Transesterification of sunflower oil with ethanol using sodium ethoxide as catalyst. Effect of the reaction conditions

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ABSTRACT

Typically, biodiesel is produced using vegetable oil and methanol as raw materials, and sodium methoxide as catalyst, whereupon the obtained product is composed of methyl esters. However, the use of ethyl esters as biodiesel presents many advantages compared to the methyl esters. In this work, the transesterification with ethanol to produce ethyl esters using sodium ethoxide as catalyst was studied. The effect of temperature and alcohol and catalyst concentration on the reaction conversion was investigated, in order to optimize these parameters while also meeting the quality standards.

It was found that the optimal reaction conditions are: 1.6 wt.% sodium ethoxide, 25 v/v% ethanol and 55 °C, which allow obtaining a biodiesel composed 100% by ethyl esters that complies with the international quality standards. On the other hand, it was observed that methanolysis reactions are faster than the ethanolysis and sodium methoxide catalyst is more active than the corresponding ethoxide, due to the higher steric hindrance of the ethoxi-radical and to the more intense saponification of sodium ethoxide in ethanol medium.

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1. Introduction

The biodiesel production is based on the chemical reaction between triglycerides and an alcohol, which is known as alcoholysis or transesterification, and the product obtained is a mixture of fatty acid alkyl esters. Both for commercial and laboratory level processes, mainly edible vegetable oils and methanol are used as reagents, and the reaction is carried out in the presence of a basic homogeneous catalyst. Recently, other oils (e.g. non edible oils and used oils) as well as other alcohols have been investigated. The use of bioethanol in the biodiesel synthesis process is beneficial because it leads to the production of a fuel entirely based on renewable sources [1]. Although ethanol is currently more expensive than methanol, it has the advantage of being more miscible in vegetable oils and has lower toxicity [2]. Compared to methyl esters, ethyl esters have higher oxidation stability [3,4], lower iodine value [3] and improved lubricity properties [4,5]. Additionally, ethyl esters have lower cloud point and pour point, which improves the engine starting at low temperatures [3], and the extra carbon atom provided by the ethanol molecule slightly increases the heat of combustion and the cetane number [1]. The evaluation of exhaust emissions (NO_x, CO_2, soot) shows that the ethyl esters have a less negative effect on the environment, compared with that caused by the methyl esters [6,7].

During the ethanolysis of vegetable oils, stable emulsions are formed which complicate the separation of ethyl esters from the ethanol–glycerol phase [8,9]. The presences of mono and diacylglycerols, as well as soaps formed by saponification, also complicate the separation and purification of esters [10,11]. Therefore, it is evident that the physico-chemical changes introduced to the system by using a longer chain alcohol, significantly affect not only the properties of the product obtained, but the evolution of the transesterification reaction.

Typically, homogeneous base catalysts are used for vegetable oil ethanolysis [12]. The most frequently used are sodium and potassium hydroxides and alkoxides. The alkoxides are more expensive and more difficult to manipulate but their use decreases the amount of water released in the ethanolysis and therefore, the soap formation during the reaction [13]. Homogeneous base catalysts show excellent activity under mild reaction conditions. On the other hand, they present some drawbacks such as non-reusability, requirement of neutralized oil as feedstock and the possibility of effluent generation due to the biodiesel washing process, which is mandatory in order to remove the catalyst and other contaminants from biodiesel [14]. In order to overcome these problems, efforts are being made to develop heterogeneous catalysts for the ethanolysis of vegetable oils. Some of the compounds studied are mixed metal oxides [15], ion exchange resins [16,17], heteropolyacids and sulfonated carbohydrates [18,19]. Due to the presence of three phases during the reaction in the case of using heterogeneous catalysts, diffusional limitations are present. As a consequence, transesterification processes based on heterogeneous catalysts often require more severe reaction conditions such as higher temperatures (up to 200 °C), higher pressure (up to 25 atm), higher catalyst

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concentration (20 mol% to oil) and higher ethanol to oil molar ratio (>30:1) in order to achieve satisfactory yield [20]. The possibility of reusing heterogeneous catalysts is one of its advantages, but so far only a few catalysts could be reused without a loss in activity [21,22]. For these reasons, all of the industrial ethanolysis processes for biodiesel production use homogeneous catalysts.

In this work, the transesterification reaction of sunflower oil was carried out using ethanol as alcohol, and sodium ethoxide ($NaCH_3CH_2O$) as catalyst, aiming at the production of a biodiesel entirely composed of ethyl esters. The ethyl ester production using sodium ethoxide as catalyst has been studied using different oils, such as castor oil [23,24], Raphanus Sativus oil [25], and sunflower oil [26]. Kim et al. [26] performed the transesterification of sunflower oil using homogeneous (sodium methoxide and ethoxide) and heterogeneous catalysts, with methanol, ethanol or mixtures of both alcohols. The reaction conversion was analyzed by measuring the ethyl ester yield, and they found no difference in conversion rates between the methanolysis and ethanolysis when using the homogeneous catalysts.

There are differences among the quality standards throughout the world, regarding the definition of biodiesel. The EN 14214 [27] defines the biodiesel as a mixture of methyl esters of fatty acids, while the ASTM D-6751 [28] defines it as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. Therefore, according to this standard, the biodiesel can be obtained using different alcohols. Similar definitions are presented by the standards in Argentina and Brazil.

In this work, the effect on the conversion (measured by the mono-, di- and triglycerides content) of the variables involved in the transesterification process such as catalyst concentration, temperature and alcohol concentration was studied. These variables were optimized in order to obtain a product (ethyl esters) that meets the specifications of international quality standards. In addition, the results obtained using methanol or ethanol and sodium methoxide or ethoxide were compared, in order to establish the influence of the methoxi- vs ethoxi-radicals on the transesterification reaction.

2. Materials and methods

2.1. Biodiesel production process

The reaction was carried out in a 0.5 L flask with magnetic stirring, using a 50 mm Teflon-coated magnetic bar at 800 rpm, at atmospheric pressure, under reflux conditions. 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, taking as zero time the moment in which all the mixture was transferred to the reaction vessel. Refined sunflower oil with acidity less than 0.1 g oleic acid/100 g sample was used as raw material. Ethanol 99.5% purity (water content 1150 ppm) from Cicarelli was used as transesterification alcohol, and the catalyst was a solution of sodium ethoxide in ethanol (21 wt.%) from Evonik.

In order to optimize the reaction conversion, different catalyst and alcohol concentrations were used, and the temperature was varied between 30 and 70 °C. In all cases, the reaction was carried out for 120 min, in a single stage. At the end of each reaction, phase separation was carried out in a separatory funnel at room temperature. The catalyst concentration is expressed as wt.% referred to the oil (g of catalyst/100 g of oil). The alcohol concentration is expressed as v/v%, also referred to the oil (mL of ethanol/100 mL of oil). In order to compare sodium methoxide and sodium ethoxide as catalysts, the same molar concentration was used. This concentration is expressed as mol% (mol of catalyst/100 kg oil), which has been previously used to compare the activity of different catalysts [29].

The biodiesel rich phase was purified using two consecutive extraction steps. In the first one, neutral water was used; and in the second one, an aqueous solution saturated with CO_2. Both extraction stages were carried out with gentle agitation at 60 °C, during 15 min. The volume of aqueous phase was 30 v/v% relative to the biodiesel phase. Afterwards, the biodiesel was dried by stripping with nitrogen at 80 °C. A detailed description of this procedure can be found elsewhere [30].

2.2. Conversion analysis

Mono-, di-, and tri-glyceride contents (MG, DG, and TG respectively) were determined according to UNE-EN 14105 [31] by gas chromatography. The total glycerin content (% G) was also calculated according to this standard.

2.3. Soap and catalyst content analyses

The soaps and catalyst contents were determined by an acid–base titration method (AOCS Cc17-95 [32] or IRAM 5599 [33]). The biodiesel sample was dissolved in a toluene–ethanol mixture, and titrated with 0.1 N HCl solution, using phenolphthalein as indicator to determine the catalyst concentration, and bromophenol blue for the soaps concentration.

3. Results and discussion

3.1. Catalyst evaluation at different temperatures

Fig. 1 shows results of experiments carried out at 30, 50, 55, 60 and 70 °C using 1.3 wt.% sodium ethoxide (EtONa) and 25 v/v% ethanol (EtOH), after 120 min of reaction time at atmospheric pressure. The alcohol amount corresponds to an ethanol:oil molar ratio of 4.25:1.

The minimum triglycerides content in biodiesel at the end of the reaction (120 min) was obtained at 55 °C, indicating that this is the optimum reaction temperature at atmospheric pressure. At lower temperatures (30 °C–50 °C) the reaction rate is lower, and probably the equilibrium cannot be reached within the reaction time employed. To verify this hypothesis, triglycerides content was measured at 2 and 8 h reaction time. In all cases (30, 55 and 70° C) triglycerides content at 8 h was almost negligible, whereas at 2 h, the values were 1.13, 0.063 and 0.222% at 30, 55 and 70 °C, respectively. These results confirm that the reaction have not reached equilibrium at 2 h reaction time at any temperature in the range 30–70 °C.

Moreover, it was observed that conversion decreased when the temperature was increased from 55 °C to 60 or 70 °C. There are two important effects when increasing the reaction temperature at atmospheric pressure. On one hand, the alcohol concentration in the liquid phase decreases as the temperature is increased, and this leads to a lower
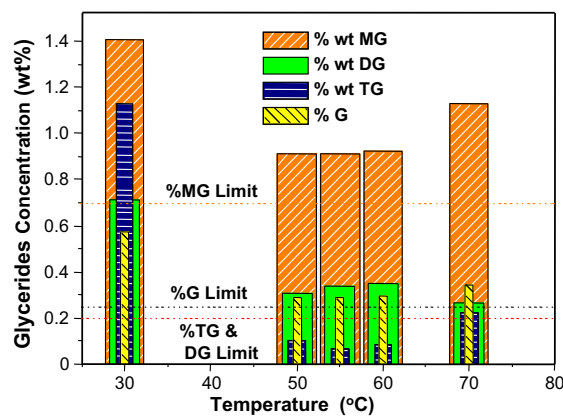

Fig. 1. Mono- (%wt MG), di- (%wt DG), triglycerides (%wt TG) and total glycerin content (% G) at different reaction temperatures. Reaction conditions: 25 v/v% EtOH, 1.3 wt.% EtONa, t = 120 min.

reaction rate. On the other hand, at higher temperatures saponification reactions of both glycerides and ethyl esters are favored, leading to catalyst consumption, which significantly decreases the reaction rate. Table 1 shows the catalyst and soap content (expressed as sodium oleate concentration) at different temperatures at 2 and 8 h of reaction using 25 v/v% EtOH and 1.3 wt.% EtONa.

At higher temperature, the catalyst concentration is lower, and the soap content (sodium oleate) higher. This confirms that the saponification reactions are favored at higher reaction temperature, causing a catalyst concentration decrease in the reaction system. Moreover, if catalyst and soap concentrations are compared at the same temperature but at different reaction times, it can be seen that at lower temperatures (30 °C) the saponification reaction reached equilibrium. On the other hand, at higher temperatures, soaps were formed even after the 2 h reaction time. It is important to note that the presence of soap in biodiesel will bring about complications during the subsequent purification stages.

It can be concluded that there is a temperature range (50–60 °C) where the unreacted material content (MG + DG + TG) at the end of the reaction does not differ significantly. These results are consistent with those observed when the catalyst employed for the sunflower oil ethanolysis was sodium methoxide [11,34]. Moreover, other authors also reported that high reaction temperatures are unsuitable because of forming soaps, when performing the ethanolysis of different vegetable oils [10,25].

It is important to note that in the experiments shown in Fig. 1 it was not possible to obtain the concentrations of mono, di and triglycerides required by the biodiesel quality standards (EN 14214 [27], IRAM 6515-1 [35]). Therefore, experiments using a higher catalyst concentration (1.6 wt.%) while keeping the other parameters constant, were performed. The results are shown in Table 2. There were no significant variations in the mono-, di- and triglyceride contents as a function of the reaction temperature at this catalyst concentration. The most important result is that at this catalyst concentration the conversion was significantly higher than using 1.3 wt.% EtONa, and made it possible to reach the desired conversion values. It can also be seen that when the temperature is increased to 70 °C, saponification reactions are favored (as shown in Table 1) thereby decreasing the conversion. However, in all the experiments shown in Table 2, the percentages of mono-, di- and triglycerides meet the quality standards. Even though the catalyst concentration decreased due to saponification reactions, the remaining concentration of EtONa in the system was enough to achieve the desired conversions.

3.2. Catalyst concentration effect

The conversion obtained in the transesterification reaction using different concentrations of EtONa was evaluated, keeping all the other operating variables constant. For this purpose, 25 v/v% ethanol, 55 °C, and 120 min reaction time were employed. The results obtained are shown in Fig. 2. The catalyst concentration is expressed as g catalyst/100 g of oil.

Fig. 2 shows that conversion increases for higher sodium ethoxide concentration and therefore lower final concentrations of mono-, di- and triglycerides were obtained. This is because, as demonstrated

Table 1
Catalyst and soap contents at different temperatures and reaction times.

Temperature (°C)	Reaction time			
	2 h		8 h	
	% EtONa	% Na Oleate	% EtONa	% Na Oleate
30	0.65	1.41	0.65	1.45
55	0.55	2.05	0.46	2.52
70	0.47	2.38	0.36	3.01

Table 2
Glycerides and total glycerin content at different temperatures. Reaction conditions: 25 v/v% EtOH, 1.6 wt.% EtONa, t = 120 min.

Temperature (°C)	% MG	% DG	% TG	% G
50	0.55	0.18	0.015	0.17
55	0.50	0.16	0	0.15
60	0.40	0.22	0.004	0.13
70	0.57	0.24	0.005	0.18

above, the transesterification reaction did not reach equilibrium in the reaction time employed.

Fig. 3 A and B show the catalyst and soaps concentrations at 120 min reaction time in biodiesel and glycerol rich phases, respectively. The larger the initial amount of EtONa, the higher its concentration at the end of the reaction in the biodiesel phase, which is the phase where the reaction occurs, thus leading to a higher conversion. The physicochemistry of the system is significantly different if methanol is used as alcohol [29]. In this case, the catalyst (sodium methoxide) fraction in the biodiesel phase at the end of the reaction was almost negligible, due to the lower solubility of the catalyst in methanol than ethanol.

Table 3 shows the EtONa contents in biodiesel phase after the reaction. The amounts of catalyst transformed into soap and the amount of EtONa available for reaction were also calculated. It is interesting to note that the fraction of catalyst consumed due to the soap formation reaction decreased as the initial catalyst content increased. It is also important to highlight that the amount of sodium ethoxide transformed into soaps was very similar in all cases, showing a little increase as a function of the initial catalyst concentration. Therefore, the higher the initial catalyst concentration, the higher the net amount available for reaction, and the higher the conversion obtained at a given reaction time. Finally, it was observed that the conversion obtained with 1.6 wt.% of catalyst, was high enough in order to meet the international quality standards (EN 14214 [27], ASTM D-6751-12 [28]).

3.3. Ethanol concentration effect

The effect of varying one of the reactants (ethanol) concentration and its impact on the glyceride conversion was evaluated. The optimal alcohol:oil molar ratio depends on the reaction temperature, the oil, the catalyst type and its concentration. Fig. 4 shows the results obtained at 55 °C, for two different EtONa concentrations.

The amount of non converted glycerides (mono + di + triglycerides) decreased when the initial ethanol concentration increased from 20 to 25 v/v%. These concentrations correspond to 3:1 and 4.25:1 ethanol/oil molar ratio, respectively. Nevertheless, when the ethanol concentration
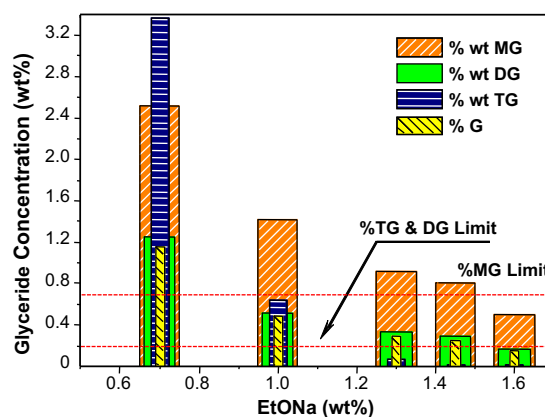
Fig. 2. Mono- (%wt MG), di- (%wt DG), triglycerides (%wt TG) and total glycerin content (% G) at different sodium ethoxide concentrations. Reaction conditions: 25% v/v EtOH, temperature: 55 °C, t = 120 min.
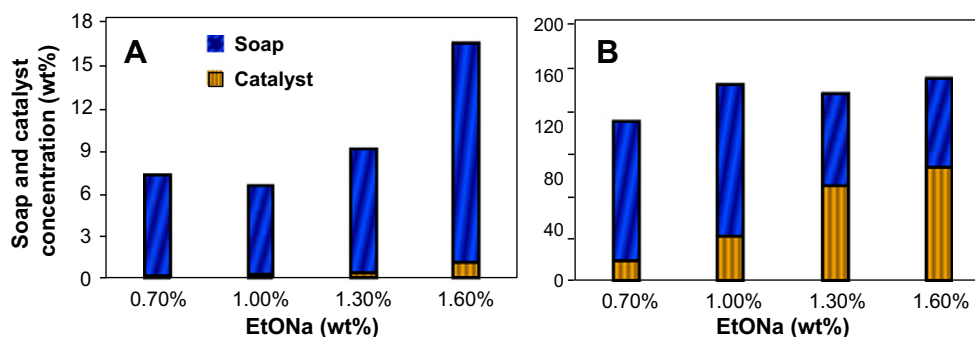
Fig. 3. Catalyst and soap distribution. (A) biodiesel phase; and (B) glycerin phase.

was further increased above 25 v/v%, the conversion decreased. This is because the higher the ethanol volume, the higher the reaction volume, and therefore, the catalyst concentration diminished with the consequent decrease in the reaction conversion.

It can be concluded that the optimum ethanol concentration is 25 v/v% (4.25:1 ethanol:oil molar ratio) for catalyst concentration in the range 1.3–1.6 wt.% and reaction temperature of 55 °C. This is in agreement with other studies reported in the literature, which recommend ethanol:oil molar ratios of 5:1 for the ethanolysis performed at low temperatures, using different vegetable oils [25,36]. Fig. 4 shows that when using 1.6 wt.% catalyst and 25 v/v% ethanol, the total glycerin percentage obtained was 0.15 wt.%, which complies with the international quality standards for biodiesel [27,28].

3.4. Reaction conversion with different alcohols (methanol–ethanol) and catalysts (sodium methoxide–ethoxide)

Fig. 5 shows the monoglycerides (A) and non converted glyceride (B) profiles, during the course of the reaction when MeONa or EtONa was used as catalysts, and methanol or ethanol was used as alcohol. The experiments were carried out under the same conditions, i.e., equal molar concentrations of catalyst and alcohol for each case. Using the same molar concentration of each catalyst, it is possible to compare their intrinsic activity. The catalysts concentration used in these experiments was 23.3 mol%, and correspond to 1.6 wt.% and 1.2 wt.% for EtONa and MeONa respectively. The aim of these experiments was to compare the activity of both catalysts for the production of ethyl and methyl esters.

As shown in Fig. 5 A, the monoglyceride evolution during reaction was very similar for both catalysts when the alcohol used was methanol. However, the maximum concentration observed at low reaction times, was higher for the case of EtONa (%MG: 2.6 wt.%) in comparison to MeONa (%MG: 2 wt.%) which implies that the rate of disappearance of these compounds was higher when the catalyst used was sodium methoxide. Similar behavior was observed when ethanol was used as transesterification alcohol. On the other hand, when MeONa was used to catalyze the ethanolysis, the maximum monoglycerides content

obtained was 4.5 wt.%, whereas the concentration measured for EtONa was 5.5 wt.%. This implies that the sodium methoxide catalyst has higher activity both for methanolysis and ethanolysis than sodium ethoxide, being this difference more pronounced when the alcohol used was ethanol. This is because the longer the carbon chain of the alcohol employed, the lower the reactivity of the alkoxide ion [17,37]. According to Reeve and Erikson [38], methanol is 4.4 times stronger as an acid than ethanol in an equimolar mixture. However, methoxide is less nucleofilic than ethoxide (0.82 times). The combination of these effects gives as a result that methoxide is 3.6 times more reactive than ethoxide. On the other hand, better solubility of ethanol in oil enhances mass transfer as compared to methanol [39]. Moreover, as it was previously discussed in Section 3.2, the phase distribution of the catalyst is more favorable for ethanol than methanol. As a consequence, the difference in reactivity is less pronounced than expected.

In the same experiment it was observed that evolution of di- and triglycerides (not shown) showed a similar pattern, but less marked than for the case of monoglycerides. Fig. 5 B shows the unreacted material percentage (MG + DG + TG) profiles obtained for each reaction. Using methanol as alcohol, in both cases with sodium methoxide and ethoxide, the amount of unreacted glycerides was lower than that observed when the alcohol used was ethanol. These results show an increased reaction rate (disappearance of mono-, di- and triglycerides) for methanolysis than for ethanolysis. Moreover, in both cases (using ethanol or methanol as alcohol) the amount of unreacted glycerides was higher when sodium ethoxide was used.

3.5. Catalyst consumption during ethanolysis. Effect on the conversion

To determine the correlation between the percentage of unreacted glycerides (or catalyst activity), and the type of catalyst and alcohol employed, experiments were conducted under identical conditions to

Table 3
EtONa percentage consumed due to saponification and available for reaction. Reaction conditions: 25 v/v% EtOH, temperature: 55 °C, t = 120 min.

EtONa concentration (wt%) [a]	% EtONa consumed [b]	EtONa consumed (wt%) [a]	EtONa available for reaction (wt%) [a]
0.7	68.9	0.48	0.22
1	47.8	0.48	0.52
1.3	41.3	0.54	0.76
1.6	37.9	0.60	1.00

[a] Relative to the oil mass (g EtONa/100 g oil).
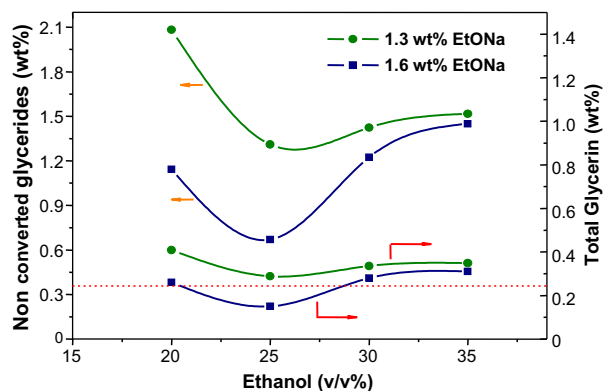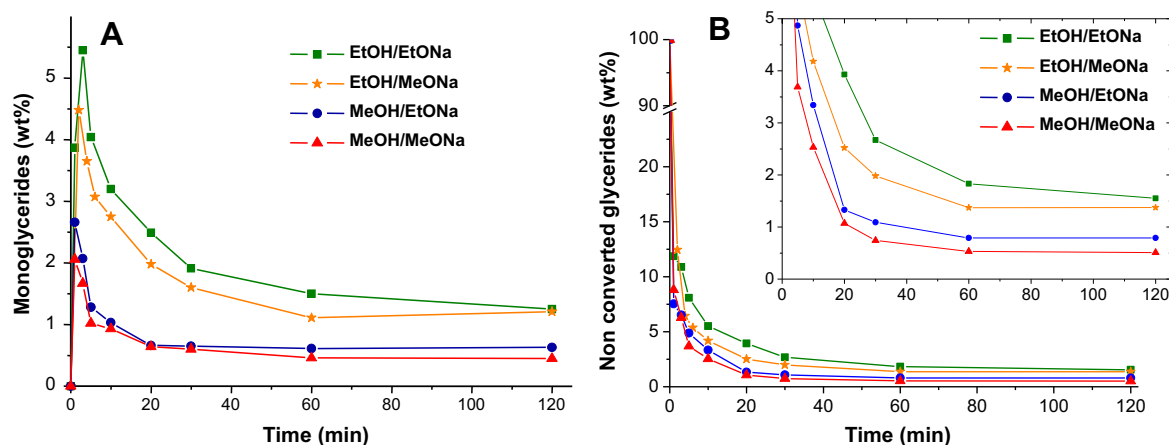[b] Relative to the initial EtONa mass.

Fig. 4. Non-converted material and total glycerin at different ethanol concentrations. Reaction conditions: temperature: 55 °C, t = 120 min.

Fig. 5. (A) Monoglycerides, and (B) Non-converted glycerides concentration vs time using different alcohols (methanol and ethanol) and catalysts (sodium methoxide and ethoxide). Reaction conditions: temperature: 55 °C, alcohol/oil molar ratio: 4.25/1, catalyst concentration: 23.3 mol% (corresponding to 1.2 wt.% MeONa and 1.6 wt.% EtONa).

those described in the previous section, determining the variation of the total concentration of catalyst with time. Catalyst consumption is shown in Fig. 6. According to these results, there is a correlation between the moles of catalyst consumed due to saponification and the activity shown in Fig. 5. The higher reaction rate was observed when MeONa was used as catalyst and methanol as alcohol. Fig. 6 shows that in this experiment, the catalyst concentration measured at 120 min of reaction was 16.31 mol%, whereas the initial catalyst concentration was 23.3 mol%. Therefore, the percentage of catalyst that disappeared was only 30% of the initial concentration, this being the smallest value observed among the experiments carried out to compare different catalysts and alcohols. Even more, it can be seen that such catalyst consumption occurred in the first few minutes of reaction and then the concentration became stabilized and remained constant until the end of the reaction. This allows the reaction system to have a high catalyst concentration during the course of the transesterification, thus increasing the reaction rate. When EtONa and ethanol were used, the percentage of unreacted glycerides was the largest, which implies the lowest reaction rate. This correlates well with the results presented in Fig. 6, which shows that 69% of the sodium ethoxide catalyst disappeared during the reaction with ethanol (final catalyst concentration: 7.08 mol%; initial catalyst concentration: 23.3 mol%). Furthermore, according to the data presented in Fig. 6, it can be calculated that at 3.5 min of reaction, only 48% of the dosed catalyst remained in the

reaction mixture EtONa/EtOH, while the remaining catalyst at the same time in the mixture MeONa/MeOH was 75%. This demonstrates that the reaction rate is not only affected by steric hindrance for the longer chain alcohol, but also is greatly affected by the catalyst disappearance. This is due to the less polar character of ethanol, which favors the saponification reactions during the transesterification to a greater extent than methanol. It can also be seen in Fig. 6 that using the same alcohol, either methanol or ethanol, sodium ethoxide showed greater tendency to form soaps than sodium methoxide, which is in agreement with its lower activity under identical conditions.

Finally, similar catalyst concentrations were measured at the end of the reactions carried out with MeONa/EtOH or EtONa/MeOH. However, during the first 60 min of reaction it can be seen that the catalyst concentration in the experiment using EtONa/ MeOH decreases slower than for the case of the mixture MeONa/EtOH. This behavior is reflected in Fig. 5 B, because the reacting system EtONa/MeOH presents a higher reaction rate (lower amount of unreacted glycerides) than the system MeONa/EtOH.

It can be concluded therefore, that the alcohol used has more influence on the reaction conversion than the catalyst, methanol being more reactive than ethanol, and sodium methoxide more active than the ethoxide.

3.6. Mass balance and biodiesel quality

Experiments were carried out to determine the ethyl esters yield of the ethanolysis reaction, when using the EtONa (21 wt.%)/ethanol solution as catalyst. In a previous work [34] it was shown that when a methanol solution of MeONa 30 wt.% was used as catalyst for ethanolysis, approximately 80% ethyl esters and 20% methyl esters were obtained. The mass balance experimentally obtained, showed that for 100 g of oil, 104 g of the methyl/ethyl esters mixture was obtained. When using the EtONa solution as catalyst, it was found that for 100 g of oil used as raw material, 105 g ethyl esters were obtained. This yield increase is because the reaction medium is free from methanol and therefore, only ethyl esters were formed. The molecular weight of ethyl esters is higher, therefore, the reaction yield (mass biodiesel obtained/oil mass) increases from 104% (methyl/ethyl esters mixture) to 105% (ethyl esters only). On the other hand, if the alcohol employed is methanol and the catalyst a solution of sodium methoxide, as commonly occurs in the biodiesel industry, the maximum yield that could be obtained would be 100% (g methyl esters/g oil). Therefore, the production increase obtained by generating ethyl instead of methyl esters, if extrapolated to large scale, has a significant impact on the economy. It is important to note that the proposed process has no significant
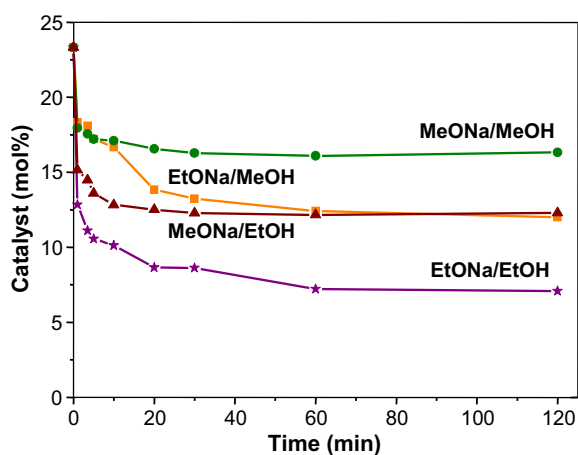
Fig. 6. Catalyst concentration vs time using different alcohols (methanol and ethanol) and catalysts (sodium methoxide and ethoxide). Reaction conditions: temperature: 55 °C, alcohol/oil molar ratio: 4.25/1, catalyst concentration: 23.3 mol%.

differences with the processes currently used on the large scale plants, which makes it an interesting alternative for biodiesel production.

Table 4 presents the properties of the ethyl ester sample obtained in the conditions of maximum conversion (55 °C, 25 v/v% ethanol and 1.6 wt.% EtONa). It should be remarked that the biodiesel produced meets the standards required by international regulations. However, taking into account the parameters related to the reaction conversion (%MG, %DG, %TG, %G), it must be mentioned that in order to accomplish the standard requirements it was necessary to use a high catalyst amount, which increases substantially the process cost. This problem can be solved by using the strategy of two-stage reaction [34]. This process allows obtaining similar conversion using a lower proportion of catalyst.

The biodiesel acidity is a property that strongly depends on the process sequence. The acid value of the obtained ethyl esters was 0.12% (0.24 mg KOH/g), although the soap content of the biodiesel phase at the beginning of the purification (after decanting) was 1.75% (expressed as g sodium oleate/100 g biodiesel). Taking into account this high soap content, it would be expected to obtain an acid value of 1.9% approximately, for a biodiesel treated with the conventional washing with hydrochloric, phosphoric or citric acid. However, the value obtained was much lower, because a different purification technique was used, which was previously developed [30]. This strategy comprises a first washing with a small volume of neutral water and a second washing with water saturated with CO_2. Other properties that depend on the type of ester (methyl or ethyl ester) and thus the alcohol and the catalyst used in the transesterification are the cloud and pour point. Because the biodiesel obtained is entirely composed of ethyl esters, the cloud and pour points measured are −2 °C and −10 °C, respectively. These are lower values than those observed in mixtures 20% methyl/80% ethyl esters, obtained using MeONa and ethanol for the biodiesel production, where the observed values were 1.5 °C and −7 °C, respectively. This is a major advantage, especially in cold climates, avoiding filters plugging or even fuel solidification in the fuel tank and pipes of the automobile. Another property that improves when the biodiesel is composed of ethyl instead of methyl esters is the iodine value. The iodine value measures the insaturation of the fuel, and a high value of this property is related with the tendency to polymerisation and formation of deposits in the injection nozzles and the piston rings. The iodine value of the ethyl ester sample obtained in this work was 114.2, whereas the corresponding to methyl esters (produced in similar conditions) was 130.5.

Table 4
Properties of the ethyl esters.

Property (units)	Ethyl esters	EN-14214	ASTM-D 6751
Density (kg m^{-3})	881	860–900	–
Viscosity (mm^2 s^{-1}) (40 °C)	4.7	3.5–5.0	1.9–6
Carbon residue (%)	3.67 10^{-3}	≤0.050	≤0.050
Pour point (°C)	−10	–	–
Cloud point (°C)	−2	–	Report
Acid number (mg KOH/g)	0.24	≤0.50	≤0.50
Monoglycerides (wt %)	0.50	≤0.70	–
Diglycerides (wt %)	0.16	≤0.20	–
Triglycerides (wt %)	0	≤0.20	–
Total glycerine (wt.%)	0.15	≤0.250	≤0.240
Free glycerine (wt.%)	0	≤0.020	≤0.020
Iodine value	114.2	≤120	–
Oxidation stability (h)	>6	≥6	≥3
Esters content (wt.%)	98.8	≥96.5	–
Phosphorus (mg/kg)	0	≤10	≤10
Flash Point (°C)	163	≥120	≥130
Sulfur (mg/kg)	0	≤10	≤15
Water (mg/kg)	180	≤500	0.050 vol.% (water and sediment)
Cetane number	51	≥51.0	≥47.0
Methanol content (wt.%)	0	≤0.20	≤0.20

4. Conclusions

The transesterification reaction of sunflower oil and ethanol using sodium ethoxide as catalyst was studied. It was observed that increasing the catalyst concentration the reaction conversion increases, due to a combination of effects: on one hand, in the reaction time employed, the reaction does not reach equilibrium, and hence the conversion measured at a certain reaction time is higher for a higher catalyst concentration. Given that in this phase is where the reaction occurs, the greater catalyst availability leads to an increase in conversion.

It was found that the maximum conversion is reached when the reaction temperature is 55 °C. At lower temperatures, the reaction rate is lower, and cannot reach equilibrium within the reaction time employed. Moreover, at higher temperatures saponification reactions of both glycerides and ethyl esters are favored, which consume the catalyst, decreasing the reaction rate. Furthermore, it was concluded that the methanolysis reactions are faster than the ethanolysis and sodium methoxide catalyst is more active than the corresponding ethoxide. This is due to two factors: first, the steric hindrance and secondly, that the saponification of EtONa in ethanol medium is greater than when using methanol, causing a decrease in the catalyst concentration and leading to lower conversion. Finally, using 25 v/v% ethanol and 1.6 wt.% sodium ethoxide at a temperature of 55 °C and 120 min reaction time, it is possible to obtain a product which conversion complies with international standards of quality.

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