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Production of methyl and ethyl biodiesel fuel from pequi oil (Caryocar brasiliensis Camb.)

CURRENT PROBLEMS. Alternative Fuels

PRODUCTION OF METHYL AND ETHYL BIODIESEL FUEL FROM PEQUI OIL
(*Caryocar brasiliensis* Camb.)

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We studied the physical and chemical characteristics of methyl and ethyl esters (biodiesel) produced by transesterification of pequi oil (Caryocar brasiliensis Camb.) in the presence of potassium hydroxide. The oil extracted from pequi seed comprises 60% of the fruit content. Such characteristics as density, acidity, viscosity, and carbon residue of the biodiesel meet ANP (Brazilian National Petroleum Agency) standards. Our tests demonstrated the feasibility of utilizing pequi oil for biodiesel production.

***Key words:** pequi, Caryocar brasiliensis Camb., biodiesel, biofuel.*

Biodiesel consists of biodegradable monoalkyl esters of fatty acids derived from renewable resources (vegetable oils and animal fats) by cracking, esterification, and transesterification. Most often biodiesel is obtained by transesterification: reaction of the oil or fat with alcohol (usually methanol or ethanol) in the presence of a catalyst (acid or base). During this process, glycerol is also obtained, which can be used in production of soap and other cosmetic products [1-8]. Biodiesel is used in diesel engines in pure form or as blends with petroleum diesel fuel. A fuel containing 2% biodiesel, for example, is called B2; pure biodiesel is called B100 [9-16].

Besides the economic and environmental advantages of biodiesel, the social aspect of its production on small farms is also important. The biodiesel production chain may provide a large number of jobs, thus promoting social integration, especially in regions that are less attractive for other economic activities. Furthermore, use of renewable fuel reduces oil and diesel fuel imports. We must also point out that using biofuel means less environmental pollution.

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Dozens of plant species grow in Brazil which can be used to produce biodiesel, including castor oil plant, palm, sunflower, baru, babassu, peanut, jatropha, soybean [8, 11, 12, 15, 17-19]. Pequi grows in the Cerrado region (Brazil), in the transitions between the Amazon forests and the Cattinga, and also in the Cerrado enclaves in the Amazon and Atlantic forests. From 5 to 43 trees can be grown per hectare.

Pequi can be used for rehabilitation and reforestation as well as for wood production. This plant is nectar-bearing and useful for medicinal purposes. The pequi fruit pulp is used as food, but the kernel is discarded even though biodiesel can be obtained from it due to its high oil content (~60%). Long roots are typical of the pequi tree, which can grow horizontally in shallow soils. This plant can grow in nutrient-poor soils and also in soils with high aluminum content [2]. The great adaptability of pequi to sandy, nutrient-poor soils, deficiencies in water and nutrients gives it potential for improving social and environmental conditions in regions with such soils [2]. Despite the possibility of using this plant in biodiesel production, few papers have been devoted to such applications. The aim of our research was to produce methyl and ethyl esters from pequi oil by its transesterification in alkaline medium and to study the properties of the biodiesel obtained, in order to determine the feasibility of using pequi as an alternative fuel source.

Preparation of biodiesel

Reagents used in this work were: ethyl acetate, acetone, hydrochloric acid, sulfuric acid, starch, sodium arsenite, sodium bicarbonate, ethanol, hexane, potassium hydroxide, methanol, methyl ethyl ketone, phenolphthalein (indicator), dimethyl ether, and sodium periodate. All reagents were analytical grade.

The oil was extracted in a 250 mL Soxhlet apparatus from dried and crushed pequi fruit. The solvents hexane, acetone, ethanol, and methanol were studied in order to select the one providing the highest oil yield. The oil yield for extraction by different solvents is given in **Table 1**. We see that hexane is the most effective solvent. Approximately 50 g of crushed fruit was placed in the Soxhlet apparatus and extraction was performed for 6.5 hours. The solvent was removed from the extracted oil by evaporation on a rotovap, and the water was removed using a high-vacuum pump.

The transesterification stage involved reaction of an anhydrous low-molecular weight alcohol (methanol or ethanol) with a mixture of triglycerides from pequi oil in the presence of potassium hydroxide:
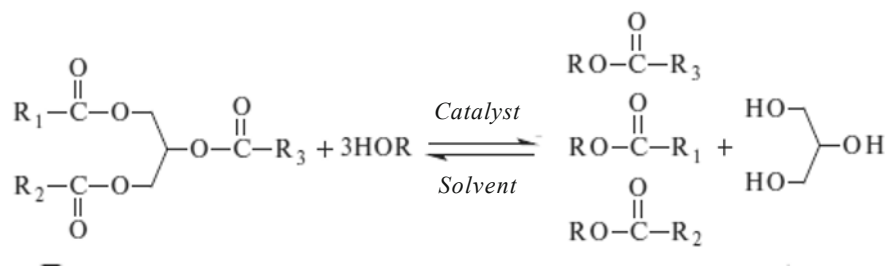

Table 1

Solvent	Required solvent volume, mL	Oil yield, mL/g of pequi fruit
Hexane	34	0.68
Acetone	27	0.54
Ethanol	21	0.42
Methanol	11	0.22

Water was previously removed from the oil by addition of sodium sulfate (about 5 g per 100 mL oil). The sodium sulfate was prepared at least one day before the experiment and was stored in a bottle sealed with parafilm. 100 mL of the dried oil was measured into a 250 mL beaker, making sure not to transfer the desiccant salt settled on the bottom. The beaker was covered with plastic film.

In parallel, a solution of 4 g potassium hydroxide in 30 mL alcohol was prepared in a 100 mL beaker. After the potassium hydroxide was completely dissolved, the solution was allowed to stand for 20 minutes to form the alkoxide. The dried oil was placed in a 250 mL Erlenmeyer flask and stirred using a magnetic stirrer. Then the alkoxide was added to the oil, and the flask was sealed to avoid contact with the atmosphere. The mixture was stirred for 40 minutes, then transferred to a separatory funnel and allowed to stand for 30 minutes to separate the biodiesel and glycerol. The separated biodiesel was washed 4 times with distilled water at room temperature, in order to remove traces of soap, byproducts, and reactants remaining in the aqueous (lower) phase. The wash water was drained into a separate vessel. The biodiesel was dried by adding 5 g sodium sulfate.

Determination of the physical and chemical characteristics of the biodiesel

The saponification number, density, acid number, carbon residue, free glycerol, oxidation stability, and viscosity of the biodiesel were determined in triplicate.

Saponification number. A 10 g sample was placed in a 250 mL round-bottomed flask, then 25 mL methyl ethyl ketone plus 25 mL of an alcoholic 0.5 mol/L KOH solution were added. The flask was connected to a reflux condenser and the system was heated for 30 minutes using a heating mantle. Then 3 drops of phenolphthalein were added to the flask, and the solution in the flask was titrated against a 0.5 mol/L hydrochloric acid solution until the pink color disappeared. The saponification number N_{sap} was calculated from the equation:

$$N_{sap} = DV_{KOH}/W$$

where D is the difference between the volume of a 0.5 N HCl solution (in mL) consumed in titration of the sample and the average volume of the solution consumed in two blank runs; V_{KOH} is the concentration of the potassium hydroxide solution, expressed in mg KOH/mL; W is the sample weight in grams.

Density. A pycnometer was dried and weighed. Then the pycnometer was filled with distilled water, making sure no air bubbles were left inside. The pycnometer was weighed after it was allowed to stand for 15 minutes to establish thermal equilibrium. We calculated the volume of the pycnometer V_p from the difference between the total weight and the weight of the empty pycnometer:

$$V_p = D_m/d$$

where D_m is the difference between the weight of the pycnometer filled with water and the weight of the empty pycnometer; d is the density of water.

The procedure described above was performed with a pycnometer filled with biodiesel.

Acid number. About 2 g of biodiesel were weighed out and placed in an Erlenmeyer flask, and then 25 mL of a 2:1 ether/alcohol mixture were added. The biodiesel sample was previously neutralized with a 0.1 mol/L sodium hydroxide solution. Two drops of phenolphthalein were added to the flask and the solution was titrated against

a 0.1 mol/L sodium hydroxide solution until the pink color disappeared. The acid number (N_{acid}) was calculated from the equation:

$$N_{acid} = 5.61 V_{NaOH} F / P$$

where V_{NaOH} is the volume of the sodium hydroxide solution consumed in the titration; F is the factor for the sodium hydroxide solution; P is the weight of the biodiesel sample in grams.

In order to determine the factor for the sodium hydroxide solution, 0.5105 g of a potassium phthalate primary standard was reacted with 25 mL of the sodium hydroxide solution. For this purpose, the standard was placed in a 250 mL Erlenmeyer flask and diluted with ~50 mL distilled water. Then 2 drops of phenolphthalein were added to the solution. The salt solution was titrated against a 0.1 mol/L sodium hydroxide solution until the color changed from colorless to pink. The correction factor for the sodium hydroxide solution was calculated from the equation:

$$F = V_{theor} / V_{spent}$$

where V_{theor}, V_{spent} are the theoretically required and the actually consumed volume of the sodium hydroxide solution.

Carbon residue. A porcelain crucible was held in an oven at 775°C for at least 1 hour. Then the oven was turned off and cooled down to room temperature. The crucible was placed in a desiccator for 1 hour and then weighed. About 50 g of the sample was added to the crucible, which was placed in the oven at 775°C. After carbonization was complete, the oven was turned off. The crucible was placed in the desiccator for 1 hour and then weighed. The residual carbon C of the sample was calculated from the equation:

$$C = (m_c - m_0) 100 / m_{sample}$$

where m_i is the initial weight of the empty crucible, m_f is the final weight of the crucible plus ash; m_{sample} is the weight of the sample in the crucible.

Free glycerol content. A 3 g biodiesel sample was placed in a 500 mL separatory funnel. 20 mL distilled water plus 0.5 mL sulfuric acid (dilution 1:4 v/v) were added to the funnel. The system was stirred and allowed to stand until it separated into two phases. The lower phase was drained off, placed in a 250 mL Erlenmeyer flask, and used to determine the free glycerol content in the sample. For this purpose, 50 mL of 5.5 g/L sodium periodate was allowed to stand at room temperature and pressure for 10 min. The sodium periodate, 4 g sodium bicarbonate, plus 1.5 g potassium iodide were added to the Erlenmeyer flask and then stirred. The solution obtained was titrated against a 0.1 mol/L sodium arsenite solution until the solution became clearer. Then 3 drops of starch solution were added to the flask and titration was continued until the solution became colorless. The free glycerol content FG in the sample was calculated from the equation:

$$FG = (VB - V_1) 0.1 T / m$$

where VB is the volume (mL) of the sodium arsenite solution consumed in titration of the blank ($VB = 26.2$ mL); V is the volume (mL) of the sodium arsenite solution consumed in titration of the sample; T is the titer of the sodium arsenite solution ($T = 2.22$); m is the weight (g) of the biodiesel sample.

Table 2

Indices	Pequi oil esters		ANP standard
	methyl	ethyl	
ASTM color, max	max 3.5	3.5	–
Density at 20°C, kg/m^3	866.3	851.5	875 – 900
Acid number, mg NaOH/g	0.7907	0.7850	max 0.8
Saponification number, mg KOH/g	58.52	51.26	–
Viscosity, mPa•sec	5	5	–
Free glycerol, wt.%	0.0438	0.651	max 0.02
Carbon residue, wt.%	0.014	0.006	max 0.05
Oxidation stability, h	5.85	–	min 6

Oxidation stability was determined on a Metrohm 743 Rancimat, in which the sample was rapidly oxidized by thermal decomposition. The decomposition products are blown by air into the measuring cell filled with distilled water. The induction period for oxidation is determined automatically from the change in the conductivity of water in the cell.

Viscosity. An ~40 mL biodiesel sample was placed in a 100 mL viscometer cylinder. A rotating rod was lowered into the cylinder so that the sample volume in the cylinder reached the 50 mL mark. The sample did not contain solid particles which could affect the viscosity measurement. The rod was placed exactly at the center of the cylinder so that it did not touch the sides of the cylinder. The digital viscometer displayed the viscosity value in cP.

The transesterification process is affected by the type of catalyst (acid or base), the alcohol:oil mole ratio, the temperature, the purity of the reactants (mainly the water and free fatty acid content in the reactants) [16]. In this work, we used base catalysis because according to some data [7, 13], this results in higher yield and selectivity and a shorter reaction time. Furthermore, using a base as the catalyst lets us avoid corrosion of the engine parts, which occurs when traces of acid are present in biodiesel [5].

Usually alkaline transesterification of vegetable oils is carried out at temperatures close to the boiling point of alcohol. However, some researchers say [7] that carrying out the reaction at a temperature above 60°C should be avoided, since high temperature accelerates the saponification reaction of glycerides by base before ester formation occurs. In order for biodiesel to be competitive on the fuel market, we need to reduce its cost. In [14], transesterification was carried out satisfactorily at room temperature. With this goal, anhydrous alcohols were used in excess, since the transesterification reaction is reversible [9, 13, 16].

The physical and chemical characteristics of the methyl and ethyl esters are given in Table 2, in which we also give the requirements for the Brazilian ANP standards. Direct use of triglycerides as fuel is not recommended, mainly due to their high viscosity. Methyl and ethyl fatty acid esters have lower molecular weight and viscosity than triglycerides, which lets us use biodiesel in existing engines with no modification [4].

The residual carbon of the fuel, characterizing its tendency toward carbon formation [6], is an important characteristic since there is a correlation between carbon residue and formation of deposits in the injector [10]. The carbon residue of methyl and ethyl esters from pequi oil are lower than the value required in the ANP standards. However, the studied biodiesel does not meet the ANP requirements (part 7) for free glycerol content and oxidation stability. The high free glycerol content may be due to problems with storage of the fuel, and therefore careful washing of the fuel to remove glycerol is important.
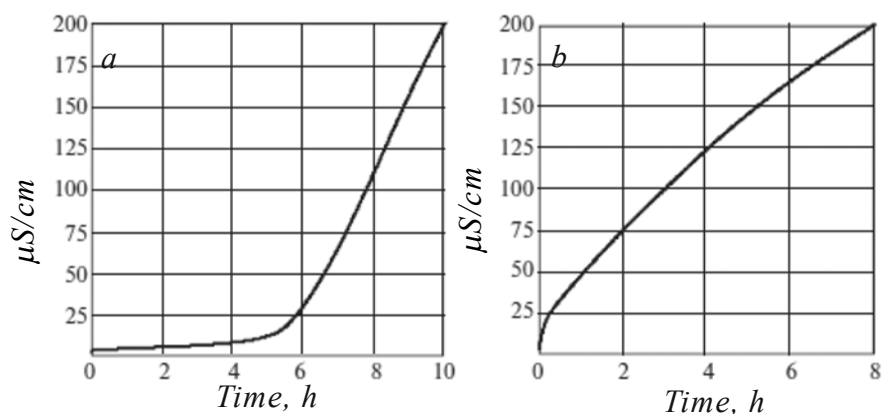
Fig. 1 Oxidation stability of pequi oil esters: a) methyl esters; b) ethyl esters.

Fig. 1 shows the oxidation stability of methyl and ethyl esters from pequi oil. The oxidation stability of the biodiesel is determined by the quality of the oil used to produce it. In this work, the pequi oil did not undergo any treatment and so the oxidation stability of the product was unsatisfactory. Thus in order to obtain better quality biodiesel, preliminary preparation of the oil is needed.

Based on the data presented, we can conclude that pequi is an alternative resource for obtaining biodiesel, since its fruits are distinguished by high (about 60%) oil content, and most of the characteristics of the biodiesel obtained meet the ANP requirements. Our work indicates that it is feasible to obtain pequi oil on industrial scales, which would enable development of regions favorable for its cultivation.

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