



Optimization of biodiesel production process using sunflower oil and tetramethyl ammonium hydroxide as catalyst



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HIGHLIGHTS

- Tetramethyl ammonium hydroxide (TMAH) is a good catalyst for the transesterification reaction.
- It is possible to obtain biodiesel with the quality specified in the EN 14214.
- The soap formation is similar to that observed with other hydroxides.
- The soap formation is considerably higher than that observed with sodium methoxide.
- TMAH favors the concentration of mono and diglycerides in the glycerin.

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ABSTRACT

In this work, the biodiesel production process by transesterification of sunflower oil was investigated using tetramethyl ammonium hydroxide (TMAH) as catalyst. The reaction conditions, such as catalyst concentration, temperature and reaction time were optimized in order to obtain a product that fulfills the quality requirements of international standards. It was found that the optimum reaction conditions were: temperature 60 °C, 1.76 wt% TMAH catalyst and 2 h reaction time. High amount of soaps were formed when using this catalyst. Therefore, an alternative purification methodology was used, especially useful for samples with high soaps content. This procedure consists of a first extraction stage using neutral water, which efficiently remove soaps. TMAH increases the solubility of mono and di-glycerides in the glycerine phase, thus decreasing their concentration in the biodiesel phase. Consequently, for a given production of mono- and di-glycerides, lower amount of these compounds were found in the final biodiesel product, being this an important advantage of this catalyst.

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1. Introduction

In recent years, increased attention has been given to biofuels, such as biodiesel, that can be used as an alternative fuel in compression-ignition engines. This fuel has many advantages with respect to petroleum-based fuel, namely, it is biodegradable, non-toxic, renewable, and it contributes to the reduction of CO₂ emissions, because it comprises a closed carbon cycle, and produces lower soot emissions in the tail-pipe exhaust gases [1,2].

Biodiesel is defined as fatty acid alkyl esters, which are typically produced by the transesterification of vegetable oils or animal fats with methanol or ethanol in the presence of a suitable catalyst. During the reaction, the triglyceride is sequentially converted into a diglyceride, monoglyceride and glycerine; 1 mol of ester being produced in each step.

Four groups of feedstock can be defined for biodiesel production [3]: edible and non-edible vegetable oils, animal fats, waste cooking oils and algal oils, which have been emerging in recent years as a feedstock of increasing interest because of their high oil content and rapid biomass production [4,5]. The vegetable edible oils such as soybean, rapeseed, sunflower or palm oil, are the main and more conventional feedstock for biodiesel production. However, their large demand as food and high prices has encouraged the use of non-edible oils as alternative feedstock. More than 26 plants species containing non-edible oil in their seeds were reported by Azam et al. [6] as potential sources for biodiesel synthesis. In addition to vegetable oils, animal fats can also be used for biodiesel production, having the advantage of a lower price. However, there exists the limitation of their availability, and consequently they will never be enough to replace vegetable oils. Another disadvantage is the higher melting point, and could complicate their processing and use [7]. Used cooking oils are priceless or at least cheaper than fresh vegetable oils, making them an interesting alternative as triglycerides source for biodiesel synthesis [8].

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However, these waste oils are usually contaminated by many types of impurities from the cooking process (polymers, free fatty acids) and their conversion to biodiesel could be complicated [9]. In recent years, biodiesel production from microalgae has received growing attention. Microalgae would offer various advantages such as: much higher biomass productivities than land plants, some species can accumulate up to 20–50% triglycerides; no agricultural land is required to grow the biomass and they required only sunlight and a few nutrients [10].

The transesterification reaction can be catalyzed both by homogeneous and heterogeneous catalysts. In general, the heterogeneous catalyzed biodiesel production processes have less number of unit operations; with simple product separation and purification steps [11]. The heterogeneous transesterification catalysts can be categorized into three main groups: acid, basic or bifunctional (acid-basic character) solids. In general, solid base catalysts are more active than solid acid catalysts, requiring relatively shorter reaction times and lower reaction temperatures [12]. However, solid acid catalysts have several advantages over solid base catalysts such as for example, that the reaction is less affected by the presence of water and free fatty acids [13]. New trends are oriented toward the search of new solid catalysts that can simultaneously carry out esterification and transesterification reaction steps, i.e., solid catalysts with combined acid and basic properties. Nevertheless, in general, heterogeneous catalysts for biodiesel synthesis are not able to achieve the conversion levels required, or need strong reaction conditions or extremely long reaction times, excluding them for their industrial application.

Currently, due to their simple usage and less time required for oil conversion, homogeneous catalysts dominate the biodiesel industry. These include alkalis and acids, being the basic catalysts the most commonly used, since the process is faster at mild reaction conditions [14]. However, their utilization in vegetable oil transesterification produces soaps due to the neutralization of the free fatty acids initially present in the oil and by triglyceride saponification that occurs when water is present in the reaction system [15]. In addition, the presence of water in the system generates further problems in the transesterification, because at high temperatures it can hydrolyze the triglycerides, producing fatty acids. Both, water and fatty acids produce a negative synergetic effect, because they partially consume the catalyst, decrease the biodiesel yield and generate soaps, complicating the separation and purification steps. Therefore, base catalyzed transesterification needs a high purity feedstock.

The most commonly used alkali catalysts are sodium and potassium hydroxides and methoxides. Many authors [15–17] have reported comparative studies between these four catalysts. However, such studies were performed using the same mass percentage of catalysts that have very different molar weights. Therefore, the results cannot be compared from a kinetic point of view. Pisarello [18] used the four alkali catalysts in the same molar concentration. The results showed that the sodium catalysts are more active than the potassium ones, and in turn, the methoxides are more active than the hydroxides [18]. From a large scale industrial production point of view, biodiesel manufacturing by homogeneously catalyzed transesterification reaction shows the disadvantages of high production costs, as the process involves washing and purification steps, and it is quite difficult to remove K and/or Na traces remaining in the biodiesel product [19]. Despite these drawbacks, currently, in large scale facilities, the sodium methoxide is exclusively used as catalyst, given its high activity at moderate reaction conditions.

The tetramethyl ammonium hydroxide (TMAH) is a strong base that constitutes an interesting alternative to the conventional alkaline homogeneous catalysts for biodiesel production. This would be specially useful in the eventual situation of a price raise or shortage of the sodium methoxide, which, as it was previously mentioned, is

the main catalyst used in the biodiesel industry. Moreover, the methyl esters obtained in these conditions would be free from Na or K, which makes them especially interesting for their potential use in turbines as fuel for electric energy generation [20]. In this application, the limit established for sodium plus potassium is 0.5 ppm, i.e. one order of magnitude lower than in the case of using the biodiesel in diesel engines. Conventional processes based on sodium methoxide do not meet this specification; therefore, the use of a catalyst such as the TMAH is an interesting alternative. In addition, the glycerine would be also free from salts, if the catalyst could be eliminated by heating. The tetramethyl ammonium hydroxide has been used as catalyst for the transesterification of cottonseed oil and used frying oil as raw materials [21]. In this work [21], the effects of methanol:oil ratio and catalyst concentration on the transesterification reaction were addressed. The effect of the reaction temperature, and the study of the other process stages, such as phases separation and biodiesel purification were not addressed. It was found that high quality methyl esters could be obtained, especially when the semi-refined cottonseed oil was used as feedstock. Lower ester yields were achieved with waste oil, which were attributed to amide formation during the transesterification reaction. Almost all glycerides were converted into esters and remained below the EN 14214 limits with a catalyst amount of 2.5 wt% or higher for cottonseed oil, and a catalyst concentration higher than 3% for used oil. Non-ionic bases have been used for vegetable oil transesterification. The catalytic behavior of guanidines, amidines and triamino(imino)phosphoranes has been reviewed by Schuchardt et al. [22]. The guanidines showed good activity with low soap formation, although the ester yield was 93% for a catalyst concentration of 3 mol%. Other guanidines displayed lower conversions. Different amines, including the TMAH were studied by Cerce et al. [23], and found that this catalyst displayed a better catalytic performance than the other amines (e.g. diethylamine, dimethylethanolamine, tetramethyldiaminoethane). However, Cerce et al. [23] showed only one experiment carried out with TMAH, using a 8.7:1 methanol:oil ratio, at 60 °C. Recently, a patent [24] reported in the use of TMAH but using co-solvents, such as tetrahydrofuran and acetone, being this an option that complicates the process design and the production costs. Tang et al. [25] also studied these amines, but in supercritical methanol and a continuous tubular-flow reactor, finding problems due to the poor mixing achieved in this configuration. Karavalakis et al. [26] studied the tetramethylguanidine as catalyst for transesterification of waste frying oil and semi-refined cottonseed oil, obtaining good results mainly with the latter.

TMAH was used to transesterify triglycerides with analytical purposes, but using reaction conditions different from those used in a commercial process [27,28]. In addition, it was considered as catalyst in order to analyze the economics of the biodiesel production process, but without including information regarding its catalytic behavior [29].

The objective of this work was to optimize the biodiesel production process using sunflower oil and tetramethyl ammonium hydroxide (TMAH) as catalyst, specially aiming to its application in the large scale industry. Therefore, the whole production process was analyzed, from the reaction stage to the quality of the final biodiesel obtained, in order to assess the possibility of using this catalyst at industrial level. The possibility of obtaining the glycerine free from salts was also explored.

2. Experimental

2.1. Materials

In order to avoid or minimize soaps formation, refined sunflower oil was used, with acidity lower than 0.02 wt% (g oleic

acid/100 g sample). Methanol p.a. (Cicarelli) with a water content of 345 ppm was used. This implies that all the soaps formed are due to the water content of both methanol and catalyst. The catalyst used was a solution of tetramethyl ammonium hydroxide 25 wt% (TMAH 25M) in methanol, provided by Sachem Chemicals. The water content, measured by the Karl–Fischer volumetric method, was 2.2 wt%. It is important to highlight that this concentration is considerably higher than the water content of sodium methoxide. Nevertheless, the commercial product contains approximately 6% water, and with this material, the conversion was much lower than with the TMAH containing 2.2 wt% water. The latter was especially prepared by Sachem Corporation in order to decrease the water content and consequently, improve the catalytic behavior. The Karl–Fischer method used to determine the water content gives wrong results if the pH is too high. Consequently, a conventional modification to this method is to add glacial acetic acid (or benzoic acid) to neutralize the OH⁻ ions. Then, the Karl–Fischer analysis is carried out, taking into account the amount of water form by neutralization.

2.2. Transesterification reaction conditions

The reaction was carried out in a 0.5 L flask, with magnetic stirring, using a 50 mm teflon-coated magnetic bar and vigorous agitation (800 rpm). Reaction temperature was varied between 45 and 70 °C, and reaction time was in all cases 2 h. The catalyst concentration was varied from 1.09 to 2.72 wt% (g TMAH/100 g oil). The total methanol content was 25 vol% relative to the oil (25 mL methanol/100 mL oil), taking into account both the pure methanol and the methanol loaded with the catalyst. This amount corresponds to a molar ratio alcohol/oil 6:1.

The oil was first loaded into 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. The addition of the alcohol–catalyst mixture was carried out within a time range of 3–5 s, taking as zero time the moment at which all the mixture was transferred to the reaction vessel.

2.3. Biodiesel purification

In the typical procedure, the phase rich in biodiesel was purified by two consecutive steps, using HCl 5 wt% aqueous solution in the first step and distilled water in the second. In both cases, the aqueous phase represented 30 vol%, relative to the biodiesel phase. Both extraction stages (commonly called biodiesel washing), were carried out with gentle agitation at 60 °C, during 15 min. Afterwards, the biodiesel was dried by stripping with nitrogen at 80 °C. An alternative purification treatment was also tested, which included two consecutive washing stages using neutral water and water acidified with CO₂ in the first and in the second stages respectively. Additional details of this procedure are given in Section 3.2.

2.4. Total glycerine analysis

The total glycerine is a biodiesel quality parameter that is related to the non-converted amount of mono-, di-, and triglycerides, and the free glycerine, as indicated in the EN14105 standard. It represents the amount of glycerine present in the system, both as free glycerine and as bound glycerine forming the unreacted mono, di, and triglycerides compounds. The total glycerine analysis was performed using both, the GC procedure and a method previously developed [30], especially useful for samples obtained from alternative raw materials and high total glycerine content, since this method has no limitations regarding the analysis range and the raw material. In this procedure, the total glycerine content was obtained after all the glycerides, i.e. mono-, di- and triglycerides, were

quantitatively transformed into methyl esters and glycerine by transesterification. Afterwards, the glycerine was extracted first with acidified water, and then with water. Finally, glycerine was titrated according to standard procedures. This method is very sensitive, and it was possible to perform the total glycerine determination with 50 g of sample or less.

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

The glycerine titration was based on its oxidation to formic acid using sodium periodate, followed by a titration with sodium hydroxide. Details of this technique can be found elsewhere [30].

2.5. Analytical methods

Several parameters were evaluated in order to assess the biodiesel quality, according to international standard methods. The following properties were determined: (i) water content, by the coulometric Karl Fischer titration method (UNE-EN ISO 12937); (ii) soap and catalyst content, according to IRAM 5599; (iii) mono-, di-, and tri-glycerides content, according to UNE-EN 14105; (iv) total esters content, according to UNE-EN 14103; (v) acid value, according to UNE-EN 14104; (vi) methanol content, according to UNE-EN 14110; (vii) total solid residue, according to UNE-EN 12662; (viii) ash content, according to ASTM D 482; (ix) sulfated ash content, according to ASTM D 874; and (x) cold soak filterability, as described in ASTM D7501.

2.6. Catalyst removal from the glycerine phase

After phase separation, the glycerine was heated under vacuum in order to eliminate the catalyst by evaporation. The temperature was 160 °C, and the treatment was applied for 2 h.

3. Results and discussion

3.1. Transesterification reaction. Effect of reaction variables on glycerides conversion

3.1.1. Catalyst concentration

Fig. 1 shows the total glycerine content of biodiesel obtained in reactions carried out with different catalyst concentrations. As the catalyst concentration increased, the total glycerine content reached a minimum. Therefore, there is an optimal catalyst concentration in relation to the acylglycerides conversion. This

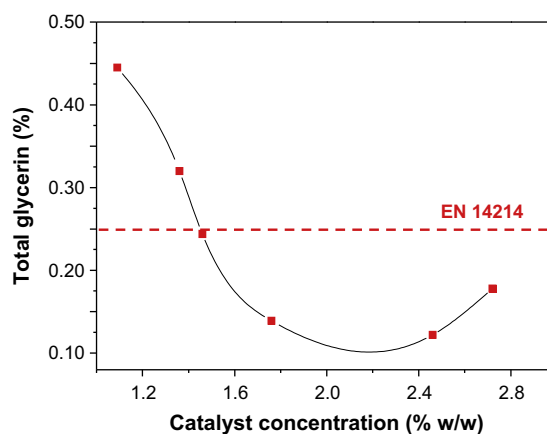


Fig. 1. Total glycerine content vs. catalyst concentration (wt% with respect to oil). Reaction conditions: temperature 60 °C; methanol/oil 25 vol% (6:1 molar ratio); reaction time 120 min.

behavior has also been observed when using conventional catalysts, such as sodium methoxide [31]. With high catalyst concentration, saponification reaction occurs in a higher extent, with the consequent inhibitor effect in the transesterification reaction.

According to EN-14214 standard, the total glycerine content must be lower than 0.25 wt%. The results obtained showed that using tetramethyl ammonium hydroxide as transesterification catalyst, it was possible to obtain good conversion levels, reaching total glycerine contents within the range established by the international standard. The total glycerine varied little for catalyst concentrations between 1.75 and 2.5 wt%, being 0.14 wt% approximately, well below the limit. Therefore, in order to decrease the catalyst consumption, it was adopted for other experiments, a TMAH concentration of 1.76 wt%. The conversion evolution with time was studied using this value and also a lower catalyst concentration (1.09 wt%) which, according to the results presented in Fig. 1, was not enough to obtain a final total glycerine value lower than 0.25 wt%. Karavalakis et al. [21] found lower activity for the TMAH. Using the same methanol:oil molar ratio as in this work, a high catalyst concentration (approximately 3 wt%) was needed to reach mono-, di- and tri-glycerides concentration according to the EN 14214 standard. It is likely that the water content in the TMAH solution used by Karavalakis et al. [21] was higher than that used in this work, although it was not reported. In preliminary experiments, we found that the TMAH as provided, had a low activity and a poor ester yield, due to a high water concentration, which was approximately 6 wt%.

Figs. 2 and 3 show the evolution of mono-, di- and tri-glycerides as a function of time. It can be seen that with the higher catalyst concentration, the triglycerides were converted at a higher rate, specially at the beginning of the reaction (Fig. 2). Table 1 presents the values obtained at the end of the reaction (120 min), as well as the limit values established by the standard EN-14214. Using the lower catalyst concentration, the conversion reached after 2 h reaction corresponded to a total glycerine content higher than 0.25 wt%. Nevertheless, the monoglycerides were within the range of the standard, whereas the diglycerides were slightly higher.

Table 2 shows the mono-, di- and triglycerides content of biodiesel samples synthesized using sodium methoxide and TMAH as catalysts. In each case, the reaction conditions were selected in order to obtain similar triglycerides contents between samples produced with the two different catalysts. In all cases, the mono- and di-glycerides were lower for the biodiesel obtained using TMAH. In order to explain this phenomenon, the glycerides distribution between the methylester rich phase and the glycerine rich phase was investigated. The samples of the glycerine phase had

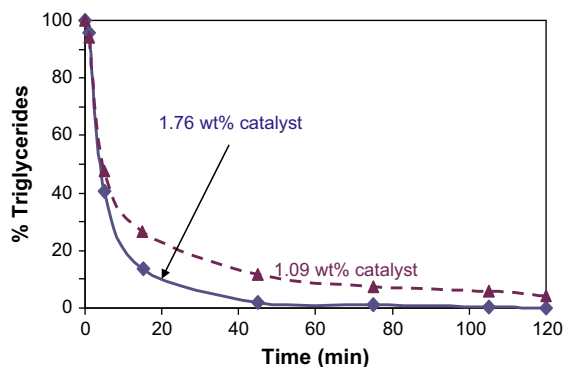


Fig. 2. Triglycerides concentration measured during the transesterification reaction using two different catalyst concentrations (wt% with respect to oil). \blacktriangle : 1.09 wt% catalyst; \blacklozenge : 1.76 wt% catalyst. Reaction conditions: temperature 60 °C; methanol/oil 25 vol%; reaction time 120 min.

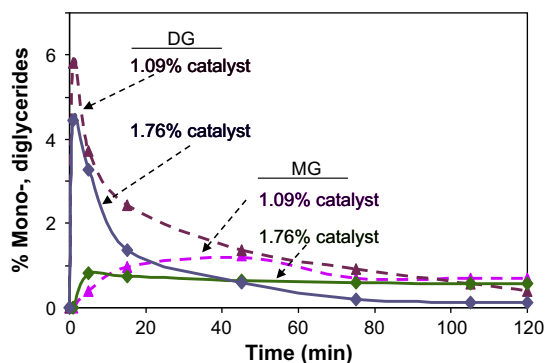


Fig. 3. Mono- and diglycerides concentrations (MG and DG, respectively) measured during the transesterification reaction using two different catalyst concentrations (wt% with respect to oil). \blacktriangle : DG, 1.09 wt% catalyst; \blacklozenge : DG, 1.76 wt% catalyst; \blacktriangle : MG, 1.09 wt% catalyst; \blacklozenge : MG, 1.76 wt% catalyst; Reaction conditions: temperature 60 °C; methanol/oil 25 vol%; reaction time 120 min.

Table 1

Mono-, di- and triglycerides content at the end of the transesterification reaction with different catalyst contents.

Catalyst	% MG	% DG	% TG
1.09% TMAH	0.7	0.4	4.21
1.76% TMAH	0.58	0.12	0.08
EN 14214 standard	0.8	0.2	0.2

Table 2

Mono-, di- and triglycerides content at the end of the transesterification reaction with sodium methoxide and TMAH as catalysts, with different catalysts concentrations. Temperature: 60 °C; 120 min reaction time.

Catalyst	Catalyst concentration		% TG	% DG	% MG
	mol cat./L oil	wt%			
CH ₃ ONa	0.066	0.40	1.23	0.55	0.77
TMAH	0.133	1.36	1.40	0.24	0.53
CH ₃ ONa	0.057	0.35	4.29	1.05	0.82
TMAH	0.106	1.09	4.21	0.40	0.73
CH ₃ ONa	0.049	0.30	5.97	1.61	1.03
TMAH	0.094	0.96	5.51	0.87	0.76

Table 3

Mono-, di- and triglycerides content in methylester and free-fatty acid rich phases at the end of the transesterification reaction, with sodium methoxide and TMAH as catalysts.

Catalyst	Methylester phase			Free-fatty acid phase ^a		
	MG	DG	TG	MG	DG	Acidity
CH ₃ ONa, 0.4 wt%	0.77	0.55	1.23	0.81	0.12	77
TMAH, 1.5 wt%	0.42	0.2	1.06	4.59	0.31	84

^a Obtained by acidification of the glycerine-rich phase.

to be acidified using diluted HCl before analysis, in order to transform soaps into fatty acids. Two phases were formed, a lighter non-polar one (esters, glycerides, fatty acids, and other non-polar substances) and a heavier polar phase (glycerine, water, salts, and other polar substances). Then, the non-polar phase was analyzed by the same GC method as the ester phase, according to EN-14105 [32]. The results obtained are presented in Table 3. As discussed above, for two samples with similar triglycerides content, the mono- and diglycerides concentrations in the methylester rich phase were lower when the biodiesel was produced using

TMAH as catalyst. However, in the free-fatty acid rich phase, the mono- and diglycerides were significantly higher for the TMAH corresponding sample. Therefore, it is concluded that the distribution of the glycerides between the two phases obtained after the transesterification reaction was very different when tetramethyl ammonium hydroxide or sodium methoxide were used as catalysts. The former one favors the distribution equilibrium of mono- and diglycerides towards the glycerine phase, thus decreasing its concentration in the methylester phase. Taking into account that the specification of mono-glycerides content on biodiesel is under discussion since these compounds primarily affects the cold flow properties, these results are very interesting. Moreover, it is probable that its concentration in the biodiesel be lowered in order to improve the fuel properties.

3.1.2. Temperature

Table 4 shows the mono-, di-, and triglycerides and the total glycerine content of biodiesel samples obtained at different reaction temperatures. The total glycerine values are also depicted in Fig. 4, where it can be clearly observed that the conversion was maximized (minimum total glycerine) at 60 °C. Moreover, according to the values presented in Table 4, the triglycerides contents of samples obtained at 55, 65 and 70 °C were above the limit value established by the EN-14214 standard, despite the total glycerine values of these samples were within the standard range. Thus, for the reaction conditions employed, the optimal reaction temperature was 60 °C.

As mentioned before, for temperatures higher than 60 °C, the conversion decreased. This behavior has also been observed in transesterification reactions using conventional catalysts, such as sodium hydroxide [33] and methoxide [34]. At lower temperatures, the reaction rate is slow, thus leading to lower conversion at a given reaction time. On the other hand, when temperature is increased above 60 °C, the methanol concentration in the liquid phase is too low to compensate the higher kinetic constant. This leads to a lower reaction rate and to samples with lower conversion values.

3.2. Purification stage. Saponification reaction

During triglycerides transesterification with basic catalysts, the saponification reaction takes place, producing an undesirable effect due to the soap formation, decreasing the conversion level and complicating the purification steps. Thus, it is important to determine the amount of soaps formed for a given set of reaction conditions.

Table 5 compares the soaps concentration measured in the methylester and glycerine phases after transesterification reaction with TMAH and with other catalysts commonly used for biodiesel production. For comparative purposes, the reactions were carried out using the same molar concentration of catalysts. As it can be seen, when TMAH was employed, the soaps concentration in both phases was considerably higher than that obtained with sodium methoxide. Nevertheless, the values obtained with TMAH are

Table 4

Conversion (mono-, di-, triglycerides and total glycerine content) at the end of transesterification, at different reaction temperatures. Reaction conditions: 1.76 wt% TMAH; methanol/oil 25 vol%; reaction time 120 min.

Temperature (°C)	MG wt%	DG wt%	TG wt%	Total glycerine wt%
45	0.54	0.23	1.44	0.32
55	0.39	0.18	0.66	0.19
60	0.44	0.12	0.08	0.14
65	0.46	0.14	0.23	0.16
70	0.44	0.19	0.73	0.21
EN-14105	0.8	0.2	0.2	0.25

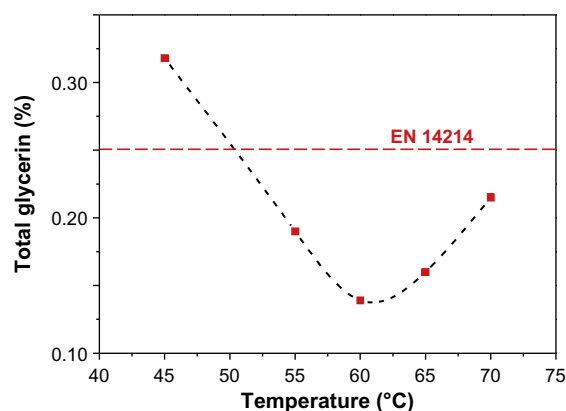


Fig. 4. Total glycerine content vs. temperature. Reaction conditions: catalyst concentration 1.76 wt% with respect to oil; methanol/oil 25 vol%; reaction time 120 min.

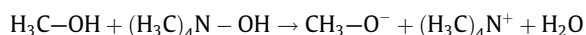
Table 5

Soaps content (g_{oleate}/kg sample) in methylester and glycerine phases at the end of the transesterification reaction of refined sunflower oil with different catalysts. Reaction conditions: temperature 60 °C, 0.019 mol catalyst/100 g oil; methanol/oil 25 v/v%; reaction time 120 min.

Catalyst	Soaps (g_{oleate}/kg) methylester	Soaps (g_{oleate}/kg) glycerine
TMAH	3.60	103.02
KOH	2.58	135.70
NaOH	4.09	113.86
CH ₃ ONa	0.98	22.96

similar to those measured for the other hydroxides. This is another important observation, and represents a disadvantage of the TMAH catalyst compared to the sodium methoxide since as above mentioned, the production of soaps is accompanied by catalyst consumption, yield loss, and problems during the purification stages.

The dissolution of hydroxides in the alcohol leads to the formation of the alkoxide, which is the compound that acts as catalyst, and water. The reaction that takes place when using tetramethyl ammonium hydroxide and methanol is the following:



According to this, one mol of water is generated by each mol of catalyst that is formed. The high soaps concentration obtained when any of the hydroxides was used as catalyst is thus attributed to the presence of water, that promotes the saponification reaction. The presence of water leads to the following problems: (i) decreases conversion, since the catalyst is consumed in soaps formation; (ii) decreases yield, since a certain amount of raw material (triglycerides) is transformed into soaps (oleates) instead of methyl esters; and (iii) the high soaps content in the methylester phase leads to a final product with high acidity, in some cases above the limit value. This is because the conventional biodiesel washing treatments employ acids (e.g. phosphoric or hydrochloric), which transform the soaps into fatty acids, which are soluble in the biodiesel phase. This can be avoided by using a special purification treatment, which will be discussed below.

An alternative washing methodology was previously developed [34], especially useful for samples with high soaps contents. This method consists of two stages: a first washing with a small amount of neutral water (7–10 vol%), followed by a second one with water saturated in CO₂. The neutral washing process is described in detail in patent AR 076851 A1 [35]. By using this treatment, two common problems derived from samples with high soaps content could be

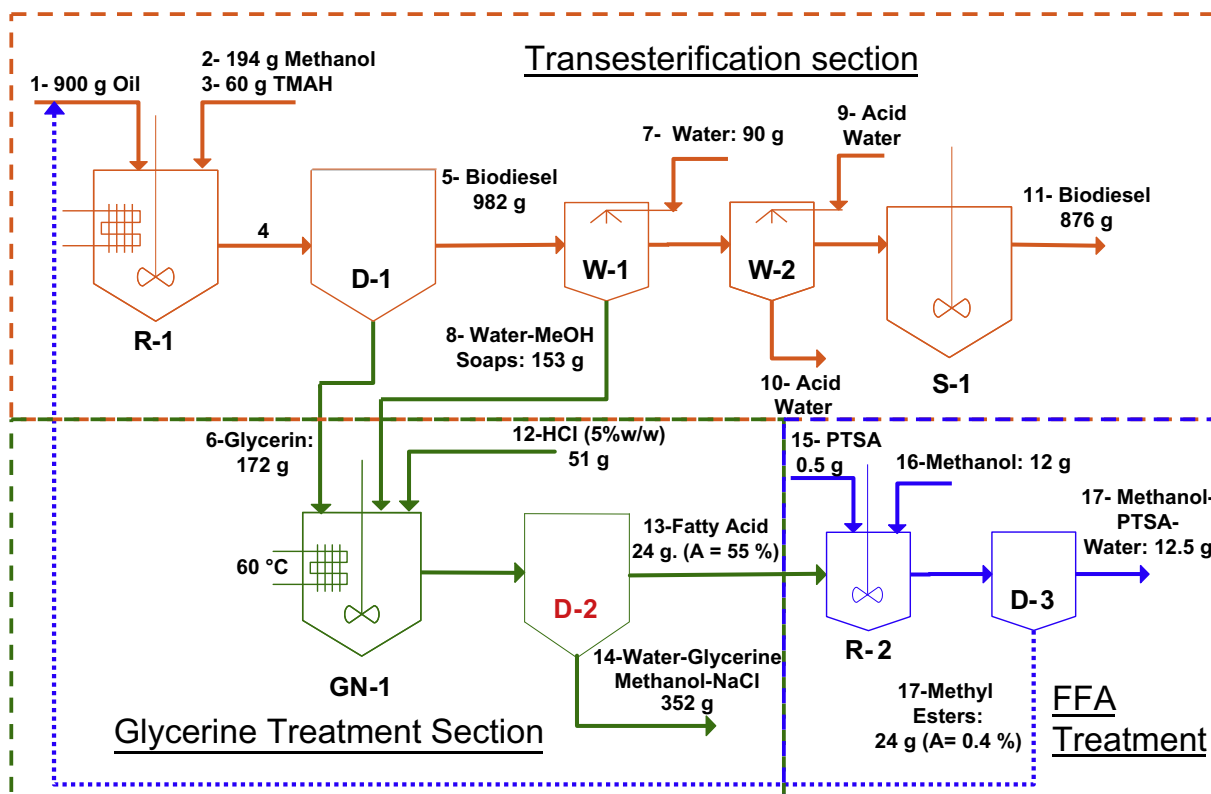


Fig. 5. Mass balance for biodiesel production using TMAH as catalyst; Transesterification Section: R-1: Transesterification reactor; D-1: Decanter (biodiesel–glycerol separation); W-1: First washing tank; W-2: Second washing tank; S-1: Drying tank. Glycerine treatment section: Glycerine treatment. GN-2: Glycerine neutralization tank; D-2: Decanter (fatty acids separation). Free-fatty acid esterification section: Esterification. R-2: Esterification reactor; D-3: Decanter.

Table 6
Properties of biodiesel obtained from transesterification of refined sunflower oil with TMAH as catalyst.

Parameter	Unit	Measured value	Limit value	Standard
Total glycerine	g/100 g	0.13	<0.25	EN 14105
Monoglycerides	g/100 g	0.42	<0.80	EN 14105
Diglycerides	g/100 g	0.11	<0.20	EN 14105
Triglycerides	g/100 g	0.08	<0.20	EN 14105
Free glycerine	g/100 g	0	<0.02	EN 14106
Acid value	mg KOH/g	0.84/0.2 ^a	<0.5	EN 14104
Total solid residue	mg/kg	16.4	<24	EN 12662
Ash content	g/100 g	0	<0.01	ASTM D 482
Sulfated ash content	g/100 g	0.01	<0.02	ASTM D 874
Total esters content	g/100 g	98.6	>96.5	EN 14103
Water content (Karl Fischer)	g/100 g	0.035	<0.050	ASTM D 4928
Methanol content	g/100 g	0	<0.2	EN 14110
Cold soak filtration test	s	130	<360	ASTM D-6751-08
Na + K	mg/kg	<1	5	EN 14108-14109

^a Values obtained with conventional purification treatment and neutral washing, correspondingly.

avoided: formation of emulsions during the purification step, and obtention of a product with high acid value. Therefore, it is concluded that this methodology is more adequate for treating the methyl esters obtained with the TMAH catalyst, due to the high soaps content measured in this product.

3.3. Fatty acids recovery

It has been previously reported the mass balance in a biodiesel production process using sodium methoxide as catalyst and

ethanol as alcohol, and including the fatty acid recovery from the glycerine phase and its esterification [36]. Fig. 5 shows a similar process scheme and the mass balance for the methyl esters production process using tetramethyl ammonium as catalyst. According to this, the yield, defined as mass of biodiesel obtained/mass of oil fed, was 97.33%. The process yield when sodium methoxide was employed as catalyst was 99.5% approximately [36]. The lower yield obtained with TMAH is due to the higher water content of TMAH, that accelerates the saponification reaction. The soaps migrate preferentially to the glycerine phase during the decantation

stage. Nevertheless, a high amount of them remained in the biodiesel phase, which are transformed into fatty acids with a conventional washing treatment using diluted acids. In this study, as it was previously explained, the first washing was performed with neutral water. Therefore, the soaps were extracted and drained with the water flow coming out of this tank (W-1). In addition, in the process scheme shown in Fig. 5, the recovery of fatty acids from the glycerine and its esterification using para-toluene sulfonic acid (PTSA) as catalyst, was included, similarly to what was explained in the case of the biodiesel production using sunflower oil, sodium methoxide and ethanol [36]. In this way, a global yield of practically 100% was obtained.

3.4. Biodiesel quality

Several quality parameters were measured in the final product. The reaction conditions employed were those which maximize conversion, according to the previous results: temperature 60 °C, catalyst concentration 1.76 wt%, 2 h reaction time.

Table 6 shows the results as well as the limit values established by the international standards. Only the acidity was out of specification in the case of using the conventional procedure to purify the crude biodiesel, i.e., a first washing with acidified water. In this case, the protons contained in the acid solution directly react with the soaps, forming fatty acids as the reaction product. This can be avoided if an alternative washing procedure is employed [35], as it was explained in Section 3.2. As shown in Table 6, when the purification was carried out using a first neutral washing, the final acidity was 0.2 mg KOH/g. Furthermore, the formation of emulsions or interphases was not detected.

3.5. Catalyst removal from the glycerine phase

The glycerine was treated at 160 °C for 2 h in order to decompose the catalyst. After this treatment the glycerine phase contained 4.6 wt% of catalyst, 11 wt% of soaps, and the ashes content was zero. The gases eliminated from the glycerine had a strong odor to ammonia. It was not possible to increase the temperature of this treatment because the glycerine would start decomposing since the pH was well above 7, and under this condition glycerine polymerization occurred. Therefore, according to these results, the removal of the TMAH catalyst from the glycerine phase is not easy, requiring long times and rather high temperatures.

4. Conclusions

The biodiesel production using tetramethyl ammonium hydroxide as catalyst was studied. It was found that using 1.76 wt% catalyst and at 60 °C, a product that meets the international standards of quality can be obtained. The purification stage was also optimized in order to reduce the acidity of the final biodiesel sample.

According to the production strategy proposed, it was shown that the TMAH catalyst could be employed in an industry operating with a conventional transesterification catalyst, such as sodium methoxide, with minor modifications. Since the price of TMAH is higher than that of sodium methoxide, it could be used only in special applications, for example in the case of producing biodiesel for its utilization in turbines, thus easily meeting the strict limit of alkaline metals. Nevertheless, it has to be emphasized that due to the higher water content and the different products distribution between the methylester and glycerine phases, higher amount of soaps were formed with this catalyst compared to the sodium methoxide. This leads to a lower process yield, unless additional operations are included, in order to treat the free fatty acid recovered from the glycerine phase.

A very interesting result obtained in this study is that the distribution of mono- and di-glycerides between the biodiesel and glycerine phases changed depending upon the catalyst used. In the case of the TMAH, the mono- and di-glycerides preferentially concentrated in the glycerine phase, thus improving the purity of the biodiesel product.

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