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Butia Yatay coconut oil: Process development for biodiesel production and kinetics of esterification with ethanol

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ABSTRACT

The aim of this work is to study biodiesel production using *Butia Yatay* coconut oil. This oil has acid values between 109 and 140 mg KOH/g, and phosphorus content in the order of 600 ppm. A three-step degumming pre-treatment of the raw material was adjusted in order to decrease the phosphorus content to approximately 200 ppm. Afterwards, a two-step esterification followed by transesterification was required in order to obtain a high-quality product.

The esterification kinetics was studied including the simultaneous reactions that take place during the esterification of free fatty acids: autocatalysis, triacylglycerides hydrolysis, transesterification, and the reaction of sulphuric acid with the alcohol, being the most important ones. The kinetic parameters for the esterification and autocatalysis reactions were also obtained, being different compared to sunflower oil, due to the presence of short chain fatty acids. The kinetic constant for the esterification reaction rapidly decreases as a function of time, due to the consumption of the catalyst by the alkyl-sulphate formation reaction.

1. Introduction

Feedstocks unsuitable for human consumption show a great potential as alternative raw materials to produce biodiesel at low cost. However, most of them contain high levels of free fatty acids (FFA). This fact turn the base-catalyzed transesterification of triacylglycerides to esters unfeasible, due to an intensive soap formation and low process yield. The conversion of triacylglycerides (TG) to methyl or ethyl ester occurs in three consecutive steps forming. diacylglycerides (DG) and monoacylglycerides (MG) as intermediate products in this reaction sequence. The free fatty acids present in the feedstock are neutralized by the catalyst (sodium hydroxide or sodium methoxide), forming soaps (e.g. sodium oleate).

An acid value lower than 4 mg KOH/g is necessary in order to carry out the transesterification step with reasonable good yields. Nevertheless, it has been found that using a step of acid-catalyzed esterification of the FFAs before the conventional transesterification makes it possible to use high-acidity raw materials to produce biodiesel.

The esterification step has the objective of reducing the concentration of free fatty acids, forming alkyesters and water. This reaction is catalyzed by acids, and depending upon the initial acidity, it may be carried out in more than one step with an intermediate phase-separation operation. With this procedure, the water formed during the reaction is separated in an hydroalcoholic phase, which also contains the catalyst. After this operation, additional alcohol and catalyst are added to the system. The reaction is reversible; therefore, it requires an excess of ethyl (or methyl) alcohol to displace the equilibrium toward the products.

Studies regarding esterification were carried out using synthetic mixtures or feedstocks with high levels of FFA. Only few of them have been made using vegetable oil, animal fat or waste grease with acidity higher than 80 mg KOH/g. Canakci and Van Gerpen [1] developed a technique to convert yellow grease (25 mg KOH/g) and brown grease (66 mg KOH/g) into biodiesel. Ramadhas et al. [2] utilized rubber seed oil (34 mg KOH/g) and Ghadge et al. [3] worked with mahua oil (38 mg KOH/g). Wang et al. [4,5] compared different processes using waste cooking oil (76 mg KOH/g). Berrios et al. [6] carried out a kinetic study of esterification of FFA by adding fatty acid to sunflower oil (7 mg KOH mg/g). Naik et al. [7] studied the biodiesel production process using Karanja oil (40 mg KOH/g) as raw material. However, none of these studies considered the secondary reactions that occur in the system. In a recent publication, Pisarello et al. [8] studied the esterification of a sunflower oil acidified in the laboratory (36 mg KOH/g), including secondary reactions in the analysis, such as esters hydrolysis, saponification of glycerides and methyl or ethyl esters, and

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sulphuric acid alkylation with the alcohol. In the present study, in addition to these reactions, autocatalysis is included. Other difficulties are the very high acidity and phosphorus content of coconut oil, both properties having a major influence in the process design.

This reaction system presents another important complication in order to obtain kinetic parameters, since in most reaction conditions two phases are present. For example, as the water concentration increases, phase separation is more likely to occur [8]. Because of this, kinetic experiments have to be carried out selecting a high enough concentration of alcohol, in order to be sure that one phase is present during the esterification, mainly at the beginning of the reaction since during this time most of the conversion takes place. On the other hand, it is desirable that phase separation occurs by the end of the reaction, because it allows separating the catalyst and most of the water from the oil-ester rich phase.

Butia Yatay is a palm that corresponds to the Arecaceae family, originated in South America, particularly in the south of Brazil, Paraguay, Uruguay and the northeast of Argentina. Its fruit contains high levels of oil, which in fact has high acidity and phospholipid levels.

Ethyl esters present a higher cetane number and calorific value, and have better cold properties (cloud point, pour point, and cold filter plugging point) than methyl esters [9], and also has lower tailpipe emissions [10,11]. There are few papers dealing with esterification and transesterification, in which ethanol is included in order to compare the behaviour with methanol [12]. However, due to its advantages, the use of ethanol has recently received more attention [8,9,13–20].

The aim of this work is to develop a process to obtain biodiesel from feedstocks with high levels of FFA and high initial phosphorus content. The study includes the kinetics and a detailed analysis of secondary reactions that occur during the esterification, such as the acid catalyzed transesterification, the contribution of the non-catalyzed esterification, esters hydrolysis, and the reaction between the alcohol and the catalyst, reaction that has a deep impact in the esterification rate. These issues have been normally neglected when analyzing the esterification reactions.

A technique is described to convert a coconut oil with initial acid value of 109–140 mg KOH/g into a high quality biodiesel. The oil obtained from *Butia Yatay* palm was used as raw material.

Most of the esterification experiments in this study were carried out using ethyl alcohol and sulphuric acid as catalyst, although methanol was also used in selected experiments. The transesterification reaction with methanol is already well known, while the use of ethanol and further purification of biodiesel has been recently addressed [18] and, consequently, the emphasis of this study was put on the esterification stages of the process.

2. Materials and methods

In order to obtain biodiesel from the *Butia Yatay* coconut oil, the following steps have been carried out:

- Degumming: to reduce the level of phospholipids.
- Esterification: to decrease the level of free fatty acids.
- Transesterification: to convert triacylglycerides to ethyl esters (or methyl esters).
- Purification: to eliminate soaps, alcohol, catalyst and free glycerine from the biodiesel-rich phase.

2.1. Materials

The oil from Butia Yatay coconuts was provided by an oil manufacturer in Paraguay. Sunflower oil (Cocinero®, Molinos Río de la Plata) previously analyzed [18] is included in order to compare the free fatty acid profiles. The free fatty acid profiles of these oils are presented in Table 1, and other properties of the coconut oil (acidity, phosphorus content, unsaponifiable matter, saponification index, density, water content, and viscosity) are shown in Table 2. It can be observed that the phosphorus and the acidity were very high, compared to other oils typically used for biodiesel production.

The alcohols used for the esterification were methanol (Cicarelli PA) and ethanol (Cicarelli PA). The water content of these alcohols, determined by a Karl-Fischer analysis was 315 ppm for methanol, and 1150 ppm for ethanol. Sulphuric acid (Cicarelli PA) was used as catalyst in this reaction. In the transesterification, sodium methoxide in methanol (30 wt%) (Evonik-Degussa) was used as catalyst.

2.2. Pre-treatment: degumming

Several tests were carried out in order to achieve the best degumming process for the *Butia Yatay* coconut oil.

Due to the very high phosphorous content in this oil, experiments were carried out mixing the coconut oil with different proportions of hydrochloric acid (5 wt%), up to 25 vol%. The mixture was stirred at 50 °C and allowed to settle at room temperature. A white phase at the bottom and solids adhered to the walls were observed. This made it difficult to distinguish the interphase. In other test, the oil was mixed with 25 vol% of phosphoric acid (4.5 wt%). In this case, it was also difficult to observe the interphase due to the formation of an emulsion.

The most appropriate degumming process consisted in heating the oil at 55 °C, adding 15 vol% of water containing 10 wt% sodium chloride and stirring for 30 min. Sodium chloride was necessary to avoid emulsion formation due to the large amount of phospholipids contained in the oil. In order to separate phases, the mixture was transferred to a separating funnel. The upper phase was then heated up to 55 °C and 0.3% in volume of concentrated phosphoric acid was added. The mixture was stirred for one hour and then the gums were separated by centrifugation. After this, 15 vol% of water was added to the oil and stirred for 30 min at 50 °C. Finally, drying was performed at 50 °C under vaccum or nitrogen flow. These pretreatment steps led to a significant reduction of the gums in order to avoid difficulties during the biodiesel production process. This degumming procedure was used in all the experiments shown throughout this work.

2.3. Acid-catalyzed reactions: influence of process variables and analysis of secondary reactions

2.3.1. Esterification

The esterification was conducted in one and in two steps, using in all cases sulphuric acid as catalyst. A one-step strategy was

Table 1
Typical distribution of free fatty acids in refined sunflower oil and coconut oils.

Fatty acids	Coconut oil (A = 130)* (wt%)	Sunflower oil (A = 0.01)* (wt%)
8:0	0.32	0.00
10:0	0.34	0.00
12:0	2.95	0.00
14:0	0.86	0.09
16:0	17.83	5.98
16:1	2.55	0.17
18:0	3.45	3.15
18:1	64.22	28.49
18:2	2.97	58.13
18:3	0.46	0.19
20:0	0.18	0.26
20:1	0.28	0.30
22:0	0.06	1.24
22:1	0.20	0.00

* Acid value expressed as mg of KOH per g of sample.