) may lead to reaction yields above 98% in short reaction times (around 30 min), a minimal presence of water greatly reduces their performance, making them unsuitable for typical industrial processes. In this contest, the hydroxides which were cited above are preferred over alkoxides because they do not require the total absence of water, and the same conversion rate of vegetable oils to esters can be achieved by increasing the catalyst concentration [13]. However, the use of homogeneous catalysis implies some disadvantages: it requires raw materials of high purity and several post-reaction steps in order to separate the reactants, the catalyst, and the reaction products (since all of them are in a same phase) [14,15].

Among the determinant factors that might affect the yield of a transesterification reaction, temperature, time, catalyst concentration, and raw material:alcohol ratio can be featured [16].

The influence degree of each factor in the reaction is greatly dependent of the TAG contents in raw material which was employed [17]. Thus, all these factors must be analyzed simultaneously, since the interactions between them can also affect the final reaction yield. In order to achieve the stated evaluations, optimization methods have been applied in the biodiesel research area. With such interaction properly studied, the yield is maximized and production costs are minimized [18,19].

Thus, the objective of this work was to optimize the mass yield of a base-catalyzed soybean oil transesterification with a response surface methodology (RSM) employing the following factors: reaction temperature, time, catalyst concentration, and oil:methanol molar ratio.

2. Methods

2.1. Materials

In this work, soybean oil acquired from Cocamar enterprise, located in Maringá (PR) city, was used. Its composition is listed in Table 1. The reference standards glycerol, mono-, di-, and triolein, 1,2,4-butanetriol, tricaprim, and methyl heptadecanoate, all with purity > 99%, were acquired from Sigma–Aldrich. The reagents methanol, NaOH, anhydrous Na₂SO₄, and HCl with analytical degree were chosen for the experiments.

2.2. Apparatus

The experiments were done in a three neck round bottom flask, employing RW20 RW20, IK Labortechnik mechanical stirrer, QUIMIS heated bath, condenser with reflux, and a 0–110 °C thermometer. The flask was kept at the desired temperature through the bath's digital controller which possesses a ±2 °C precision. After

each experiment, the remaining methanol was removed in a rotary evaporator composed of another QUIMIS heated bath, distillation apparatus, and vacuum pump. The mass yield of the reactions was determined through gravimetric method listed in Eq. (1), with a semi-analytical balance Mars, model AS2000C [5]:

$$\text{Yield (wt/wt\%)} = \frac{M_{\text{biodiesel}} \times 100}{M_{\text{oil}}} \quad (1)$$

In which $M_{\text{biodiesel}}$ is the “biodiesel” mass, in grams. It is important to cite that all the transesterification products in this work will be labeled as “biodiesel” for a better understanding; M_{oil} is the mass, in grams, of used oil.

2.3. Transesterification reactions

Initially, 200 g of oil was added in the flask adapted to a reflux condenser in order to avoid methanol losses due to evaporation [20], and then, the stirring system was turned on. Soon after, reaching the desired temperature, NaOH dissolved in methanol was added and reaction time countdown started. The reactional parameters of the experiments can be observed in Table 2.

In the end of each experiment, the flask content was transferred to a separatory funnel and allowed to rest for 2 h so that the formed glycerol could decant. The superior layer was collected and transferred to the rotary evaporator, in which the methanol in excess was removed and discarded. The product was transferred to another separatory funnel where an HCl 1% (v/v) solution was added in an amount equal to 15% of product volume, in order to avoid emulsion formation. After 30 min, the lower layer (water, soap, glycerol, salts, and eventual methyl esters) was discarded, and the product was washed with water heated to 50 °C (amount equal to 15% of product volume) until pH 6.5. Soon after, this product was filtered through a funnel of analytical degree paper, with anhydrous sodium sulfate, a compound which is highly suitable for removal of small amounts of water that might be adsorbed in the product [21].

2.4. Experimental design

The independent variables influence (Table 3), in function of mass yield, were evaluated through central composite rotary design applied to a response surface methodology (RSM) with five levels and four variables, totalizing 27 experiments composed of 16 factorial points, eight axial points, and three central points. The employed variables and intervals were previously defined by bibliographic research [22]. Since the parameters for the biodiesel transesterification reaction are very well-known from the literature, the optimum points which were previously determined by them were included in the intervals of variables which were employed in this work [23,24].

Table 1
Characterization of the soybean oil which was employed for reactions.

Analysis	Results
AI ^a (mgKOH/g sample)	0.08 ± 0.02
PI ^b (meq/kg)	6.92 ± 0.18
MAG ^c (% m/m)	ND
DAG ^d (% m/m)	1.54 ± 0.33
TAG ^e (% m/m)	97.46 ± 0.25

^a AI, acid index.

^b PI, peroxide index.

^c MAG, monoacylglycerol.

^d DAG, diacylglycerol.

^e TAG, triacylglycerol.

Table 2
Experimental range and levels of independent process variables for transesterification reactions.

Independent variable	Range and level				
	−2	−1	0	1	2
Temperature, X ₁ (°C)	50	60	70	80	90
Catalyst concentration, X ₂ (wt/wt%)	0.5	1.0	1.5	2.0	2.5
Oil:methanol, X ₃ (molar ratio)	1:3	1:6	1:9	1:12	1:15
Time of reaction, X ₄ (min)	15	30	45	60	75

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