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

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A B S T R A C T

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.

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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

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 pre-treatment 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.

Table 2
Properties of the coconut oil, biodiesel-rich phase after esterification and biodiesel (final product), using methanol both in the esterification and transesterification steps (sample MME), and ethanol in the esterification and methanol in the transesterification (sample EME).

Sample	Phosphorus content (ppm)	Unsaponified material (%)	Saponification index (mgKOH g^{-1})	Relative density at 40 °C (g L^{-1})	Acid value (mgKOH g^{-1})	Water content (ppm)	Kinematic viscosity (mm^2 s^{-1}) at 40 °C
Crude coconut oil	617.5	1.60	207.3	914.8	112.70	9400	51.7
Degummed coconut oil	229.5	1.30	208.2	917.9	128.00	400	33.6
FAME/oil[a]	47.2	1.20	221.0	823.5	5.00	14,600	8.5
Biodiesel MME	4.2	0.65	221.2	868.6	0.50	300	5.1
Biodiesel EME	3.5	0.80	214.0	862.4	0.45	354	5.3

[a] Bottom phase after first step of esterification (biodiesel-oil mixture): Reaction conditions: FFA:methanol ratio of 5.2, 0.75 vol% of sulphuric acid, 65 °C, 1.5 h.

mainly used to determine kinetic parameters and to compare the results with the two-step esterification.

2.3.1.1. One-step esterification. The reaction was conducted in a 250 ml glass batch reactor, placed in a thermostatic water bath, and using magnetic stirring at 600 rpm. The mixture was stirred at the same rate in all runs.

The degummed coconut oil was heated up to the reaction temperature, and then the alcohol containing the sulphuric acid was added. The moment at which the alcohol–sulphuric acid mixture was added to the reactor was taken as the starting point of the reaction (time zero). Since the alcohol reacts with the sulphuric acid, this mixture was prepared right before adding it to the reaction vessel. The amount of catalyst was calculated as a percentage relative to the total liquid volume loaded into the reactor, and was varied between 0.3 and 0.75 vol%.

The molar ratio FFA:alcohol (FFA:OH) is an important parameter, since it determines if a single phase or a two-phase reacting system is obtained. As this ratio decreases, the system shifts from a two-phase to a single-phase reacting media. In the kinetic studies performed in this work, and based on many preliminary experiments, this ratio was selected in order to have only one liquid phase during the reaction. This permitted to obtain homogeneous samples, and to study the system in chemically controlled regime. Both ethanol (99.5 wt%) and methanol (99.5 wt%) were used in the esterification. The FFA:ethanol molar ratios used were 1:7 and 1:12. For comparison purposes, methanol was used with a molar ratio FFA:methanol of 1:7.

In order to follow the free fatty acids concentration during the esterification stage, the acidity was measured as a function of time. Small aliquots (2 ml) were taken from the reaction mixture at different reaction times. Each sample was washed immediately in a test tube with water at 4 °C in order to separate the alcohol and the catalyst and to stop the reaction. To improve the separation of phases, each sample was centrifuged. The lower layer (organic phase) consisted of fatty acids, triacylglycerides and esters, and the upper phase (aqueous phase) contained mainly alcohol, water, and sulphuric acid. To determine the acidity, a sample of the organic phase was titrated according to UNE-EN 14104. The acidity is reported in this work as milligrams of KOH needed to neutralize one gram of sample (mg KOH/g).

The water affects both the kinetics and the equilibrium conversion. The effect of the initial water content in the system was studied changing the composition between 4 and 19 mg/g.

Total ester content, and total glycerine analyses were carried out according to EN 14103 and EN 14105 standards respectively, and the phosphorus and water contents by the EN14107 and ASTM D-4948 standards, respectively. Density and viscosity were determined followed the ISO 3675 and ASTM D-445 standards, respectively.

The reproducibility of the reacting system was studied carrying out the same experiment three times.

2.3.1.2. Two-step esterification. The esterification was carried out also using a two-step reaction strategy in order to displace the equilibrium by separating one of the products after the first reaction. This product is the water that was concentrated in the polar phase, which contains mainly alcohol, catalyst, and water [8]. In order to compare with the experiment carried out in one-step, the same total quantity of alcohol and catalyst concentration was used. In the case of the two-step reaction, the amount of alcohol loaded in the first step was 60 vol% (100 * volume of ethanol/volume of oil), which corresponds to a FFA:ethanol ratio of 1:5.2. In the second step 40 vol% of alcohol was used (FFA:ethanol = 1:3.4). The sulphuric acid concentration was 0.75 vol% in both stages. In the case of the experiment carried out in one reaction step, the amounts of alcohol and catalyst loaded were 100 vol% (FFA:ethanol = 1:8.6) and 0.75 vol%, respectively.

2.3.2. Reaction in the absence of added catalyst

Even though there is no direct evidence regarding the catalytic effect on the esterification of the compounds contained in the coconut oil, it is reasonable to assume that the acidity generated by the free fatty acids dissociation has a catalytic effect. Accordingly, throughout this work, the experiments in which no catalyst (sulphuric acid) was added will be referred to as auto-catalyzed.

The reaction was carried out at 70 °C, using ethanol as alcohol with a FFA:alcohol molar ratio of 1:12, and measuring the acidity as a function of time.

2.3.3. Acid catalyzed transesterification

During the esterification of free fatty acids catalyzed by sulphuric acid, the conversion of triacylglycerides was followed analyzing the ester-rich phase by gas chromatography in order to determine the ester, mono-, di-, and triacylglycerides content, as described in the EN 14103 and EN 14105.

2.3.4. Sulphuric acid alkylation

The sulphuric acid concentration was determined in the reaction media by titrating the phase with NaOH before and after washing the phase with water. In this way, the total acidity (corresponding to the FFA and sulphuric acid) and the acidity that corresponds to the FFA were obtained, correspondingly. Additional details of the experiments are presented in Section 3.4.4.

The sulphuric acid alkylation that occurs when the acid is mixed with an alcohol was followed by titrating the alcohol–sulphuric acid mixture with NaOH.

2.3.5. Summary of esterification experiments

Many different experiments were carried out in this study, particularly in the esterification stage. These experiments are summarized in Table 3, and a number is assigned to each of them to facilitate the discussion. Note that the experimental design was carried out with different purposes. In some of the experiments, the conditions were chosen with the objective of developing the process, and in other cases, with the objective of determining kinetic constants.

2.4. Transesterification and biodiesel purification

Once the acidity was reduced to less than 4 mg KOH/g, the organic phase was loaded into the reactor to continue the process with an alkaline-catalyzed transesterification. The amount of alcohol added in the transesterification step was calculated taken into account that a certain amount of alcohol remained in this phase after the esterification. The catalyst used was sodium methoxide 30 wt% in methanol (Evonik-Degussa). The amount of catalyst loaded in the reactor was calculated as a percentage of the oil (typically 0.5 g $NaCH_3O$/100 g oil), being it necessary to add an additional amount in order to neutralize the free fatty acids present in the mixture. The reaction was carried out during 2.5 h, using methanol at 60 °C, in a 250 mL glass batch reactor, placed in a thermostatic water bath, and using magnetic stirring at 600 rpm. In this way, the final product contains in the order of 75–80% of ethyl esters formed during the esterification, and 20–25% of methyl esters formed during the transesterification.

The amount of triacylglycerides that entered the transesterification stage was well below 30 wt% due to the very high FFA content of the raw material. Because of this, and depending upon the type and concentration of the alcohol used in this reaction, phase separation at the end of the reaction might not occur since the amount of glycerine formed due to the transesterification of the triacylglycerides was not enough to form a new phase. Consequently, the purification step has to be re-designed for this situation. In methanol-based processes, the purification steps typically include

consecutive liquid extraction steps, followed by a drying operation. Normally, the first washing step consists in mixing an aqueous solution of HCl 5 wt% with the biodiesel phase followed by a second step with fresh water. Nevertheless, due to the large percentage of short-chain esters contained in a coconut oil-based biodiesel, washing with acid solution is complicated due to the tendency of these compounds to form emulsions. To overcome this difficulty, we used a first washing with non-acidified water, using 8 vol% water referred to the biodiesel phase, at 60 °C. The water phase contained a large amount of soaps after this step. In previous studies [18], it was found that this procedure was the most effective one in order to start the biodiesel washing in cases in which the soap concentration in the crude biodiesel was high, e.g. when using high acidity raw materials or when using ethanol in the transesterification. Then, a second step with an aqueous solution of HCl 5 wt% was performed. The final washing was carried out again with non-acidified water. The volume of aqueous phase for the last two steps was 30 vol% relative to the biodiesel phase. All extraction stages were carried out with gentle agitation at 60 °C, during 15 min. Afterwards, the biodiesel was dried by stripping with nitrogen at 100 °C.

3. Results and discussion

3.1. Coconut oil characterization

Table 1 shows the fatty acid distribution of *Butia Yatay* coconut oil after the degumming treatment. There is a significant proportion of short chain fatty acids, such as C8, C10, C12, and C14, compared to other oils typically used for biodiesel production such as sunflower, rapeseed, and soybean oils. These short-chain acids, which were then converted into esters, introduced complications during the production process due to their tendency to form stable emulsions [21,22]. For comparison purposes, Table 1 also includes the fatty acids profile of sunflower oil.

The amount of phosphorus and other properties of the crude oil are presented in Table 2. It can be observed that the phosphorus content was very high, above 600 ppm, while in other cases such as crude soybean oil, a typical value is around 200 ppm. The saponification index was higher than 200, which was an indication of the existence of short chain fatty acids. As this index increased, the mean molecular weight of the fatty acids decreased. For example, sunflower oil, which contains C16 (5.6 wt%), C18 (94 wt%), and C20 (0.4 wt%) fatty acids, has a saponification index of 180 and does not contain fatty acids with a carbon chain shorter than 16 carbon atoms.

3.2. Oil degumming

The use of non-degummed coconut oil in the esterification led to an intensive formation of precipitates, complicating the biodiesel production process. During both acid and based-catalyzed steps, precipitation of gums occurred. These compounds also appeared as an intermediate phase material accumulated between the ester and the aqueous phases during the washing step. For these reasons, a degumming step was necessary as an oil pretreatment, following the procedure described in Section 2.1.

Properties of the degummed oil are shown in Table 2. It can be seen that the phosphorus was efficiently removed from the crude oil, decreasing its content from more than 600 ppm to 230 ppm. The acidity of the crude and the degummed coconut oil were 113 and 128 mg KOH/g, respectively. This increase is due to the oil treatment in water and in phosphoric acid that leads to glycerides hydrolysis, thus forming FFA.

Table 3
Summary of esterification experiments.

Exp.	Alcohol	Alc:FFA	SO$_4$H$_2$ conc. (vol%)	Temp. (°C)	Added water conc. (mg/g)
One-step esterification					
1	Ethanol	7	0.3	70	4.07
2			0.6	70	
3	Ethanol	7	0.3	30	4.07
4				50	
5				70	
6	Ethanol	12	0.3	70	4.03
7					5.34
8					19.47
9	Ethanol	7	0.3	65	4.07
10	Methanol				
11	Ethanol	8.6	0.75	70	0.00
Two-step esterification					
12	Ethanol	5.2	0.75	70	0.00
13		3.4	0.75	70	0.00
14	Methanol	5.2	0.75	65	0.00
15		3.4	0.75	65	0.00
Auto-catalyzed					
16	Ethanol	12	0.0	70	0.00
17	Ethanol	12	0.0	70	0.08–0.4 M
Sulphuric acid alkylation					
18	Methanol	7	0.3	60	0.00
19	Ethanol	–	1.0	70	0.00

3.3. Esterification

The esterification was carried out using the degummed oil, which had an acidity of 128 mg KOH/g. The experiments carried out to determine the reproducibility of the esterification experiments, showed that the acidity as a function of time did not differ in more than 15% at any time during the run.

3.3.1. Effect of catalyst concentration

Fig. 1A shows the acidity evolution as a function of reaction time, at two different concentrations of sulphuric acid: 0.3 vol% and 0.6 vol%, referred to the total volume of reactants (oil and ethanol). In both cases, the reaction was performed at 70 °C, FFA:Alcohol molar ratio of 1:7, and the same amount of initial water (4.07 mg/g oil) (Experiments 1 and 2, Table 3). Sulphuric acid has been used in the esterification of raw materials containing significant levels of free-fatty acids [23–26].

It can be observed that as catalyst concentration increased, the acidity decreased more rapidly, reaching a lower acidity level at a given reaction time. Nevertheless, the reaction progressed rapidly during the first minutes in both cases. The final value was the same regardless the catalyst concentration, indicating that the system reached the equilibrium stage.

Results shown in Fig. 1A indicated that when 0.6 vol% of catalyst was used, a reaction time of 50 min was enough to reach the final acidity. Nevertheless, using a lower amount of catalyst it is possible to obtain the same final acidity at a longer reaction time. With 0.6 vol% of sulphuric acid, the final acidity was reached in 60 min, and with 0.3 vol% it was reached at 120 min approximately.

3.3.2. Effect of temperature

According to the Arrhenius equation, a temperature increase favours the reaction rate. However, in the case of non-pressurized systems involving volatile reactants, the temperature effect is not straightforward due to the decrease of the concentration in the liquid phase at higher temperatures.

Fig. 1B shows the results obtained with ethanol at 30 °C, 50 °C, and 70 °C. In all cases, the reaction was carried out using 0.3 vol% of sulphuric acid, FFA:Ethanol molar ratio of 1:7, and the same amount of initial water (Experiments 3, 4, and 5, Table 3).

It can be observed that when using ethanol during the esterification at atmospheric pressure, 70 °C was the best temperature regarding the reaction rate and the final acidity that can be obtained. However, when the temperature was above 70 °C, the concentration of ethanol in the liquid phase dropped since the reactor was at atmospheric pressure (at reflux), and this led to a lower overall reaction rate (result not shown). If a pressurized reactor is used, then it can be expected that the observed reaction rate would be higher at temperatures higher than 70 °C.

3.3.3. Effect of initial water concentration

Water is one of the products of the esterification and, therefore, its initial content in the reaction mixture negatively affects both chemical equilibrium and reaction rate because at higher water concentration the rate of the reverse reaction increases.

Fig. 2A shows activity results obtained in experiments with different initial water content. All runs were carried out under the same conditions: 70 °C, with ethanol 99.5%, and 0.3 vol% of sulphuric acid (Experiments 6, 7 and 8, Table 3). Comparing the runs carried out using a FFA:OH molar ratio of 1:12, it can be observed that the reaction rate decreased as the initial water content increased (note for example, the differences in the slope of the different curves at times of reaction near zero). Moreover, the final acidity, which corresponds to the equilibrium value, was higher as the initial water content increased. In the experiment carried out with 19.47 mg water/g, the final acidity was 13.8 mg KOH/g, while for 5.34 mg water/g it was 8.20 mg KOH/g. The value of 19.47 mg water/g is equivalent to half the theoretical amount of water, which would be generated if complete esterification of the fatty acids were assumed. These results show the importance of controlling the water content in the reactants.

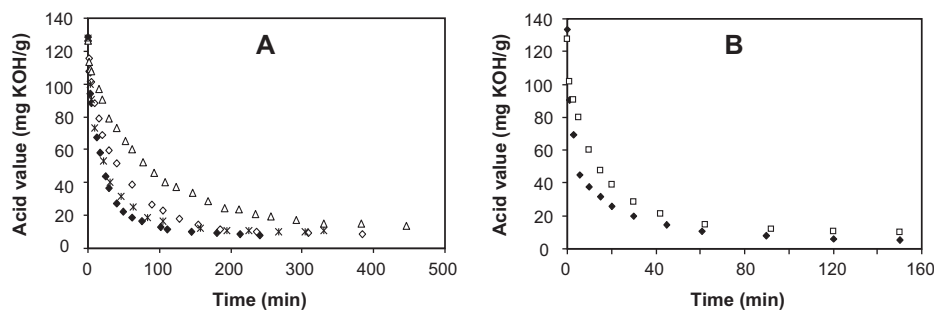#### 3.3.4. Effect of ethanol concentration

Fig. 2A also shows results of two experiments obtained with different FFA:OH molar ratio (1:12 and 1:7, Experiments 5 and 6), the other reaction conditions being the same. As expected, the reaction rate was higher for the experiment in which a molar ratio 1:12 was used, being the final acidity 7.9%, lower than in the case of using a molar ratio of 1:7, that resulted to be 9.9% (see Fig. 2A). It has to be pointed out that the alcohol amount should not be increased up to very high values because after a certain percentage no phase separation is observed at the end of the reaction. If this occurs, a different design for the purification process must be considered because it will be necessary to remove the water and the catalyst (sulphuric acid) before feeding the organic phase to the basic-catalyzed transesterification step. This can be performed by adding water at the end of the reaction in order to form a hydro-alcoholic phase. In the case of the coconut oil used in this study (128 mg KOH/g, 4 mg water/g), the maximum ethanol amount loaded to the reactor in order to adjust the production process was 60 vol%; otherwise, no decantation occurred at the end of the reaction.

3.3.5. Effect of the alcohol

Fig. 2B compares the evolution of the acidity when using methanol and ethanol as reagents. It can be observed that when
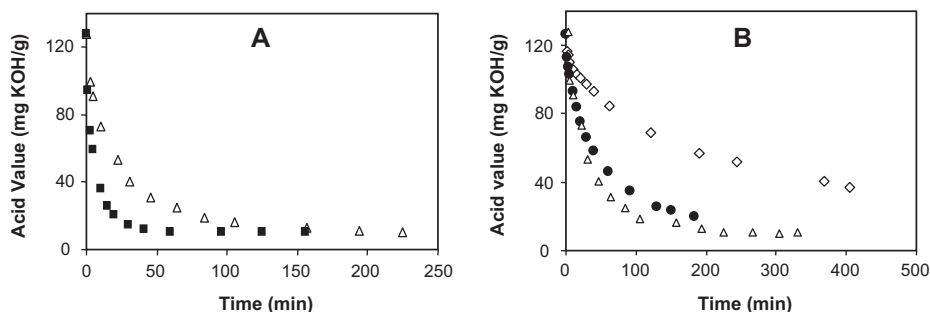
Fig. 1. Evolution of acid value during the esterification. *Reaction conditions*: Coconut oil (128 mg KOH/g), ethanol 99.5%, molar ratio FFA:Ethanol = 1:7, initial water content: 4.07 mg/g oil; (A) Effect of catalyst concentration. 70 °C, (△) 0.3% H₂SO₄, (■) 0.6% H₂SO₄. (B) Effect of the reaction temperature. 0.3% of sulphuric acid, (◇) 30 °C, (●) 50 °C, (△) 70 °C.

Fig. 2. Evolution of acid value during the esterification. *Reaction conditions*: Coconut oil (128 mg KOH/g), 0.3% of sulphuric acid. (A) Effect of initial water concentration (expressed as mg of water per g of reactants, oil plus alcohol), ethanol 99.5% , 70 °C; (♦) 4.03 mg water/g (FFA:OH 1:12), (◇) 5.34 mg water/g (FFA:OH 1:12), (△) 19.47 mg water/g (FFA:OH 1:12), (×) 4.07 mg water/g (FFA:OH 1:7). (B) Effect of the type of alcohol. 65 °C, FFA:OH molar ratio of 1:7, and initial water content of 4.07 mg/g oil. (□) ethanol, (♦) methanol.

methanol was used, the acidity decreased faster and the final value was lower than in the case of ethanol. Both runs were performed at 65 °C, a FFA:OH molar ratio of 1:7, and 0.3 vol% sulphuric acid (Experiments 9 and 10). The final acidity was 5.3 mg KOH/g with methanol and 10.2 mg KOH/g with ethanol.
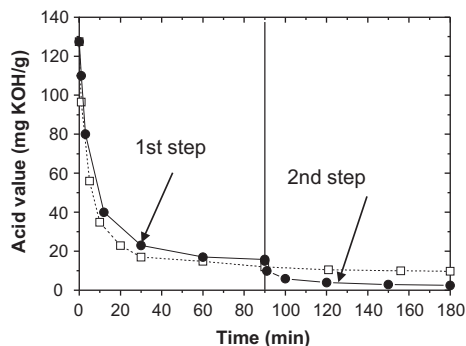
Note that none of the experiments in this study achieved the goal of reducing the acidity to 2 mg KOH/g in a *single reaction step*, in order to feed this mixture to the transesterification reactor. These results indicated the necessity of performing additional esterification steps in order to reach the target value.

3.3.6. Effect of reaction strategy

Fig. 3 shows the evolution of acidity as a function of time obtained during esterification in one-step with 100 vol% of ethanol (FFA:OH = 8.6) and in two consecutive steps using 60 vol% (FFA:OH = 5.2) and 40 vol% (FFA:OH = 3.4) of ethanol in each one (Experiments 11, 12 and 13).

The final acidity obtained in one-step was 14 mg KOH/g. This value was too high to perform the transesterification.

In the case of a two-step esterification strategy, the final acidity obtained was 15 mg KOH/g after the first step and 1.8 mg KOH/g at the end of the second step. Between the first and second steps, the reacting mixture was placed in a separation funnel, and the hydro-alcoholic phase was separated. In this way, most of the water was purged from the system. It is very important to emphasize that when using the same total amount of alcohol the final acidity was largely improved applying the two-step esterification procedure. Two effects explain this improved performance when doing the esterification in two steps. First, most of the water is formed

in the first part of the reaction. Fig. 3 shows that the acidity drops from 128 mg KOH/g to approximately 15 mg KOH/g in 50 min. This means that most of the water is formed at the beginning of the reaction. If the water is maintained in the reacting system, it limits the conversion since this reaction is equilibrium limited. By removing the water, it is possible to increase the conversion by shifting the equilibrium towards the products. On the other hand, the lower the amount of water, the lower the possibility of forming two phases [8], and therefore, the alcohol and the catalyst are preferentially concentrated in the FFA-rich phase, thus increasing the reaction rate. It can be observed that at the beginning of the second step (Fig. 3), there is a major acceleration of the esterification rate.
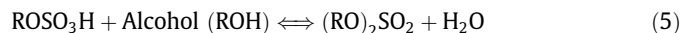
Another important result is that during the esterification, the phosphorus content is also significantly reduced, due to the phospholipids hydrolysis. Table 2 shows that during the first step of the esterification, the phosphorus decreased from 229.5 to 47.2 ppm.

3.4. Analysis of secondary reactions

As described in the introduction section, the kinetics of the fatty acid esterification has been studied by several authors considering only the reversible reaction [6,16,27,28]. However, recent publications have demonstrated that other reactions that take place in this system have a non-negligible effect on the product distribution. For example, the triacylglycerides transesterification can take place by an acid mechanism forming methyl or ethyl esters in significant amounts [8]. In addition, according to Pisarello et al. [8], the esters hydrolysis leads to the formation of FFA, and this reaction path is the cause of the appearance of a minimum in the evolution of acidity as a function of time during the esterification. This has very important consequences regarding the process design, since after a given reaction time the acidity not only does not decrease but also starts increasing. On the other hand, another very important reaction is the esterification of sulphuric acid, which has been reported in homogenous esterification of FFA in the publication of Pisarello et al. [8]. This reaction consumes a very high fraction of the catalyst forming mono and dialkyl sulphates. In addition, these reactions form water, thus limiting the equilibrium conversion. Another reaction pathway that has not been taken into account in previous studies regarding FFA esterification is the catalytic effect of the FFA.

Therefore, in addition to transesterification and esterification reactions catalyzed by acids, the following reactions take place during the acid-catalyzed esterification:

$$TG + H_2O \Longleftrightarrow DG + FFA \tag{1}$$

$$DG + H_2O \Longleftrightarrow MG + FFA \tag{2}$$

Fig. 3. Evolution of acid value in esterification performed in two consecutive steps and in only one-step. *Reaction conditions*: Coconut oil (128 mg KOH/g); alcohol: ethanol. (□) esterification in one step, 0.75 vol% sulphuric acid, FFA:OH = 1:8.6 (●) esterification in two steps 0.75 vol% sulphuric acid in each step. FFA:OH = 5.2 and 3.4 in the first and second step, respectively. Temperature: 70 °C.

$$MG + H_2O \Longleftrightarrow G + FFA \qquad (3)$$

$$SO_4H_2 + Alcohol\ (ROH) \Longleftrightarrow ROSO_3H + H_2O \qquad (4)$$

$$ROSO_3H + Alcohol\ (ROH) \Longleftrightarrow (RO)_2SO_2 + H_2O \qquad (5)$$

3.4.1. Auto-catalyzed esterification

An experiment was carried out without catalyst, using a FFA:Ethanol molar ratio 1:12 (Experiment 16). It was found that after 12 min of reaction, the acidity was reduced from an initial value of 128 mg KOH/g to 114 mg KOH/g, indicating that the reaction can proceed either by a non-catalytic pathway or due to a catalytic effect of the FFA (autocatalytic pathway). After 145 min of reaction without catalyst the reduction of the acidity was only 14.9%, i.e., the acidity decreased from 128 to 108.9 mg KOH/g. This level of conversion is much lower than the one produced in the presence of catalyst. In the latter case, for example after 12 min of reaction the acidity was reduced from 128 mg KOH/g to 65.7 mg KOH/g.

3.4.2. Acid-catalyzed transesterification

The transesterification of triacylglycerides can also proceed by an acid-catalyzed mechanism. Typically, this reaction has been considered to be significantly slower than the base-catalyzed reaction [29] and, additionally, it is inhibited by the presence of water generated as the esterification proceeds [1,30,31]. However, it was found that the percentage of diglycerides, monoglycerides and esters formed by acid-catalyzed transesterification has a significant contribution to the overall reaction rate [8].

In order to analyze the effect of the transesterification during the esterification when using coconut oil as raw material, the total esters content was measured after each acid-catalyzed step. The batch of oil used in this experiment had an initial acidity of 140.7 mg KOH/g. The first esterification step was carried out with a FFA/methanol ratio of 1:5.2, and the second one 1:3.4 (Experiments 14 and 15). Both steps contained 0.75 vol% of sulphuric acid and lasted 1.5 h at 65 °C. After the first step the amount of esters was 64.5%, the water concentration 1.46%, and the acid value 14 mg KOH/g. Before the second step, the sample was dried to reduce water content down to 0.16%. After the second esterification step, the sample contained 81.3% of esters and its acid value was 1.5 mg KOH/g. However, the theoretical amount of esters formed exclusively by esterification of the FFA was 71.9% (calculated taking into account that each mol of esterified FFA forms one mol of ester). Consequently, this difference between the amount of esters found at the end of the esterification (81.3%) and that formed from the esterification of FFA (71.9%) was due to the acid-catalyzed transesterification.

When a similar experiment was conducted using ethanol and a coconut oil with an initial acidity of 127.4 mg KOH/g (Experiments 12 and 13), the amount of esters after the first esterification step was 68.0% and after the second, it was 76.2%. The theoretical amount of esters formed exclusively by esterification of the FFA was 64.5%. Therefore, 15.3% of the total amount of esters has been formed by the transesterification catalyzed by the sulphuric acid. It can be concluded, that during the esterification of an oil containing high proportion of FFA, esters are formed both by the reaction between the FFA and the alcohol, and by the transesterification of triacylglycerides, both reactions being catalyzed by the sulphuric acid. According to the values found in this work, this second reaction has a non-negligible contribution to ester formation during the esterification stage.

3.4.3. Esters hydrolysis

At long reaction time during the esterification with ethanol, a rise in the acid value was observed, as shown in Table 4. Pisarello et al. [8] also observed this tendency during the esterification of sunflower oil with an acidity of 36 mg KOH/g. It was determined that this increase in acidity was due to the glycerides hydrolysis (reactions 1, 2 and 3). Therefore, during the processing of *Butia Yatay* oil, these reactions were also taking place during the esterification. On the other hand, it has to be pointed out that this effect was not very important with this raw material, since the increase in acidity was only 0.44 mg KOH/g in one hour (compare data taken at 267 and 330 min, Table 4).

3.4.4. Sulphuric acid alkylation

The reactions between sulphuric acid and alcohol to form mono- and dialkyl-sulphates (reactions 4 and 5) were also taken into account. Suwannakarn et al. [32] and López et al. [33] observed these reactions during a heterogeneous catalyzed reaction at 120 °C, and Liu et al. [31] studied the reaction of acetic acid and methanol using sulphuric acid as catalyst. Pisarello et al. [8] reported the consumption of sulphuric acid due to the alkylation with alcohol, during the esterification of the free fatty acids contained in sunflower oil. These reactions have a negative effect because they consume both methanol (or ethanol) and sulphuric acid and produce water, which affects the reaction rate and the equilibrium conversion of the FFA.

The content of sulphuric acid in the reaction medium at the beginning and after 1.5 h of reaction was measured. One of the experiments was conducted at 60 °C, with a FFA:methanol molar ratio of 7 and 0.3 vol% of sulphuric acid (Experiment 18). At the end of the reaction, the system was formed by two phases. The methanol-rich phase was titrated with sodium hydroxide. To determine if sulphuric acid was dissolved in the organic phase, this phase was titrated before and after being washed with water. No sulphuric acid was detected in this phase. The initial sulphuric acid concentration was 0.136 N and after 1.5 h, it was 0.0891 N. It can be seen that a significant proportion of the added acid was consumed during the esterification.

Similar results were obtained with ethanol. Table 5 shows the acidity evolution that occurs when 1 ml of concentrated sulphuric acid was mixed with 100 ml of ethanol at 70 °C (Experiment 19). The significant decrease of the sulphuric acid concentration after 1.5 h of reaction can be observed. In addition, an experiment with coconut oil, 100 vol% of ethanol (FFA:Ethanol = 1:8.6) and 0.75 vol% of sulphuric acid at 70 °C was performed (Experiment 11). The acidity due to the catalyst was measured as a function of reaction time. These results are also shown in Table 5. The catalyst consumption was also very important. As shown in Fig. 1A, the concentration of catalyst has an important impact on the kinetics of the system and, therefore, the sulphuric acid consumption (reactions 4 and 5) decreases the kinetic constant of the acid-catalyzed esterification as the reaction proceeds. Consequently, the kinetic parameters determination must consider this effect, since the kinetic constant for the esterification changes as a function of time,

Table 4
Acidity versus time. Reaction Conditions: Ethanol 99.5%, FFA:OH molar ratio of 1:7, 70 °C, 0.3 vol% of H_2SO_4, 4.07 mg initial water/g.

Time (min)	Acidity (mgKOH g^{-1})	Time (min)	Acidity (mgKOH g^{-1})
0	128.00	194	10.82
5	90.79	225	10.52
31	40.32	267	10.18
46	31.25	304	10.36
84	18.47	330	10.62
157	12.47	345	10.70

Table 5
Variation of H_2SO_4 concentration in ethanol and reaction medium at 70 °C.

Time (min)	H_2SO_4 content in ethanol (meq g solution^{-1})	H_2SO_4 content in reaction medium (meq g solution^{-1})
0	0.46	0.42
1	0.40	0.39
5	0.35	0.36
15	0.27	0.31
30	0.24	0.26
60	0.22	0.26
90	0.22	0.26

as shown in Section 3.5.1. The kinetic constant for the sulphuric acid alkylation reaction has been determined, using the data obtained in experiment 11. As discussed by Pisarello et al. [8], the monoalkyl sulphate formation is more important than the dialkyl sulphate formation. With this approximation, the direct and inverse kinetic constants obtained for reaction (4) (monoethyl sulphate formation) were 0.00418 lt mol^{-1} min^{-1} and 0.23 lt mol^{-1} min^{-1}, respectively. With these values, it is possible to estimate the real catalyst concentration during the esterification reaction.

3.5. Simplified kinetic modelling

3.5.1. Reversible esterification

As a first approximation, the system was modelled considering only the reversible esterification. The reaction rate expression for this situation is the following [6]:

$$r = -\frac{dC_F}{dt} = kC_F C_A - k'C_E C_W \quad (6)$$

where k and k' are the kinetic constants of the direct and reverse reactions respectively, and include the effects of catalyst concentration and autocatalysis. C_F, C_A, C_E and C_W are the concentrations of free fatty acids, alcohol, ester and water, respectively. Data shown in Figs. 1A and 2A were used to obtain these kinetic constants.

The parameters of Eq. (7) were determined using the experimental data adjusted by a non-linear regression using the Scientist® program. The value of k and k', and the equilibrium constant $K = k/k'$ were obtained.

Fig. 4 shows an example of results obtained in experiments carried out with coconut oil (acidity 128 mg KOH/g) and ethanol, 0.3 vol% sulphuric acid as catalyst and a FFA:Ethanol molar ratio of 1:12 (Experiment 8). The acidity obtained with the model is also included. It can be seen that this simple model fitted very well the experimental data. As shown in Fig. 4, it is possible to predict the
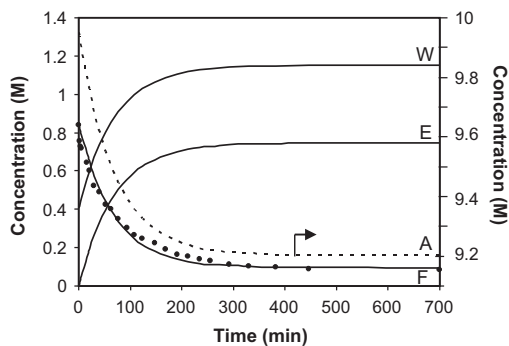
Fig. 4. Evolution of acid value during the esterification. *Reaction conditions:* Coconut oil (128 mg KOH/g), ethanol 99.5%, 70 °C, initial water content: 19.5 mg/g oil, and 0.3 vol% of sulphuric acid. F: FFA content, E: ester concentration, W: water content (left axis), A: ethanol concentration (right axis), calculated with the parameters obtained by the model in moles per litre; (•) experimental data, (lines) simulated data.

concentration of the other species as a function of time by mass balances. The concentrations of FFA, ester, water, and ethanol were calculated with the parameters obtained by the model, in moles per litre. The values of k, k' and K in this case are 0.001035 M^{-1} min^{-1}, 0.001335 M^{-1} min^{-1}, and 0.775, respectively. Nevertheless, these values of the kinetic constants represent average values, since as discussed in Section 3.4.4, the consumption of the catalyst during the alkylation of sulphuric acid led to a reduction of the kinetic constants as the reaction proceeded. In addition, the ester concentration is underestimated, due to the contribution of the acid-catalyzed transesterification. In order to obtain a more realistic value of kinetic constant k, it was also obtained from the initial reaction rate, using the data shown in Fig. 1. The kinetic constant obtained in this way corresponds to the sulphuric acid concentration initially loaded in the system. Table 6 shows these values. There is a large difference between the constant obtained by regression of the complete experiment ($k = 0.001035$ M^{-1} min^{-1}) and that obtained from the initial reaction rate ($k = 0.013$ M^{-1} min^{-1}, Table 6). To explain these results, the constant was also calculated using the integrated form of Eq. (7), obtaining k every time a sample was taken. The k obtained in this way represents the average value in the time interval used to calculate it. These values are presented in Fig. 5. This is a very interesting result, and agrees with the results and discussion presented in Section 3.4.4. The very important decrease of the apparent kinetic constant with reaction time is due to catalyst consumption, since this parameter has a direct effect on the kinetic constant. The k obtained using the experimental conversion measured at 1 min of reaction time was 0.011 M^{-1} min^{-1}, while the value obtained from the initial reaction rate shown in Table 6 was 0.013 M^{-1} min^{-1}, in perfect agreement.

Data shown in Table 6 at different reaction temperatures made it possible to estimate the activation energy. An Arrhenius plot gave a perfect straight line, resulting an activation energy for the direct reaction $E = 7.1$ kcal mol^{-1} K^{-1}.

3.5.2. Autocatalytic effect in the reversible esterification
3.5.2.1. Kinetic constant determination for the autocatalytic reaction.
The acid catalyzed esterification of acetic acid with methanol was studied by Liu et al. [31] considering that the kinetic constants include the effect of the acid catalyst and the autocatalysis. It was reported that auto-catalyzed esterification, i.e. when the reaction is carried out in the absence of added catalyst, followed third-order kinetics. This model was expressed as:

$$r_{AUTO} = -\frac{dC_F}{dt} = (k_{AUTO}C_F)C_F C_A - (k'_{AUTO}C_F)C_E C_W \quad (7)$$

where k_{AUTO} and k'_{AUTO} are the kinetic constants of the direct and reverse auto-catalyzed esterification, respectively.

As previously mentioned (Section 3.4.1), autocatalysis led to a small conversion of FFA. Experiments were carried out with different initial water concentrations, in the range from 0.08 to 0.4 M (Experiment 17). The kinetic constants obtained in these cases were very similar, suggesting that the effect of water in the autocatalytic conversion was small. The average value was 2.85×10^{-5} M^{-2} min^{-1}. Comparing with the values shown in Section 3.5.1 for the k obtained in the presence of sulphuric acid,

Table 6
Direct kinetic constants obtained from the initial reaction rate.

Temperature (°C)	SO$_4$H$_2$ Conc. (vol%)	k (M^{-1} min^{-1})
30	0.3	0.0033
50	0.3	0.0066
70	0.3	0.013
70	0.6	0.023
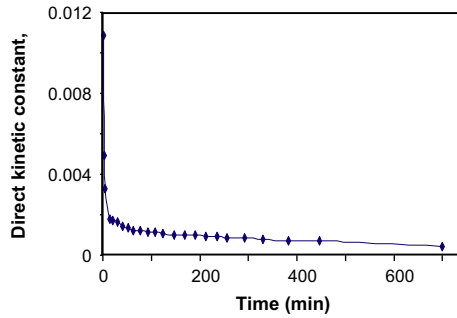
Fig. 5. Average direct kinetic constant for the esterification, calculated at different reaction times. *Reaction conditions:* see Fig. 4.

the autocatalytic kinetic constant was three orders of magnitude smaller.

3.5.2.2. Kinetic constant determination: autocatalysis and catalytic effects.

The model proposed by Liu et al. [31] includes the effect of autocatalysis in combination with the catalyzed esterification, as follows:

$$r = -\frac{dC_F}{dt} = (k_C C_C + k_{AUTO} C_F) C_F C_A - (k'_C C_C + k'_{AUTO} C_F) C_E C_W \quad (8)$$

where k_C, k'_C are the kinetic constants of the direct and reverse acid-catalyzed esterification. The values of k_{AUTO} and k'_{AUTO} were already obtained with the experiment carried out without catalyst.

In terms of FFA conversion and assuming that at the beginning of the reaction $k = k_C C_C + k_{AUTO} C_F \approx k_C C_C + k_{AUTO} C_F^0$ the expression for esterification kinetic at reaction times near zero is:

$$\frac{dx}{dt} = \left(k_C C_C + k_{AUTO} C_F^0\right) C_F^0 (1-x) \left(\frac{C_A^0}{C_F^0} - x\right)$$

$$= k C_F^0 (1-x) \left(\frac{C_A^0}{C_F^0} - x\right) \quad (9)$$

Integrating Eq. (10), the result is:

$$k\, C_F^0 t = \frac{1}{\left(\frac{C_A^0}{C_F^0} - 1\right)} \ln \left(\frac{\frac{C_A^0}{C_F^0} - x}{1-x}\right) - \frac{1}{\left(\frac{C_A^0}{C_F^0} - 1\right)} \ln \left(\frac{C_A^0}{C_F^0}\right) \quad (10)$$

This equation allowed the determination of k (obtained by extrapolation to time zero) at different initial water concentrations. With these values, k_C was obtained as a function of the initial water content. Results are shown in Fig. 6. This plot permitted to evaluate the effect of initial water on the rate constant, using an empirical equation previously proposed by Liu et al. [31]. The relationship found was:

$$k_C \,[\mathrm{M}^{-2}\,\mathrm{min}^{-1}] = 0.0014 \left(C_W^0\right)^{-1.468} \quad (11)$$

This figure also shows the data obtained for a sunflower oil acidified in the laboratory (A = 36 mg KOH/g) for comparison purposes. It can be observed that the relationship between k_C and C_W^0 has a similar tendency following a potential law. In this case, the average value of the autocatalysis constant $k_{AUTO(S)}$ was $2.53 \times 10^{-5}\,\mathrm{M}^{-2}\,\mathrm{min}^{-1}$. The higher value of this constant for coconut oil ($2.85 \times 10^{-5}\,\mathrm{M}^{-2}\,\mathrm{min}^{-1}$) compared to that of sunflower oil can be attributed to the presence of short chain fatty acids, which have higher dissociation constants than the long-chain acids.

Furthermore, the value of the equilibrium constant for coconut oil esterification was around 1.25 and for sunflower oil, it was 0.45. This difference could also be due to the different composition of these oils, in agreement with previous findings [31].
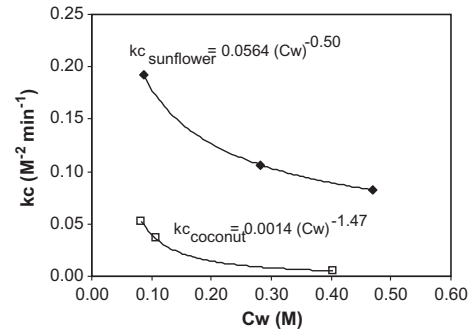
Fig. 6. k_C as a function of initial water concentration. *Reaction conditions:* For Coconut oil (128 mg KOH/g): ethanol 99.5%, molar ratio FFAs:OH of 1:12, 70 °C; for sunflower oil (36 mg KOH/g): ethanol 99.5%, molar ratio FFAs:OH of 1:16, 70 °C; Symbols: experimental data: (□) coconut oil, (♦)sunflower oil; (line) regression.

In conclusion, the two models used in this study can properly adjust the experimental data and predict the results under different reaction conditions.

Nevertheless, none of these models could predict the minimum in the acidity observed in some experiments, such as the example shown in Table 4. The other reactions must be taken into account to explain and model this behaviour.

It is important to emphasize that this simple model using only an average value for the kinetic constant in the esterification makes it possible to predict the evolution of acidity as a function of time and, consequently, it is very useful in order to pre-design the esterification reactor. However, the model has to be considered as an empirical model, since the full description of the process should include the other reactions that, as shown in previous sections, occur to a significant extent. Moreover, the average value of k is strongly dependent on the time interval in which the experimental data were determined, since the longer the reaction time, the smaller the k, due to the catalyst consumption and water production.

3.6. Process development

As previously described, a degumming and drying step were required as a pre-treatment for the coconut oil used in this study. Besides, it was shown that in order to decrease the acidity to 4 mg KOH/g, large amounts of alcohol and catalyst are needed. As established by Canakci et al. [1], it is possible to reduce the acid level to the target value using a smaller quantity of alcohol and sulphuric acid by means of a multi-step process.

The esterification procedure was similar when using methanol or ethanol, with the same FFA:Alcohol molar ratio, sulphuric acid concentration and reaction time, following a two-step reaction strategy. The difference was the reaction temperature, which was 60 °C for methanol and 70 °C for ethanol. Based on the results shown in previous sections, the process variables were selected in order to obtain the target acid value (in the order of 2 mg KOH/g), with the lowest possible alcohol consumption and catalyst concentration. The first esterification step was carried out with FFA:alcohol molar ratio 1:5 and a sulphuric acid concentration of 0.5 vol%. The second step was carried out loading alcohol equivalent to a FFA:alcohol molar ratio of 1:4, since alcohol was already present in the biodiesel-rich phase coming from the first reaction step. To calculate the amount of alcohol to be added, the initial amount of FFA in the oil was considered. Again, 0.5 vol% of sulphuric acid was used as catalyst. After an hour of reaction, the mixture was allowed to settle in a separatory funnel.

After each esterification, two phases were formed. The upper phase contained mainly alcohol, sulphuric acid and water, and the lower phase contained the methyl esters formed during the

esterification, the oil and the alcohol. Properties of this phase are shown in Table 2. It can be seen that an important amount of phosphorus was eliminated from the biodiesel phase during the esterification, in agreement with results obtained with soybean oil [34]. This phase was then transesterified using sodium methoxide as catalyst and purified, as described in Section 2.3. The purification steps, as described in Section 2.3, are a key issue in order to obtained a biodiesel that meet the acid value specified in the quality standards. Several properties of the biodiesel obtained are shown in Table 2. The value of total glycerine was 0.20 g of glycerine/100 g of sample, being the maximum value allowed by the standards 0.24 g of glycerine/100 g of sample. Both the acidity and the phosphorus content were within the limits established by the EN 14214 or ASTM D6751 standards.

In the case of using ethanol in the esterification stage, the conditions selected were those of Experiments 12 and 13. Afterwards, the transesterification was carried out as described in Section 2.4, using methanol. The final product also met the specifications established in the EN 14214 standard. The final acidity and phosphorus content, although close to the upper limits of the standard, met the specifications.

This means that the procedure used in this work, starting with a very low quality raw material, makes it possible to obtain biodiesel that meets international specifications.

4. Conclusions

A biodiesel production process using a raw material with very high acidity and phosphorus content was developed. The process involves a degumming step, two stages of esterification and one of transesterification. The side reactions that affect the global kinetics were quantified. The esters formed during the esterification due to the acid-catalyzed transesterification of triacylglycerides represent a significant proportion of the total amount of esters formed in this system.

A simple kinetic model was proposed, considering the reversible esterification. This model adjusts well the experimental data. However, it is shown that other reactions affect the esterification kinetics and should be taken into account to properly estimate the amount of alkyl ester formed during this reaction. The kinetic constant of the esterification decreases as a function of time for several reasons: (i) the sulphuric acid is consumed forming alkyl-sulphates (methyl or ethyl), (ii) the consumption of FFA due to the esterification decreases the autocatalytic effect, and (iii) the water formed during the reaction introduces an inhibition effect decreasing the constant.

Another important conclusion is that the kinetic constant depends on the raw material, being different for the esterification of coconut and sunflower oils, which is attributed to the presence of short-chain fatty acids in the former.

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