



Non-edible babassu oil as a new source for energy production—a feasibility transesterification survey assisted by ultrasound

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ABSTRACT

Ethyl esters of babassu oil were synthesized by alkaline catalysis to make the green production of biodiesel feasible with simple methods and available technology. Babassu oil is a transparent, light yellow oil extracted from the seeds of the babassu palm (*Orbinya* sp), and due to its high saturated fatty acid composition (83%), it is considered a non-edible oil. Transesterification using ethanol represents a valid alternative to using methanol because of ethanol's lower toxicity and the higher yield on weight compared to methanol. Statistical methodology was applied to optimize the transesterification reaction, which was promoted by ultrasonic waves and mechanical agitation. Nuclear magnetic resonance spectroscopy was used to quantify the conversion attained. Alkaline transesterification assisted by ultrasound produced the best results with respect to reaction time and the phase separation step. The model obtained showed that conversions higher than 97% may be achieved in 10 min with correct tuning of the process variables.

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1. Introduction

The use of edible vegetable oils for biodiesel production has recently been of great concern because they compete agriculturally with food crops, specifically with regard to rural investment, infrastructure, water, fertilizers, and skilled labor, resulting in food shortages and price increases [1]. The contribution of non-edible oils such as babassu, a generic name given to palm oil belonging to the *Palmae* family and members of the genera *Orbignya* and *Attalea*, dispels biodiesel production issues related to the use of edible vegetable oils. Babassu oil constitutes 66% of the babassu kernel weight, with 83% of the grease composition made up of saturated oils, making it an excellent candidate for biodiesel production. In the Brazilian market, a range of oilseed crops can be used in biodiesel production, although currently, most manufacturing processes use soybean oil as the main raw material. Some of these oilseeds, such as soybean oil, are a part of the food industry market, and an extensive farming area must be used to afford good production. In this sense, non-edible crops such as babassu oil that present favorable annual productivity and a good yield per hectare [2] will be significant as a non-edible plant oil source for biodiesel production [3].

Vegetable oil transesterification yields biodiesel as the main product. However, the final mixture is composed of free glycerol,

alcohol, catalyst and unreacted mono-, di- and triglycerides [4]. These contaminants can lead to several environmental and operational problems. Achieving a high conversion of mono-alkyl esters to ensure the removal of free glycerin, catalyst, alcohol and fatty acids in biodiesel is a critical issue for biodiesel quality control and one of the main challenges in the feasible industrial production of these fuels. Another significant factor influencing the performance of biofuels is the fatty acid composition of vegetable oils because carbon chains with high numbers of unsaturation are more susceptible to oxidation and exhibit better performance at low temperatures. Saturated chains are desirable [5,6] due to their higher oxidation resistance and improved cetane number. As can be seen in the literature [7], babassu oil has a high saturated chain composition. However, in view of its elevated cloud point, the feasibility of babassu oil use depends on the temperatures that will be reached, which is a concern in cold climates.

In this work, the ethanolysis of babassu oil is presented as a source for biodiesel production, employing the most commercially used hydroxides, sodium and potassium, which were evaluated independently. The aim was to study the process performance aided by ultrasound fields. The statistical methodology proposed by Taguchi [8] to obtain robust processes, i.e., processes with low variation due to uncontrolled variables, was employed. The homogeneous alkaline transesterification reaction was evaluated in the presence of saponification and hydrolysis side reactions, which accompany and are inherent to the use of these hydroxides to generate effective catalysts [9].

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2. Material and methods

2.1. Materials

Refined babassu oil was kindly provided by COGNIS (Jacarei, SP, Brazil), with the following fatty acid composition (w/v): 3.5% caprylic, 4.5% capric, 44.7% lauric, 17.5% myristic, 9.7% palmitic, 3.1% stearic, 15.2% oleic and 1.8% linoleic, with an average molecular weight of 709.90 g/mol. Analytical grade NaOH (99%), KOH (85%), Na₂SO₄, anhydrous ethanol (99.8%) and hexane were obtained and used as received. All other reagents were of analytical grade.

2.2. Properties of babassu oil

Physicochemical properties (iodine value, saponification value, acid value) were determined by methods described by the Association of Official Analytical Chemists [10].

2.3. Conventional transesterification reaction: general procedure

The catalyst and anhydrous ethanol were premixed at 40 °C under magnetic stirring either for 20 min or until complete dissolution. Then, the solution of the corresponding ethoxide was added to 70 g of refined babassu oil, previously heated at the same temperature. The reactions were performed in a 300 mL jacketed glass reactor connected to a reflux condenser, with the reaction temperature controlled by a thermostatic bath. Stirring was performed using a mechanical stirrer and glass double-curved blades, with an IKA RW20-digital mixer for rotation control. After the predetermined time for each reaction, the reaction mixture was transferred to a vessel to allow for phase separation between the ethyl esters and glycerol.

2.4. Transesterification reaction with ultrasound

In a 125 mL Erlenmeyer flask, 22 g of refined babassu oil was added. In parallel, appropriate amounts of anhydrous ethyl alcohol and sodium or potassium hydroxides were added to a glass flask equipped with a reflux condenser and mixed under moderate magnetic stirring for 20 min at 40 °C until they were dissolved completely. This prepared ethoxide catalyst solution was then added to the flask containing the babassu oil, which had been preheated to 30 °C. An ultrasonic bath (Model Kerry Pulsatron 600) was filled with 300 mL of distilled water, and the flask containing the reactants was placed inside. The temperature in the ultrasonic bath was maintained at 30 °C, and the flask was not tightly sealed because at this temperature, the evaporation of ethanol is negligible. The position inside the tub and the height of the flask were standardized with markers to ensure that the same three-dimensional position was always used. The ultrasonic bath was set to operate at 600 W and 20 kHz. After the predetermined time for each reaction, the reaction mixture was transferred to a vessel to allow for phase separation between ethyl esters and glycerol.

2.5. Experimental design

The Taguchi designs with orthogonal arrays were performed according to the factors and levels presented in Tables 1 and 2 for conventional agitation and the ultrasound method, respectively. The levels on these arrays were selected according to the headings of previous works [11,12].

2.6. Downstream procedure

After phase separation and removal of the glycerol produced (lower phase), 200 mL of hexane was added to the upper phase,

Table 1

Levels and controllable factors used in the babassu oil ethanolysis reaction with conventional agitation.

Factor	Units	Levels	
		1	2
Turbulence	Rpm	200	400
Temperature	°C	30	60
Molar ratio ethanol/oil	Mol	4:1	6:1
Hydroxide/oil ratio	% By weight	0.5	1.0
Reaction time	Min	30	60
Hydroxide type		NaOH	KOH

Table 2

Levels and controllable factors used in the babassu oil ethanolysis reaction with ultrasound agitation.

Factor	Units	Levels	
		1	2
Molar ratio ethanol/oil	Mol	3:1	6:1
Hydroxide/oil ratio	% By weight	0.5	1.0
Reaction time	Min	10	20
Hydroxide type		NaOH	KOH

which contained the non-reacted intermediates and ethyl esters. This addition promoted further glycerol phase separation. After collecting the new phase, an additional step involving several washings with a 0.1 mol L⁻¹ solution of HCl was carried out to attain a neutral pH. After rinsing, the phase was dried with approximately 0.5 g of anhydrous Na₂SO₄ to remove remaining water, followed by vacuum filtration; then, residual alcohol and hexane were evaporated by a rotary evaporator at 72 °C for 20 min under atmospheric pressure.

2.7. Proton nuclear magnetic resonance spectrometry (1H NMR)

The conversion into ethyl esters was evaluated by NMR in a Mercury 300 MHz – Varian spectrometer, with 5 mm glass tubes, using CDCl₃ as the solvent and 0.3% TMS as the internal standard. The calculations involving the conversion of esters were performed using the equation proposed by Garcia [13] Eq. (1). This methodology allowed for the identification of molecules by ¹H NMR, with peaks present in the region from 4.05 to 4.35 ppm during the transesterification reaction. A calibration plot using Eq. (1) and the known concentrations of ethyl esters and babassu oil was performed; the correlation coefficient obtained was 0.998.

$$\%EE = [(Ac_4 \times 8) / (Add + ee)] \times 100 \quad (1)$$

Where:

Ac₄ = Component 4 area

Add+ee = Whole signal area between 4.35 and 4.05 ppm

%EE = Yield of fatty acid ethyl esters (FAEE)

In this equation, the Ac₄ values were obtained from the integration of the peak at 4.08 ppm. The area obtained corresponds to 1/8 of the whole ethoxi-carbons hydrogen area (–OCH₂), whose signals appear in the region ranging from 4.05 to 4.20 ppm. The region near 4.08 ppm is the only region where crossover does not occur, and this integrated signal can be successfully assigned to ethyl esters.

3. Results and discussion

3.1. Chemical properties of babassu oil

The chemical properties of babassu oil were determined, and the results of the free fatty acid content, saponification and iodine

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