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High performance purification process of methyl and ethyl esters produced by transesterification

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HIGHLIGHTS

- Purification of crude biodiesel containing high amount of soaps requires a non-conventional procedure.
- A first washing with neutral washing removes a part of the soaps from the crude biodiesel.
- The volume of water used in the first washing is critical to avoid emulsion formation.
- The second washing with CO_2 saturated water is a better option than other mineral acids.

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ABSTRACT

The aim of this work is the obtention of high quality methyl and ethyl esters, particularly in those cases in which conventional purification procedures fail such as in the production of ethylesters or in the case of methylesters obtained from high acidity raw materials, e.g. in the range 1–4%. Three different methodologies were employed, according to the soap content of the crude biodiesel: (a) one washing step with a CO_2 saturated solution; (b) two consecutive washing steps with CO_2 saturated solutions; (c) first neutral washing using a small volume of water and a subsequent washing with a CO_2 saturated solution. These procedures were compared with the classical method that uses a first acid washing followed by a neutral one. The washings with CO_2 saturated solutions showed excellent performance, giving a final product with quality parameters similar to the ones obtained with conventional methods (washing with HCl solution). It was demonstrated that the utilization of a first neutral washing to purify biodiesel with high soap content is highly efficient since it abates a high percentage of these soaps without generating phase separation or problems of emulsion formation. Furthermore, this acid solution (water saturated with CO_2) is less corrosive than the solutions normally used (hydrochloric, sulfuric, phosphoric, or citric acid). It was found that in order to decrease the sterol glucosides deposition in the final biodiesel, the combination of longer washing times and centrifugal separation was very effective in reducing these contaminants in the final product.

1. Introduction

In the last few years, the growing energy demand, the decrease of petroleum reserves, and the more stringent requirements in terms of gaseous emissions have encouraged the development of alternative fuels being biofuels among the most important ones. These biofuels are liquid or gaseous fuels produced from renewable raw materials or biomass [1]. The ASTM 6751 standard defines biodiesel as a fuel composed by mono-alkyl esters of long chain fatty acids derived from vegetal oils or animal fats.

Biodiesel presents many advantages with respect to petroleum derived diesel: it is biodegradable, non-toxic, sulfur free, and does not contribute to global warming since it presents a closed carbon cycle [2]. Besides, CO and soot emissions are lower [3]. Biodiesel can be mixed with petroleum derived diesel and used in diesel engines with minor or none modifications.

At industrial level, biodiesel is most commonly produced by the transesterification reaction. During this reaction the triglycerides contained in vegetal oils (soybean, sunflower, rapeseed, jatropha, etc.), animal fats (cow, pork, chicken) or microalgae derived oils react with an alcohol (methanol or ethanol) to give mono-alkyl esters and glycerol. This reaction takes place in the presence of basic catalysts, which have very good performance and higher reaction rates at moderate temperature and pressure conditions than the acid catalysts [4,5]. The most commonly used catalysts are sodium and potassium hydroxides and methoxides. The latter are more reactive than their corresponding hydroxides, but they are more expensive. On the other hand, methoxides present higher reaction rates, lower water content and subsequently, lower tendency to

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produce soaps than hydroxides. As a consequence, higher yields can be obtained, and on the other hand, problems during purification steps are avoided or minimized, making these catalysts the preferred option in large scale industries.

According to the transesterification reaction stoichiometry, three moles of methanol react with one mol of triglyceride to give three moles of alkyl esters and one mol of glycerol. The overall reaction involves three consecutive reversible reactions, with mono- and diglycerides as intermediate products. Once the reaction has finished, the glycerol is separated from the crude biodiesel phase by gravitatory decantation or centrifugation. The crude biodiesel is composed mainly of alkyl esters but it also presents impurities such as soaps, catalyst, water, alcohol and free glycerol, which must be eliminated in the subsequent purification stages [6] in order to satisfy the quality standards (EN 14214, IRAM, ASTM, etc.). These impurities cause different engine problems, as reported by Berrios et al. [7].

Ethyl esters have numerous advantages over methyl esters. From an environmental point of view, ethyl esters produce lower emissions of particulate matter and greenhouse effect gases, such as carbon monoxide and nitrogen oxides (NO_x), and they are more biodegradable in water than methyl esters [20]. Besides, they present better physical properties, such as cetane index, cloud point, pour point and flash point. Another advantage is that ethanol is obtained from agricultural sources, making ethyl esters a completely renewable and petroleum independent fuel. Due to the higher ethanol molecular weight with respect to methanol, yields higher than 104% with respect to oil can be obtained in the ethyl ester production process, which represents an important economic advantage [14,15].

The most frequently used alcohol for transesterification is methanol, owing to its historically lower price in comparison with other alcohols. Nevertheless, the growth of ethanol production and consumption as gasoline additive led to the situation that it was on certain occasions less expensive than methanol, e.g. in 2007 and 2008 in Brazil [8,9]. This situation has resulted in an increasing motivation for the study of the ethyl esters production process [10–15]. However, a production process based on alkaline transesterification using ethanol instead of methanol presents the serious problem of excessive soap formation. The amount of soaps formed is three or four times higher than in the methanolysis reaction under similar conditions [14,15]. The saponification reaction is highly undesirable because it not only consumes the catalyst but also causes phase separation problems and emulsion formation during the purification stages [16]. In addition, in all the conventional purification methods industrially used – such as washings with phosphoric, citric or hydrochloric acid, or utilization of ionic exchange resins – the soaps are neutralized yielding free fatty acids. Therefore, the presence of high amounts of soaps in crude biodiesel leads to a high acidity in the final product, which might be significantly higher than the maximum value established by international standards.

The most widely used methods for biodiesel purification at industrial level can be classified under two categories: dry and wet. Most large facilities use wet purification with two consecutive washing steps. During the first one, neutralization is achieved by means of hydrochloric, phosphoric, sulfuric or citric acid; in the second washing, neutral water is used to eliminate acid excess. The main drawbacks of this process are the corrosion provoked by the acids in equipment and pipes, and the hydrolysis of soaps forming free fatty acids.

The so-called dry washings are performed using ion-exchange resins or magnesium and calcium silicate powders. These methods have the disadvantage of requiring methanol elimination by evaporation. Besides, resins are very expensive and the fine magnesium silicate powders are difficult to remove [7]. It is important to highlight that for the industrial production of ethyl esters, none of these treatments can be employed due to the high soap content in the crude biodiesel.

This work focussed on the study of an alternative acid (carbonic acid) to perform the first purification stage in order to avoid the system corrosion. Besides, a suitable method for the purification of biodiesel with high soap content was investigated. This is especially useful for the case of ethanol-based biodiesel as well as for samples produced from oils with high acidity. The procedure was optimized in order to avoid emulsion formation, and to facilitate its application at industrial level. Different raw materials were employed, such as crude soybean oil, beef tallow and sunflower oil. This procedure has been recently summarized in a patent by Mendow and Querini [17].

2. Experimental

2.1. Biodiesel production process

2.1.1. Transesterification reaction and phase separation

The reaction was carried out in a 0.5 L flask, with magnetic stirring, using a 50 mm teflon-coated magnetic bar, and 1200 rpm. The reaction temperature was in the 55–65 °C range, and the reaction time varied between 1 and 2 h. Refined sunflower oil with acidity less than 0.1 mg KOH/g sample; two samples of beef tallow with acidities of 5.6 and 0.50 mg KOH/g sample (refined beef tallow); three samples of crude soybean oil with acidities of 5.4, 4.6 and 1.6 mg KOH/g sample, and rapessed oil with acidity 3.3 mg KOH/g sample were used as raw materials.

The oil was loaded in the reactor and the temperature adjusted to the desired value. Once the oil reached this value, the alcohol containing the catalyst was added to the reactor. Methanol 99.8% purity (water content 350 ppm) from Cicarelli and ethanol 99.5% purity (water content 1150 ppm) from Cicarelli were used as transesterification alcohols. The catalysts were sodium hydroxide dissolved in methanol or ethanol, and sodium methoxide (30 wt.% in methanol) from Evonik. The catalyst concentration was in the range 0.45–1.5 g catalyst/100 mL oil. The catalyst amount was calculated in order to neutralize the free fatty acids, plus the amount needed to catalyze the reaction. The phase separation was carried out in a separatory funnel at room temperature.

2.1.2. Alcohol evaporation

After the reaction and before the phase separation, the methanol was evaporated from the reaction vessel by applying a vacuum of 80 mmHg at 60 °C. The vacuum was applied during 15 min, in order to evaporate the methanol. The next step was the phase separation, which was achieved in a separatory funnel allowing a 15 min settling time. After this settling time, glycerine and biodiesel phases were separated.

2.1.3. Biodiesel purification

The biodiesel rich phase was purified using two consecutive extraction steps. In the first one, distilled water, or an aqueous solution containing 5 wt.% of HCl, 300 mg/L of H_3PO_4, or CO_2-saturated water were used. In the second washing step, fresh water or CO_2-saturated water were used. Both extraction stages (commonly called biodiesel washing) were carried out with gentle agitation at 60 °C, during 1–10 min. Afterwards, the biodiesel was dried by stripping with nitrogen at 80–100 °C.

2.1.4. Fatty acid recovery from the glycerine phase

The recovery of the fatty acids was carried out as currently practiced by the biodiesel industry. The glycerine-rich phase was mixed with all the water used in the washing steps, adding concentrated

hydrochloric acid while stirring at 60 °C. The amount of acid used in the neutralization was calculated in order to obtain a final pH = 4, in such a way that the catalyst was neutralized and the soaps were completely transformed into fatty acids. The contact time was 15 min. After mixing, the sample was allowed to settle, forming an upper layer rich in fatty acids and a lower layer rich in glycerine, salts and water. Figs. 1 and 2 show the scheme of methyl and ethyl esters production processes, respectively.

2.1.5. Esterification

The fatty acids recovered as described in Section 2.1.4 were esterified using p-toluene sulfonic acid dissolved in methanol as catalyst. The reaction was conducted at 60 °C with vigorous stirring for 135 min. The ethanol/oil ratio loaded in the reactor was selected depending on the initial acidity of the raw material. In the case of the fatty acids recovered from the glycerine phase obtained from soybean oil and beef tallow, the following conditions were used, respectively: 60 and 40 v/v% ethanol (referred to the oil volume), and 0.66 and 0.56 v/v% p-toluene sulfonic acid (relative to the total volume loaded into the reactor, i.e. ethanol plus oil). After each esterification, the system was allowed to settle. The upper phase containing mainly ethanol, p-toluen sulfonic acid and water was sent to the ethanol recovery step. The lower phase was a mixture of ethylesters and glycerides. This product was mixed with the feed of the transesterification reactor, in which the acylglycerides fraction was converted into ethyl esters. During the esterification, the acidity was measured as a function of time in small aliquots of the reaction mixture taken from the reaction vessel. The acidity was determined as described in the European Standard EN 14104, after washing the sample with cold water and centrifuging at 3500*g* for 2 min in order to eliminate the catalyst. Measurements were carried out by duplicate, and fell within a 15% interval of the average value. Two different acidity analyses of the same sample did not differ by more than 5%.

2.1.6. Mass balance – methyl ester production

Mass balances were performed for three different raw materials, such as refined sunflower oil, refined beef tallow (A = 0.5 mg KOH/g) and crude soybean oil (A = 4.6 mg KOH/g). Sodium methoxide was used as catalyst, methanol as alcohol, agitation speed 1200 rpm, temperature 60 °C and 2 h reaction time. After 15 min decantation, the first washing was performed with 10 v/v% neutral water, and a second washing using 30 v/v% water saturated in CO_2. Finally, the biodiesel obtained was dried at 90 °C in N_2 stream.

2.1.7. Sterol elimination

Three experiments were carried out varying the washing times. The influence of centrifugal or gravitatory separation was also investigated. Neutralized soybean oil (A = 0.05 mg KOH/g) was used as raw material, sodium methoxide solution (30% in methanol) as catalyst, and methanol as alcohol. The reaction was carried out at 60 °C, with agitation speed 1200 rpm, 2 h of reaction time, 25 v/v% methanol and 2.3 wt.% $NaCH_3O$ solution. After the reaction, the mixture was allowed to settle for 15 min.

Three different purification strategies were employed:

1. 1st and 2nd washing with 10 v/v% phosphoric acid solution (300 ppm).
2. 1st washing with 5 v/v% neutral water and 2nd washing with 10 v/v% water saturated in CO_2.
3. 1st and 2nd washing with 10 v/v% CO_2 saturated solution.

In all cases, the agitation speed was 500 rpm. After the washing steps, the samples were dried at 90 °C in N_2 flow. Each washing step was 1 min long.

2.2. Biodiesel analyses

2.2.1. Soap and catalyst analyses

Small samples of the biodiesel or glycerine phases were taken at different process stages. These samples were used to determine the soap and catalyst content by an acid–base titration method (AOCS Cc17-79 or IRAM 5599). The biodiesel sample was dissolved in a toluene–ethanol mixture, and titrated with a 0.1 N HCl solution, using phenolphthalein as indicator to determine the catalyst concentration; and bromophenol blue to determine soap concentration.

2.2.2. Free glycerine analysis

Free glycerine was determined by extraction with water, followed by titration as indicated in the ASTM D-1615, IRAM 41089, BS-5711, or AOCS 14-56.

Details of this technique can be found elsewhere [18]. Results have been verified using the procedure described in the standard EN 14105. It has to be emphasized that in several cases the GC

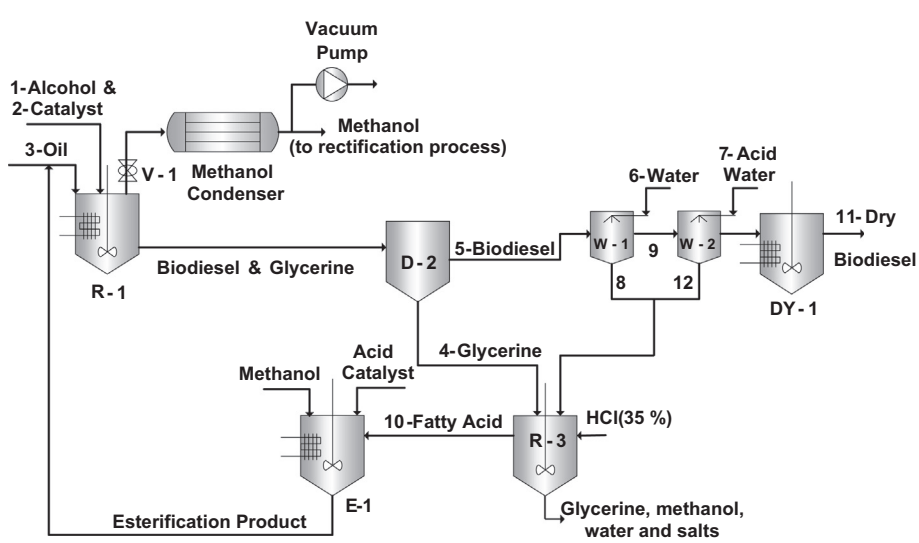

Fig. 1. Scheme of the methyl ester production process with one-stage transesterification.

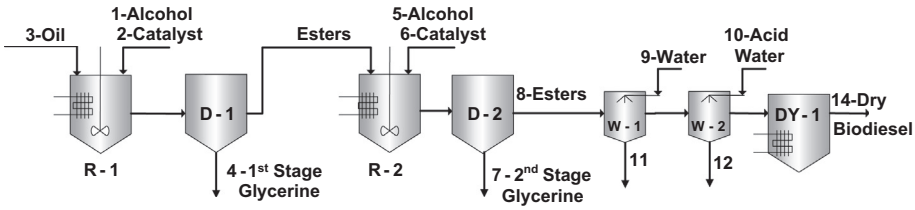

Fig. 2. Scheme of the ethyl ester production process with two-stage transesterification.

Table 1
Biodiesel produced from crude soybean oil partially degummed (A = 1.6 mg KOH/g) without alcohol evaporation.

Purification	Free glycerine (%)	Acidity (mg KOH/g)	Soaps (mg_{oleate}/kg)
One washing with 40 v/v% CO_2 saturated solution	0.007	0.84	0.02
Two washings: (1) 10 v/v% neutral water and (2) 20 v/v% water saturated in CO_2	0	0.14	0
Two washings: (1 and 2) 20 v/v% water saturated in CO_2	0	0.76	0
Two washings: (1) 20 v/v% HCl 5 wt.% and (2) neutral water	0	0.98	0

procedure has to be modified in order to extend the applicability range, since as described in the standard it can be used only up to a glycerine content of 0.05%. Because of this, the volumetric procedure as developed by Pisarello et al [18] present advantages since it has no calibration limitations.

3. Results and discussion

3.1. Methyl ester purification

The following four different purification strategies were used: (i) one washing step using 40 v/v% CO_2 saturated water; (ii) first washing with 10 v/v% neutral water and second washing with 20 v/v% CO_2 saturated water; (iii) two washings with 20 v/v% CO_2 saturated water; (iv) first washing with 20 v/v% HCl solution and second washing with 20 v/v% distilled water (similar to the industrial process currently in used). After each treatment, free glycerine and soap content as well as acidity were measured. The latter procedure corresponds to the process used in the industry, and is included for comparison purposes.

It is important to highlight that two consecutive washings with neutral water lead to the formation of stable emulsions, so that it is not possible to carry out this alternative in order to purify crude biodiesel.

3.1.1. Production process without alcohol evaporation

Fig. 1 shows the schematic process employed in these experiments. In this case, the V-1 valve remained closed, and no methanol evaporation was carried out after the end of the reaction. Table 1 shows the results obtained using crude soybean oil partially degummed (acidity 1.6 mg KOH/g) and sodium methoxide as catalyst.

It can be observed that when the first washing was performed with acids (hydrochloric or carbonic), the acidity of the biodiesel obtained was in both cases significantly higher than the maximum permitted by international standards, which requires an acidity lower than 0.5 mg KOH/g. On the contrary, when a small amount of neutral water was employed (10 v/v% with respect to oil) as the first washing step, the acidity notoriously decreased. It is important to remark that when neutral water was used in the first purification stage, a fast phase separation was observed, with no emulsion formation (see Fig. 3). On the other hand, when 30 v/v% of water were used, a very stable emulsion was formed, which prevented the separation of the biodiesel and water phases, even when using centrifugal separation (see Section 3.1.4 for an explanation of this behavior). Therefore, in order to use a first washing with non-acidified water, the volume of this phase should be properly selected, and must be in the order of 10 v/v%.

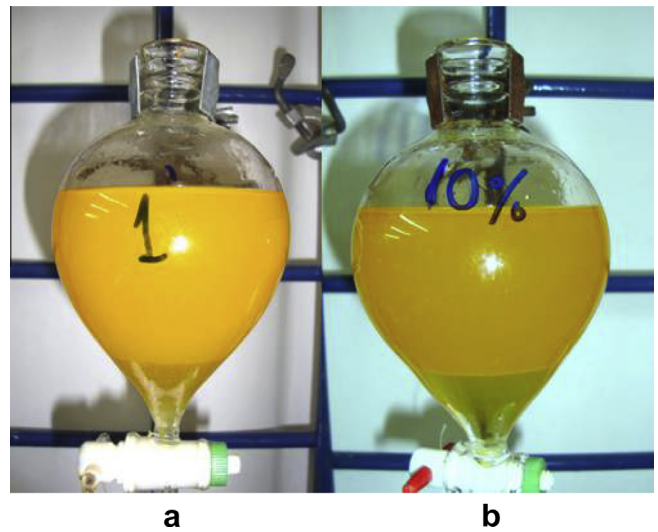

Fig. 3. Photo of the system during settling, after the first washing with neutral water. (a) 5 v/v% water and (b) 10 v/v% water.

Table 2 presents the results corresponding to experiments performed with rapeseed oil as raw material (acidity 3.3 mg KOH/g). Even though the acidity was almost the double than that of the crude soybean oil, the final acidity results were very similar (compare Tables 1 and 2). High acid values were measured when the first washings were carried out with acids (CO_2-saturated water in the first and third strategies, and HCl in the fourth one, Table 2), which was due to soap hydrolysis. The best performance was obtained using a small volume of neutral water in the first washing because in this process strategy soaps were extracted by water without forming free fatty acids.

3.1.2. Production process with alcohol evaporation

Crude soybean oil with high acidity (acidity 4.6 mg KOH/g) was used as raw material to evaluate the effect of including a methanol evaporation stage in the process, right after the reaction. Fig. 1 schematizes the process stages. In this case, the V-1 valve was opened once the reaction was finished, applying vacuum to the reactor (absolute pressure 80 mmHg) at 60 °C.

The presence of methanol increases the polarity of the biodiesel phase, thus increasing the concentration of impurities, such as soaps and catalyst. Therefore, the removal of methanol favors the

Table 2
Biodiesel produced from rapeseed oil (A = 3.3 mg KOH/g) without alcohol evaporation.

Purification	Free glycerine (%)	Acidity (mg KOH/g)	Soaps (mg_{oleate}/kg)
One washing with 40 v/v% CO_2 saturated solution	0.0023	0.94	0.24
Two washings: (1) 10 v/v% neutral water and (2) 20 v/v% water saturated in CO_2	0	0.18	0
Two washings: (1 and 2) 20 v/v% water saturated in CO_2	0	0.98	0
Two washings: (1) 20 v/v% HCl 5 wt.% and (2) neutral water	0	1.02	0

Table 3
Biodiesel produced from crude soybean oil partially degummed (A = 4.6 mg KOH/g), and sodium methoxide as catalyst. Alcohol evaporation after the reaction.

Purification	Free glycerine (%)	Acidity (mg KOH/g)	Soaps (mg_{oleate}/kg)
One washing with 40 v/v% CO_2 saturated solution	0.0015	0.56	0
Two washings: (1) 10 v/v% neutral water and (2) 20 v/v% water saturated in CO_2	0	0.12	0
Two washings: (1 and 2) 20 v/v% water saturated in CO_2	0	0.52	0
Two washings: (1) 20 v/v% HCl 5 wt.% and (2) neutral water	0	0.64	0

transference of these compounds to the glycerine-rich phase, which has a high polarity. This is the reason of evaporating methanol before phase separation, i.e. to decrease the solubility of soaps in the biodiesel phase [19]. As a result of this operation, it was observed that the phase separation during the decantation stage was improved, and the soap content of the biodiesel rich phase entering the washing steps was lower. The soap content in the biodiesel phase before evaporation was 8.5 g_{oleate}/kg, and decreased to 4.8 g_{oleate}/kg after the alcohol evaporation, in which 32% of the total methanol was eliminated.

The results obtained in these purification experiments are shown in Table 3. When the first washing was performed with acid solutions, the final biodiesel acidity was practically the same independently of the acid used. However, it is very important that this acidity was lower than in the cases in which no alcohol evaporation was carried out (compare Table 3 with Tables 1 and 2). In all cases, two washings steps were enough to completely eliminate the free glycerine and soaps. No emulsion formation or phase separation problems were observed in these experiments.

Another set of experiments was carried out using beef tallow with high acidity level (5.6 mg KOH/g) as raw material. The catalyst used was sodium methoxide. Results are presented in Table 4. The behavior was similar to the one previously observed for the other raw materials. When acid water was used in the first washing stage, the biodiesel acidity was higher. Besides, the acid values decreased when the methanol evaporation was performed, although the final acidity was out of specification. Free glycerine and soap contents were almost negligible in all the purification strategies employed.

3.1.3. Production process without alcohol evaporation using NaOH as catalyst

Sodium hydroxide is frequently used as catalyst in small facilities to produce biodiesel, since it is less expensive than sodium methoxide. However, it generates water when it is dissolved in methanol, according to the following reactions:

$$\begin{array}{ccccccc} H_3C{-}OH & + & NaOH & \rightarrow & H_3C{-}O^-Na^+ & + & H_2O \\ \text{Methanol} & + & \text{Sodium Hydroxide} & & \text{Sodium Methoxide} & + & \text{Water} \end{array}$$

A similar reaction occurs when it is dissolved in ethanol. As mentioned above, water promotes soap formation, and if conventional purification is carried out using a first washing with an acid solution, the final biodiesel acidity would be too high.

The production of biodiesel from a high acidity raw material, such as crude soybean oil (A = 5.4 mg KOH/g) using NaOH as catalyst, is a difficult challenge. Therefore, in this case we tested a purification method where the first stage consisted of a neutral washing using 10 v/v% of water followed by a second stage with CO_2 acidified water. The soap and glycerine contents of the final product were undetectable, and the final acidity was 0.2 mg KOH/g, which is a very good result taking into account the raw material and the catalyst used in this case.

These are very interesting results concerning their possible application in small scale facilities installed by farmers, who frequently use this type of raw materials (high acidity oil and NaOH) to produce biodiesel for self-consumption.

3.1.4. Effect of water volume fed in the first washing (W-1)

Systematic experiments were carried out in order to assess the effect of the water amount in the first washing step, expressed as v/v% with respect to the oil. The other variables involved were maintained constant: washing time 5 min, agitation speed 1200 rpm, temperature 60 °C, and decantation time 10 min. The washes were performed after the separation of glycerol without methanol evaporation. The results are shown in Fig. 4.

The soap content was 2.43 g_{oleate}/kg biodiesel, and the catalyst content 0.13 gMeONa/kg biodiesel at the initial value. Using 3 v/v% water in the first washing, the soap content was reduced to approximately half the initial value and the catalyst was completely eliminated. As the volume of water increased, the soaps left in the biodiesel decreased notoriously. The best results were obtained with 10 v/v% water, since the final soap content in biodiesel was 0.48 g/kg, i.e. 0.048 wt.%. This means that the final biodiesel acidity after acid washing would be 0.08 mg KOH/g approximately, considering that all the remaining soaps were transformed into fatty acids. It can also be observed that the catalyst content is negligible in all cases, which is due to the high affinity of the methoxide salts for water. It is concluded then that the optimal water content for the first washing is 10 v/v% with respect to the oil.

This behavior is due to the combined effects of water and methanol concentration in the system. In the cases in which a small amount of water was added, the amount of soaps extracted was limited by the distribution constant, since at high soap concentration in the water phase (as those obtained when using small amounts of water), the soap concentration in the biodiesel is correspondingly high. As the amount of water increased, the amount of soaps transferred to the aqueous phase increased, thus reducing the final soap concentration in biodiesel.

On the other hand, methanol plays a major role as an inhibitor of emulsion formation. Results obtained in our laboratory indicate that the addition of methanol (or ethanol) to an emulsified system

Table 4
Biodiesel produced from beef tallow with high acid value (A = 5.6 mg KOH/g), with alcohol evaporation.

Purification	Free glycerine (%)	Acidity (mg KOH/g)	Soaps (mg_{oleate}/kg)
One washing with 40 v/v% CO_2 saturated solution	0.0032	0.46	0
Two washings: (1) 10 v/v% neutral water and (2) 20 v/v% water saturated in CO_2	0	0.2	0
Two washings: (1 and 2) 20 v/v% water saturated in CO_2	0	0.56	0
Two washings: (1) 20 v/v% HCl 5 wt.% and (2) neutral water	0	0.52	0

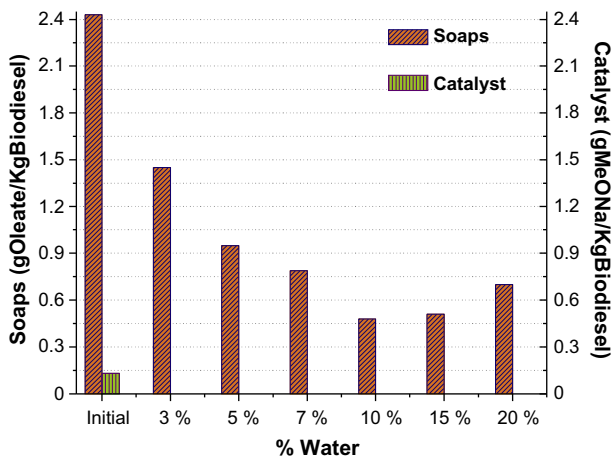

Fig. 4. Soap and catalyst contents after the first washing, using 3, 5, 7 and 10 v/v% water.

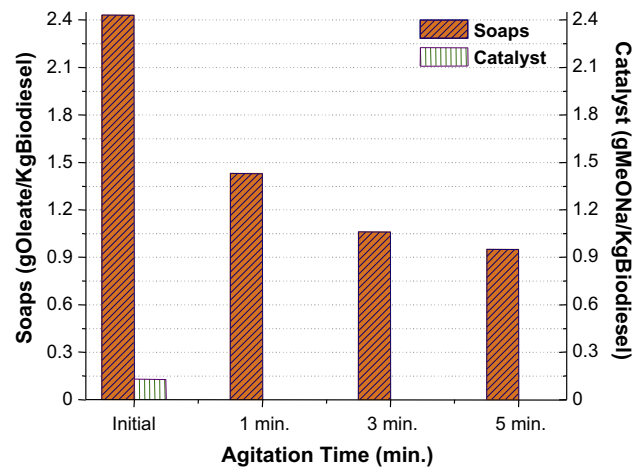

Fig. 5. Soap and catalyst content after the first washing, with agitation during 1, 3 and 5 min.

containing water and crude biodiesel is adequate in order to break the emulsion.

Therefore, as more water was added to the system, a higher dilution of the methanol occurred and as a result, the emulsion was formed. Consequently, small drops of water containing soaps were dispersed in the biodiesel phase, thus increasing its soap concentration. This emulsion formation also occurred when two consecutive washings using neutral water were carried out, as above described. This is because in the second washing the methanol concentration is too low to avoid emulsion formation.

3.1.5. Effect of mixing time during neutral washing (W-1)

A set of experiments was carried out in order to assess the optimal washing time necessary to maximize soap extraction. The other variables involved were maintained constant: amount of water 5 v/v% (with respect to oil), agitation speed 1200 rpm, temperature 60 °C, and decantation time 10 min. The results are shown in Fig. 5.

The initial soap content was 2.43 g_{oleate}/kg biodiesel, and the catalyst content 0.13 gMeONa/kg biodiesel. It can be observed that with 1 min agitation the soap content decreases to approximately half of its initial value. As the agitation time increases, the soap content slightly decreases from 1.43 g_{oleate}/kg for 1 min agitation to 0.95 g/kg for 5 min. This value represents 0.095 wt.%, which implies that the acid value of the final biodiesel would be 0.18 mg KOH/g approximately. Therefore, it is concluded that short washing times are suitable to eliminate a high fraction of soaps, 5 min being enough to reach a satisfactory level of purity.

3.1.6. Mass and soap balance

The soap and catalyst contents in the crude biodiesel depend on a number of factors, such as concentration and type of catalyst used in the transesterification, decantation time, process design (e.g. alcohol evaporation), water content and acidity of the raw material. As it can be observed in Figs. 4 and 5, the biodiesel phase after decantation contains a certain amount of catalyst. This catalyst, in the presence of water and saponifiable material (esters or unreacted glycerides), can react forming soaps. When the first washing is performed with an acid solution the saponification reaction cannot take place, since the acid neutralizes the basic catalyst. On the contrary, when the first washing is performed with neutral water, the neutralization cannot occur, hence saponification takes place, provoking a yield loss. This loss occurs because the soaps generated are extracted by water, and as a result, a certain amount of esters are eliminated from the system. For these reasons, the yield loss that occurs with this purification strategy was studied in this work. It is important to highlight that the second washing was performed with a CO_2 saturated solution, since at the end of the first washing with neutral water a certain amount of soaps was still present in the biodiesel phase. It was observed that if the second washing was performed with neutral water, a stable emulsion was formed very fast, since the soaps act as emulsifying agents. Besides, the CO_2 saturated solution entails two additional advantages: it produces negligible corrosion and the remaining acid after the second biodiesel washing can be eliminated during the drying step, as gaseous CO_2. Therefore, a third washing step becomes unnecessary, whereas it is mandatory if the acid used is either HCl, H_3PO_4 or citric.

In each step, the weight of each phase was registered, as well as the soaps and catalyst contents of streams 5, 8 and 9 (see Fig. 1). Tables 5 and 6 show the results. In Table 5, the% Theoretical Yield is included, and defined as% Theoretical Yield = mass of biodiesel × 100/(mass of oil − mass of FFA (mass of biodiesel × 100/(mass of oil − mass of FFA). It takes into account the initial acidity (content of FFA), which are lost due to saponification and extraction during the washing steps. It can be observed in Table 5 that when refined sunflower oil was used, the amount of water leaving the first neutral washing (stream 8) was much higher than the amount obtained with the other two raw materials. During the washing step, emulsions were formed, and as a consequence biodiesel was retained in the aqueous phase. The problem of emulsion formation was not detected when beef tallow or crude soybean oil

Table 5
Mass balance in methyl ester production process. % Real Yield = Mass of biodiesel obtained × 100/mass of oil fed; % Theoretical Yield = mass of biodiesel × 100/(mass of oil − mass of FFA).

Stream	Raw material		
	Refined sunflower oil	Crude soybean oil	Refined beef tallow
1 – Alcohol (g)	224	224	224
2 – Catalyst (g)	22.3	37.5	23.8
3 – Oil (g)	1000	1000	1000
4 – Glycerine (g)	163.4	195.2	170.1
5 – Esters (g)	1082.9	1066.3	1077.7
6 – Water (g)	103.7	104	112.6
7 – Acid water (g)	339	339	339
8 – Water out (g)	337	171.3	171.7
9 – Washed ester (g)	849.6	999	1018.6
10 – Fatty acid (g)	169.3	38.2	6.6
11 – Biodiesel (g)	836	967	998.4
Real Yield (%)	83.6	96.7	99.84
Theoretical Yield (%)	100.5	98.2	100.25

were used. Table 6 shows that the soap content in the biodiesel phase before entering the first neutral washing was 1.674 g for refined sunflower oil, 2.413 g for beef tallow and 9.092 g for raw soybean oil. The increase in the amount of soaps during the neutral washing, i.e., the soap content in streams 8 and 9 compared to stream 5 (Fig. 1), was higher as the initial soap content was lower. The results shown in Table 6 indicate that the increase in the amount of soaps was 73% and 53% for refined sunflower oil and beef tallow, respectively. On the contrary, for a high acidity raw material, such as the crude soybean oil (4.6 mg KOH/g), soap generation by saponification was not detected. These results indicate that the extraction with neutral water as a first purification step is not complicated by a higher amount of soaps; moreover, according to the data shown in Table 6, apparently this procedure is more efficient in the case of a higher soap concentration. Finally, by comparing the maximum yields expected with those experimentally obtained (Table 5), it can be seen that for the case of crude soybean oil and beef tallow, these values resulted very similar. On the other hand, when refined sunflower oil was employed, the yield decreased considerably since as above discussed, an important amount of biodiesel was left on the water phase in the first purification step. According to this, it can be concluded that the neutral washing as a first stage in the purification treatment is particularly useful and avoids yield losses in the case of high soap-containing samples.

As shown in the process scheme (Fig. 1), the glycerine stream discharged from the transesterification reactor (stream 4), and the aqueous streams coming from the washing steps (streams 8 and 12) are sent to the neutralization reactor (R-3). In this equipment, HCl 35 wt.% was dosified, in order to neutralize all the catalysts and soaps entering the reactor. As a result, an aqueous phase was obtained which contained salts, glycerine and methanol, and an organic phase constituted mainly by fatty acids and a small amount of esters. The resulting fatty acid contents in the organic phase after neutralization were 2.24%, 82% and 77% for refined sunflower oil, crude soybean oil and beef tallow, respectively. The low acidity corresponding to the refined sunflower oil was because in the first neutral washing a great amount of biodiesel became emulsified with water, subsequently entering the neutralization reactor (R-3). Finally, the phase rich in fatty acids was fed to an esterification reactor.

3.2. Ethyl ester purification

The ethyl esters production process is shown in Fig. 2. In previous studies [14,15], it has been shown that ethanolysis reactions generate a great amount of soaps, almost three times higher than the amount formed in methanolysis under similar operating conditions. For this reason, the ethyl esters purification stages result highly complex [21]. There are no reports concerning this problem or how to solve it. Therefore, the purification step is one of the major hindrances in the development of the ethyl esters industrial process. Taking this in consideration, different purification methodologies were studied, such as the utilization of ion exchange resins, acid washings (CO_2, Citric acid, HCl, H_3PO_4) and neutral washing. Table 7 shows the soaps and free glycerine content after each of these treatments, and the acidity of the final biodiesel obtained in the production process. All these alternatives were successful in order to eliminate soaps and free glycerine. On the other hand, it can be clearly observed that when either exchange resins or acids were employed in the first purification step, all the soaps initially present in the ester phase were transformed into fatty acids. This is because in the commercial ion exchange resins, Na^+ ions present in crude biodiesel were exchanged with the H^+ ions from the resin. These protons reacted with soaps forming fatty acids, leading to an increase in the acid value of the final biodiesel. A similar phenomenon took place during the washing with hydrochloric, carbonic, citric or phosphoric acid solution. For this reason, the biodiesel samples obtained by any of these treatments have similar acid values, and are considerably higher than the maximum permitted by the international standard (EN 14214: acid value = 0.5 mg KOH/g). In this way, it is concluded that the utilization of resins or the conventional washings with acid solutions are not suitable for this process, because of the high soap content of the crude biodiesel.

The most efficient methodology involved one first washing with neutral water, followed by a second washing with water saturated in CO_2. This process is described in detail in patent AR 076851 A1 [17]. It could be observed that this treatment was highly efficient, since the obtained biodiesel showed negligible amounts of soaps, catalyst and free glycerine, with an acid value considerably lower than the limit established by the international standards. Moreover, no emulsions were detected among the samples treated with this procedure.

Another strategy to decrease the soap content in the ester phase after the basic transesterification reaction consists in distilling the remaining alcohol. In our case, ethanol distillation was carried out at 60 °C, under vacuum (60 mmHg absolute pressure). It was observed that after a few minutes of distillation the reaction mixture turned into a gel. This is because the soap content was significantly

Table 6
Soap balance based on 1000 g oil.

Raw material	Refined sunflower oil		Crude soybean oil		Refined beef tallow	
	Catalyst (gMeONa)	Soaps (g Na-Oleate)	Catalyst (gMeONa)	Soaps (g Na-Oleate)	Catalyst (gMeONa)	Soaps (g Na-Oleate)
5 – Esters	0.066	1.674	0.319	9.092	0.158	2.413
8 – Water out	0.066	2.4	0.319	7.735	0.158	2.108
9 – Washed ester	0	0.497	0	1.366	0	1.591
Soap generation	–	73%	–	0.10%	–	53%

Table 7
Acidity, soap and free glycerine content obtained using different purification methodologies for ethylesters. Second washing was performed with water saturated in CO_2, followed by drying at 90 °C in N_2 stream. Initial soaps = 11.28 g_{oleate}/kg, initial free glycerine = 0.39%.

1st Wash	Final biodiesel soaps (g_{oleate}/kg)	Final free glycerine (%)	Final acidity (mgKOH/g)
HCl	0	0	1.29
H_3PO_4	0	0	1.32
Citric acid	0	0	1.23
Neutral	0	0	0.14
CO_2 saturated water	0	0	1.41
Resin	0	0	1.36

higher than that formed during methanolysis. For this reason, it is concluded that this alternative is not suitable for purifying biodiesel samples obtained by basic transesterification with ethanol.

3.3. Sterol elimination

Sterolglucosides are one of the problems of the biodiesel industry based on soybean oil. These compounds are transformed into a non-acylated form during the transesterification, which has a very low solubility in biodiesel and slowly precipitates in the final product [22].

A set of experiments was performed in order to determine the effect of the proposed purification strategy on the sterol content by measuring the total contamination of the biodiesel right after preparation, according to the procedure described in standard EN 12662 [23].

The results showed that for the three different washings performed as described in Section 2.1.7, the soluble impurity content was 29.5, 26.2 and 28.7 mg/kg, respectively. The values obtained were very similar, indicating that the presence of sterols in the washed biodiesel was not related to the type of acid used in the purification. It should be noted that in all cases, the soluble impurity content was higher than 24 mg/kg, which is the limit value according to the international standards (EN 14214). However, this is because there was no maturing and separation of the sterols crystals as normally carried out in industry.

An additional experiment was carried out, washing with 5 v/v% neutral water followed by water saturated in CO_2 but using a 15-s washing time instead of 1 min, and 500 rpm agitation speed. The biodiesel obtained contained insoluble sterols and soaps (1 g_{oleate}/kg biodiesel). The total contamination value was 154 mg/kg, which was considerably higher than the values obtained in the previous experiments. Therefore, it can be concluded that the presence of soaps increased the insoluble impurity content, most probably due to the co-precipitation of both types of compounds. In addition, as discussed in the following paragraph, the shorter washing time has a negative effect on the total contamination value.

The influence of washing time in the sterol content was also investigated. Two experiments were performed with identical operation conditions as those previously employed, but increasing the washing time to 5 min. The insoluble impurities were 9.7 mg/kg and 13.9 mg/kg when phosphoric acid and water saturated in CO_2 were used in the washings, respectively. These values are significantly lower than the values obtained when the washings were performed during 1 min. Moreover, they were within the limits of the international standard (<mg/kg), even no maduration and decantation operations were carried out.

Finally, the effect of the type of separation was studied. The washings were performed for 5 min, but using centrifugal separation instead of gravitatory. It was observed that the insoluble impurity content was undetectable when centrifugal separation was employed. It is concluded that the combination of a longer washing time with centrifugal separation completely eliminates the sterols from the biodiesel phase.

4. Conclusions

Different methodologies for biodiesel purification were studied, according to the soap content of the crude samples. It was found that the utilization of carbonic acid (water saturated in CO_2) can replace the inorganic acids that are currently being used, thus avoiding the corrosion issues in equipment and pipes. It was also observed that the representative parameters of an effective purification (acidity, soaps and free glycerine content) meet the limit values established by the international standards when using the proposed methodology. When carbonic acid is used in the purification, a second washing step can be avoided, thus decreasing the equipment requirements. An important part of the purification process is the alcohol evaporation before phases separation, since this operation favors the transference of soaps to the glycerine phase.

An adequate methodology was developed to purify biodiesel with high soap content without generating acidity in the final product. This was accomplished using low amounts of neutral water in a first washing step. It was also found that the efficiency of the treatment increases with the soap content of the sample to be purified.

This is a very efficient strategy for ethyl-ester purification, being the only adequate methodology to purify samples with very high soap contents, such as the ones generated by ethanolysis.

The combination of a longer washing time with centrifugal separation completely eliminates the sterols from the biodiesel phase.

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