Catalyst consumption during one and two steps transesterification of crude soybean oils

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HIGHLIGHTS

- Catalysts (sodium and potassium hydroxides and metoxides) are consumed by saponification reactions.
- Up to 80% of the catalysts were consumed forming soaps with acid oils.
- Sodium soaps are more soluble than potassium soaps in the biodiesel phase.
- The total soaps formation in a two-step reaction was exactly the same as in one step.
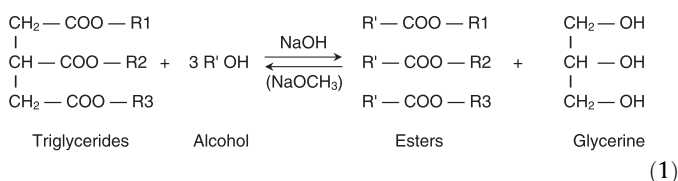
ARTICLE INFO

ABSTRACT

In this work, the transesterification reaction of refined and crude oils was studied. The reaction was carried out using methanol, with the aim of studying the effect of different catalysts, such as sodium and potassium hydroxides and methoxides, all of them in the same molar concentration. The saponification is an important side-reaction in this system, and was carefully analyzed in order to compare the yields and the rate of soaps formation with each catalyst. Significant differences among them have been found. The catalyst and soaps distribution between the biodiesel and the glycerine phases was also determined. It was found that a very important fraction of the hydroxides, both sodium and potassium, are consumed by the saponification reaction, thus decreasing the final acyl-glycerides conversion. Carrying out the reaction in two steps, it was found that not improvement was obtained regarding the catalyst consumption and soap formation, what indicates that the water fed to the system and the water formed by free fatty acid neutralization, determine these values independently of the reaction strategy followed in the process.

The importance of this study is that in medium and small scale plants, the biodiesel production is often carried out with crude oils, and consequently, the selection of the catalyst that minimizes soap formation and its solubility in the biodiesel phase, is an important issue.

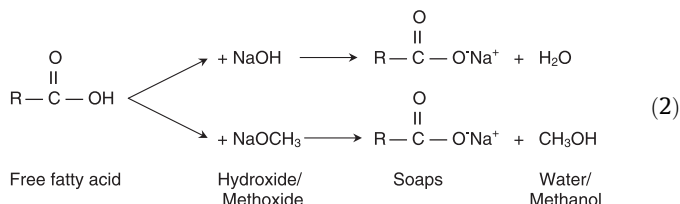© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Biodiesel is commonly obtained by transesterification of vegetable oils or animal fats, with short-chain alcohols (Eq. (1)). In order to obtain high reaction rates, basic or acid catalysts can be used. However, basic catalysts are more active than acid catalysts and consequently, the former are the preferred option [1,2].
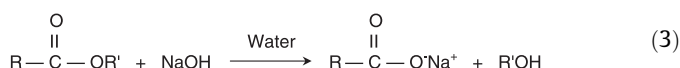
Basic catalysts present the disadvantage of soaps formation, either by free fatty acid neutralization (Eq. (2)) or by acyl-glycerides saponification (Eq. (3)), which occurs in the presence of water. Soap formation is undesirable since it consumes catalyst, hinders phase separation and biodiesel purification, and diminishes the process yield [3]. Low yields are mainly due to the occurrence of these two reactions.

$$
\begin{array}{c}
CH_2-COO-R1 \\
| \\
CH-COO-R2 \ + \ 3\,R'\,OH \ \underset{(NaOCH_3)}{\overset{NaOH}{\rightleftharpoons}} \\
| \\
CH_2-COO-R3
\end{array}
\begin{array}{c}
R'-COO-R1 \\
| \\
R'-COO-R2 \ + \\
| \\
R'-COO-R3
\end{array}
\begin{array}{c}
CH_2-OH \\
| \\
CH-OH \\
| \\
CH_2-OH
\end{array}
$$

Triglycerides   Alcohol   Esters   Glycerine

(1)

Transesterification reaction with alkaline catalyst.

$$
\underset{\text{Free fatty acid}}{R-\overset{\overset{O}{\|}}{C}-OH}
\begin{cases}
+\,NaOH \longrightarrow R-\overset{\overset{O}{\|}}{C}-O^-Na^+ \ + \ H_2O \\[2mm]
+\,NaOCH_3 \longrightarrow R-\overset{\overset{O}{\|}}{C}-O^-Na^+ \ + \ CH_3OH
\end{cases}
$$

Free fatty acid   Hydroxide/ Methoxide   Soaps   Water/ Methanol

(2)

Free fatty acid neutralization reaction.

$$
R-\overset{\overset{O}{\|}}{C}-OR' \ + \ NaOH \ \overset{Water}{\longrightarrow} \ R-\overset{\overset{O}{\|}}{C}-O^-Na^+ \ + \ R'OH
$$

(3)

Ester group saponification reaction.

There are several publications in which the transesterification reaction has been addressed, using different raw materials such as: sunflower [4], rapeseed [5,6], palm [7,8], soybean [9,10], rice oils [11], beef tallow [12–14], and used vegetable oil [15]. The effects of the presence of water and free fatty acids, temperature, alcohol/triglyceride ratio, and catalyst concentration have been analyzed. In some cases, comparative studies using different raw materials have been presented [1,9,16,17].

Basic catalysts such as sodium methoxide, potassium methoxide, sodium hydroxide, and potassium hydroxide have been previously used in the acyl-glycerides transesterification reaction. In few cases, these catalysts have been compared [3,15,18]. However, the comparison was done working at the same wt% concentration. Since the molecular weights of these catalysts are different, in order to compare their intrinsic activity and the side-reactions conversions, the same molar concentration must be used. In general, the publications focussed in the comparison of different raw materials with a given catalyst [19,20], or different catalysts with a given raw material [3,14,15,18,21]. In very few papers the comparison of catalysts using different raw materials have been addressed [22,23]. Dias et al. [22] studied the behavior of sodium and potassium hydroxides, and sodium methoxide in the transesterification of used and crude vegetable oils. In this latter study, the catalysts have been used in the same mass concentration. Leung and Guo [23] reported the used of these three catalysts at approximately the same molar concentration, with rapeseed oil and used vegetable oil. In the latter, similar conversions have been observed at 30 min of reaction with the three catalysts, being the yield obtained with the methoxide higher than with the hydroxides (89% and 86% respectively).

Metallic alkoxides are more active than the hydroxides since in fact, the species that catalyzes the transesterification reaction is the alkoxide ion. The hydroxides dissolved in methanol forms methoxide and water, according to the following equation:

$$OH^- + CH_3OH \rightleftarrows CH_3O^- + H_2O \qquad (4)$$

Methoxide formation from methanol in basic media.

Water in the reaction media is undesirable since it favors the saponification reaction (Eq. (3)).

There are several publications in which the yield loss has been attributed to the saponification reaction, but no soaps determinations were carried out. In few papers these measurements have been done [3,24–27]. Vicente et al. [3] studied sodium and potassium hydroxides and methoxides catalysts, using refined sunflower oil, but using the same mass concentration, instead of the same molar concentration. This variable is relevant regarding not only the catalytic effect, but also the amount of soaps that can be formed. In other cases, reacting systems using potassium hydroxide have been studied; evaluating the amount of soaps formed depending upon the acidity of the raw material [25] and the initial amount of water [26]. In the latter work only the glycerine phase was analyzed, since in this phase most of the soaps were concentrated, approximately 90–95% of the total amount. However, the biodiesel phase contained both, soaps and catalysts, as will be shown in the present work. There are no reports regarding the distribution of soaps between both phases. On the other hand, it has been suggested that as the soap concentration in the glycerine phase increases, the amount of esters present in this phase also increases. However, there are no measurements of these amounts. The amount of esters in the glycerine phase was calculated by mass balance [25,26] and other indirect measurements as the saponification index of the glycerine phase [3]. However, the presence of mono-, di- and triglycerides in the glycerine phase does not allow obtaining a precise result.

In this work, the transesterification reaction of raw materials such as refined and crude soybean oils, having different acidity, is studied. The alcohol and catalysts concentrations are those typically used at industrial level. The objective is to compare the behavior of the catalysts that are most commonly used, including sodium and potassium hydroxides and methoxides, **at the same molar concentration**. The aim is to obtain information regarding the effect of each of these four catalysts not only on the activity for the transesterification reaction, **but also for the saponification reaction and catalyst consumption**. The distribution of the catalyst and soaps formed during the reaction, between the glycerol and biodiesel phases, is addressed. These are distinctive features compared to previous works.

2. Experimental

2.1. Transesterification reaction

2.1.1. Reaction in one step

The reaction was carried out in a 0.5 L flask, with magnetic stirring, using a 50 mm Teflon-coated magnetic bar, and 800 rpm, working at atmospheric pressure, under reflux conditions, condensing the methanol vapours with water at 20 °C. The reactor was immersed in a thermostatic water-bath at 60 °C, which was the reaction temperature in all the experiments. Throughout this work, the acidity of the raw material is expressed as (g oleic acid/100 g sample), and referred to as acidity %. Refined sunflower oil with acidity less than 0.1 g oleic acid/100 g sample, and crude soybean oils with acidity 0.41, 1.13 and 1.85 g oleic acid/100 g sample were used as raw material. In all cases, methanol was used (99.8% purity, water content 350 ppm, from Cicarelli), loading 25 vol% (volume of methanol per volume of oil*100). This amount corresponds to a methanol/oil molar ratio of approximately 6:1, i.e. 100% excess relative to the stoichiometric value, being the latter 12.8 vol% or 11.1 wt%, in both cases relative to the oil. The catalyst was either sodium or potassium hydroxide dissolved in methanol, and sodium or potassium methoxide (30 wt% and 32 wt% in methanol respectively) from Evonik. In all cases the same molar concentration was used, 7.83 mol/100 kg of (oil + methanol), and will be indicated as mol% throughout this work. This concentration expressed in wt% (g catalyst/100 g of oil + methanol) is for each catalyst, as follows: NaOH 0.31 wt%; KOH 0.44 wt%; NaOCH$_3$ 0.42 wt%; KOCH$_3$ 0.55 wt%. The advantage of using the mol% concentration, is that it is the same for all the catalysts, and also that there is a one-to-one relationship between the soap formation and the catalyst consumption. If the wt% scale is used, this relationship is different for each catalyst, and the comparison among them is not straightforward. Instead of using mol/kg, the values are presented throughout this work as mol/100 kg just to re-scale the numbers.

Depending upon the oil acidity, an extra amount of catalyst has to be added in order to neutralize the free fatty acids. For the oils with acidities 0.41%, 1.13% and 1.85%, the amount of catalyst needed to neutralize the free fatty acids were 1.2, 3.3 and 5.4 mol%, respectively. These amounts represent 13.3%, 29.6%, and 40.8% of the total amount of catalyst loaded in the reactor for the oils with acidities 0.41%, 1.13%, and 1.85%, respectively. This extra amount reacts with the free fatty acids, and consequently is consumed very fast in the reaction media, forming soaps. Table 1 shows the concentrations needed for each catalyst and oil, in order to neutralize the oil and catalyze the reaction. The concentrations are expressed both in wt% and mol%. As above mentioned, the wt% values are different for each catalyst and raw material, thus complicating the direct comparison of the intrinsic activities for

Table 1
Catalysts concentrations used with crude oils of different acidities.

Catalysts	Acidity of the raw material			
	0.01%	0.41%	1.13%	1.85%
Catalyst concentration wt% (g/100 g (oil + methanol))				
NaOCH$_3$	0.42	0.48	0.54	0.59
KOCH$_3$	0.55	0.62	0.71	0.77
NaOH	0.31	0.35	0.40	0.44
KOH	0.44	0.50	0.57	0.62
Catalyst concentration mol% (mol/100 kg(oil + methanol))				
All catalysts	7.8	9.0	11.1	13.2

the transesterification and the saponification reactions. On the other hand, the mol% values for all the catalysts are the same value, and only depend on the oil acidity.

The reaction was carried out loading first 250 mL of oil into the reactor. Once the reaction temperature was reached, the alcohol containing the catalyst was added, taking this as zero time. The reaction was carried out for 90 min.

2.1.2. Reaction in two steps

Crude oil with acidity 1.85% was used as raw material, carrying out the reaction both in the conventional way as above described in one step of 90 min, and in two steps of 90 min each, at 60 °C. In the first case, 25 vol% methanol was loaded, together with the sodium methoxide used as catalyst (7.8 mol%, equivalent to 0.51 g NaCH$_3$O/100 g oil) plus the amount needed to neutralize the free fatty acid (5.4 mol%, equivalent to 0.21 g NaCH$_3$O/100 g oil). In the second case, i.e. reaction in two steps, half of the total amount of methanol (12.5 vol%) was added in the first stage, adding the catalyst needed to neutralize the free fatty acids (5.4 mol% equivalent to 0.21 g NaCH$_3$O/100 g oil) plus half the amount used as catalyst (i.e. 3.9 mol% equivalent to 0.26 g NaCH$_3$O/100 g oil). In the second stage the other half of methanol and catalyst were added, after the first reaction step, settling and phase separation. In all cases, the zero time for the reaction was taken as the moment in which the methanol, containing the catalyst, was added to the preheated oil.

At the end of each reaction step, the system was allowed to settle for 10 min at 60 °C, and then the mass of each phase was determined, and analyzed in order to obtain the catalyst and soap concentrations.

2.2. Sampling and analysis

The samples were taken from a lateral outlet, in which a refrigerant was also included to condense the alcohol vapours, preventing its escape during sampling. The reaction evolution was followed taking samples of the reacting mixture at 1, 2, 3, 5, 10, 20, 30, 60 and 90 min. In order to rapidly stop the reaction, the sample was placed in a water bath at 4 °C during 5 min to separate the glycerine. The upper phase (biodiesel-rich phase) was washed with a solution of HCl 5 wt%, and then centrifuged to separate the water phase. Finally, the biodiesel was dried at 50 °C while stripping with nitrogen.

The total ester content was determined in each sample by GC analysis, as described in UNE-EN 14103 standard.

The samples taken from the reactor cannot be directly washed because large amount of soaps are produced, changing the sample composition. This problem was solved allowing the sample to settle, since in preliminary experiments it was found that 90–95% of the soaps and the catalyst were concentrated in the glycerine phase. In a second step, the biodiesel phase was washed. It has to be taken into account that the reaction proceeds during decan-

tation, even though the reaction rate is considerably slower due to the low temperature selected to carry out this step (4 °C).

In order to verify that this procedure to handle the samples does not introduce significant errors, reaction experiments at 4 °C were carried out using a stirred reactor. The conversion was 3.1% and 4.7% at 5 and 10 min respectively. Considering that during the settling step there is no stirring, it can be expected that the conversion will be significantly smaller than 3.1%. Another reason to expect conversion values smaller than the one determine in a stirred reactor, is that the reactant concentration during settling are already diminished due to the conversion obtained during the reaction.

After 90 min of reaction, the compositions of the biodiesel and glycerine phases were determined, after settling during 10 min. This settling time was chosen in order to minimize the changes in composition due to the advancement of the reaction during this operation. Methanol (UNE-EN 14110), catalyst and soaps (IRAM 5599), and mono-, di-, and tri-glycerides (UNE-EN 14105) were determined in the biodiesel-rich phase. In the glycerine-rich phase, methanol, water, and catalyst and soaps were determined. As above mentioned, the concentration of soaps and catalysts in each phase (biodiesel and glycerine) are presented as mol/100 kg of phase (mol%). Methanol in the biodiesel phase was determined following the UNE-EN 14110 standard by head-space gas chromatography, with a calibration curve carried out to determine up to 5 wt% methanol. Similar procedure, with a calibration curve up to 35 wt% methanol, was followed to analyze this parameter in the glycerine-rich phase.

The analysis of soap and catalyst is not required in the quality standards. However, these are very important parameters in order to monitor the process. This is particularly important in the case of using acid crude oils as raw materials, such as those used in this study. The soap content in the system is related to the rate of the saponification reaction, which is strongly affected by the water content in the system and the catalyst. According to the IRAM 5599 standard, soaps in vegetable oils are determined by titration with HCl 0.1 N, using bromophenol blue as indicator, and acetone as solvent. In the case of a system containing both catalyst and soap, it is necessary to determine in a first step the catalyst content, using a toluene/ethanol (1:1 in volume) mixture as solvent and phenolphthalein (10 g/lt in ethanol 95%) as indicator. In a second step, the soaps are titrated according to the procedure described in the above mentioned standard. In this procedure, HCl 0.1 N was used to titrate catalysts and soaps.

The total and free glycerine content was determined as described in the UNE-EN 14105, i.e. by gas chromatography, determining the amount of mono, di, and triglycerides as well as the dissolved glycerine present in the sample. The total glycerine content is one of the most important parameter regarding biodiesel quality. It is related to the amount of glycerine present in the system, both as free and bound glycerine, forming mono, di and triglycerides.

The mass balance was determined in experiments carried out specifically with this objective, in order to eliminate the uncertainties introduced by the sampling throughout the run.

3. Results and discussion

3.1. Transesterification reaction

3.1.1. Influence of the raw material

3.1.1.1. Soap formation and catalyst consumption. Table 2 shows results of compositions obtained after 90 min of reaction, using the refined and crude oils as raw materials, and NaCH$_3$O as catalyst.

Table 2
Composition of mono- (M), di- (D), and tri-glycerides (T) after 90 min of reaction for different raw materials, and catalyst and soaps concentration in biodiesel (BP) and glycerine (GP) phases. Catalyst: NaOCH₃, methanol: 25 vol%, at 60 °C. BG: bound glycerine.

Raw material	Composition							
	M (wt%)	D (wt%)	T (wt%)	BG (wt%)	Catalyst mol% (wt%)[b]		Soaps mol% (wt%)	
					BP	GP	BP	GP
Refined oil A = 0.01%	0.39	0.09	0.07	0.12	0	54.0 (2.92)	0.53 (0.16)	7.9 (2.4)
Crude oil A = 0.41%	0.66	0.17	0.10	0.20	0	22.9 (1.24)	1.10 (0.33)	46.7 (14.0)
Crude oil A = 1.13%	0.74	0.23	0.12	0.23	0	21.9 (1.18)	1.62 (0.49)	53.3 (16.0)
Limits EN 14214	⩽0.8	⩽0.2	⩽0.2	TG⩽0.25[a]	–	–	–	–

[a] TG: total glycerine.
[b] Number between brackets corresponds to concentrations in wt%.

In all cases, the conversion was very good. The composition of non-converted acyl-glycerides is within the limits established in the EN 14214 standard, except in the case of the di-glycerides concentration obtained with the oil that has the highest acidity value.

In order to evaluate the influence of the acidity of the raw materials in the saponification reaction, the catalyst and soaps concentrations were determined after the reaction and decantation stages in both phases. These concentrations are presented in Table 2, in a mol% scale (mol/100 kg) and in wt% (numbers between brackets). It can be observed that there was no catalyst in the biodiesel phase (BP). In the glycerine phase (GP) the NaOCH₃ concentration diminished as the acidity of the raw material increased, while the soap formation increased. It is also important to highlight that both components, the catalyst and the soaps, were concentrated in the glycerine phase (GP).

The total amount of catalyst used with each raw material was different, since it was calculated as the sum of the amount needed to neutralize the free fatty acids, plus the amount selected to catalyze the reaction. In this study, the latter was 7.8 mol% for all the catalysts. The total amount of catalyst loaded in the reacting system was 7.8, 9.0, and 11.1 mol% for the oils with acidities 0.01%, 0.41%, and 1.13% respectively (Fig. 1, bars labelled "I"). The percentage of catalyst needed to neutralize the FFA represented 0.4%, 13%, and 30% of the total amount of catalyst loaded in the reactor for the raw materials with acidities 0.01%, 0.41%, and 1.13%, respectively, and are represented in Fig. 1 at the top of the bars labelled "I".

Taking into account the concentrations of catalyst plus soaps detected at the end of the reaction shown in Table 2, and the mass

of each phase determined at the end of the reaction (not shown), the total amount of moles of catalyst plus soaps in the system was calculated. These results are shown in Fig. 1 (bars labelled "A"). The total amount found at the end of the reaction were 7.9, 9.0 and 11.0 mol% for the three raw materials, being in excellent agreement with the initial values of catalyst loaded in the reactor (compare the heights of the bars labelled "I" and "A" for each raw material). The acidity of the refined oil was very low (A = 0.01%), being necessary only 0.4% of the catalyst loaded in the reactor to neutralize it. The soaps formed above this level, reaching a value of 18% of the total amount of catalyst loaded in the system, were due to the saponification reactions.

In the case of the oils with 0.41% and 1.13% acidity, 71% and 75% of the catalyst initially loaded in the system was transformed into soaps, while the amount of soaps formed due to the neutralization of the free fatty acids represented only 13% and 30% respectively, of the catalyst initially loaded. Therefore, it can be observed that in the case of the crude oils a high fraction of catalyst was consumed forming soaps by saponification reactions. It has to be highlighted that at the end of the reaction, the amount of catalyst available for the reaction represented 82%, 29% and 25% of the total amount loaded in the reactor, for the raw materials with acidities 0.01%, 0.41%, and 1.13%, respectively. These results clearly show that when using raw materials with high acidity, the catalyst are consumed by lateral reactions (neutralization, hydrolysis, saponification) and after some time of reaction, there is only a small fraction of catalyst available for the reaction. Consequently, once this state is reached, the reaction proceeds very slowly. Another very important observation is that the catalyst was concentrated
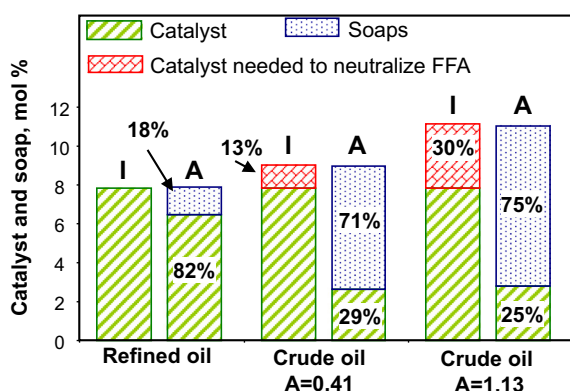
Fig. 1. (I) *Initially*: catalyst (NaOCH₃) loaded in the reactor for different raw materials. The numbers in the bars indicate the percentage of catalyst needed to neutralize the FFA. (A) *After reaction and decantation*: total amount of soaps and catalyst (measured in both phases). The numbers in the bars indicate the percentage of catalyst and soap at the end of the reaction, referred to the total number of moles of catalyst loaded in the system.
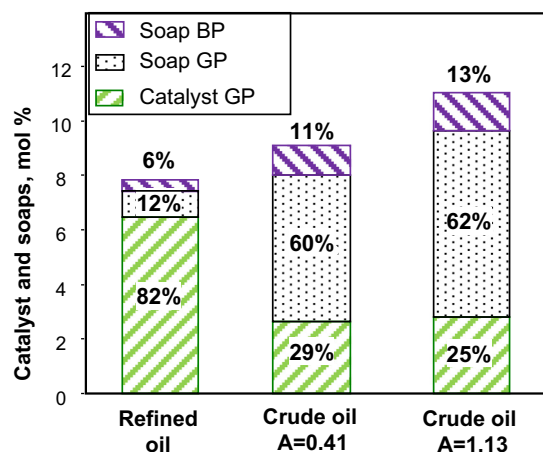
Fig. 2. Soaps and catalyst concentration in biodiesel and glycerine phases, referred to the total system mass. Methanol 25 vol%, Catalyst: NaOCH₃. Numbers in the bars represent the percentage of moles of catalyst initially loaded that remained as catalyst, or as soaps in the biodiesel and glycerine phases.

in the glycerine phase, thus being very important the level of agitation in the system, in order to have a highly dispersed glycerine phase, thus favouring the contact between the reactants and the catalyst.

3.1.1.2. Distribution of soaps and catalyst. After settling, the catalyst and the soaps were distributed between the glycerine and the biodiesel phases. Fig. 2 shows the results. In the case of the refined oil, 82% of the initial amount of catalyst was in the glycerine phase, while 18% was converted into soaps (as shown in Fig. 1). These soaps were distributed between the two phases, 67 of the soaps in the GP and 33% in the BP.

In the case of using crude oils, approximately 80–85% of the soaps formed and all the catalyst present in the reacting system were concentrated in the glycerine phase. However, the soaps concentration in the biodiesel phase was enough to complicate the purification stages, since it was above the value that leads to acidity in the final product above the limit established in the standards. This is because the conventional operation carried out after the reaction is the neutralization of the biodiesel phase, using hydrochloric, phosphoric, or citric acids. In this operation, the catalysts are neutralized and also the soaps are hydrolyzed forming free fatty acids, which are soluble in the biodiesel phase, and consequently, increasing the final acidity of the product. Taking into account that the limit for the acidity in biodiesel is 0.50 mg KOH/g, the maximum amount of soaps that can be present in the biodiesel before entering the neutralization steps is 0.89 mol%. In the case of the crude oils with acidities 0.41% and 1.13%, the concentration of soaps in the biodiesel phase after the reaction was 1.10 and 1.62 mol% (Table 1), and therefore, after neutralization a product out of specification would be obtained.

Recently, an alternative purification procedure was proposed, in order to process this type of raw materials [28]. Briefly, this procedure has a first washing step using neutral water, followed by an acid extraction step, thus decreasing the level of soaps in the biodiesel phase before the neutralization.

3.1.2. Catalyst consumption mechanism

Eq. (3) shows the reaction that occurs in a basic media, in the presence of water. This reaction indicate that the hydroxides are consumed, forming one molecule of soap per molecule of hydroxide. In the case of the methoxide catalysts, there is not a direct participation of methoxide ions in the saponification reaction. However, in the reaction media and in the presence of water, the reverse of Eq. (4) occurs. Therefore, a small amount of hydroxide ions are present in the system, according to the equilibrium of Eq. (4). These hydroxide ions are consumed in the saponification reaction, thus displacing the equilibrium consuming more methoxide and producing more hydroxides that react according to Eq. (3) forming soaps.

3.1.3. Influence of the catalyst

The transesterification reaction was carried out with the crude oils (A = 0.41% and A = 1.13%), using sodium and potassium hydroxides and methoxides. Results obtained during the initial 30 min of reaction using the oil with acidity 0.41%, are shown in Fig. 3. The four catalysts have good activity. At a reaction time of 10 min the ester concentration was approximately 90%. However, in order to meet specifications higher conversions are needed. The total ester content in the final product has to be above 96.5%, as established in the EN 14214 standard. This value was reached at 30 min of reaction in the case in which the catalyst was NaOCH$_3$, and in 60 min in the case of KOCH$_3$ and NaOH, while in the case of the KOH the maximum ester concentration reached at 90 min was 95%.
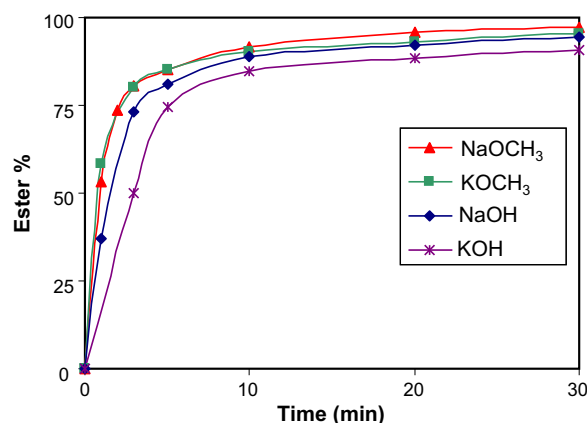

Fig. 3. Ester content as a function of time during soybean oil (A = 0.41%) transesterification. Methanol 25 vol%; catalyst concentration 9.03 mol%, temperature 60 °C.

Leung and Guo [23] reported the ester content at 30 min of reaction, using vegetable oil having an acidity of 1% and comparing different catalysts. It was found that NaOH led to a higher ester concentration (94%) compared to KOH (92.5%) and NaOCH$_3$ (92.8%). However, Leung and Guo [23] use the same catalyst concentration in a mass basis, and consequently, the molar concentrations were different. In a molar basis, the NaOH concentration was 12.5% higher than in the case of the NaOCH$_3$, and 3% higher compared to KOH concentration. This explains the difference in relative activities with results shown in the present study in Fig. 3.

Table 3 shows the acyl-glycerides concentration after 90 min of reaction, obtained with the four catalysts studied. The NaOCH$_3$ catalyst showed the highest activity. The composition of mono-, di-, and tri-glycerides were within the EN 14214 specification. In the case of KOCH$_3$ and NaOH the di-glycerides concentrations do not meet the specification, although for a little amount. In the case of the KOH, the tri-glycerides concentration was much higher than the allowed limit.

Results shown in Fig. 3 and Table 3 indicate that the sodium catalysts are more active than the potassium catalysts for the transesterification reaction, and that the methoxides are more active than the corresponding hydroxides. Comparing these catalysts at the same molar concentration, the order of activity is the following:
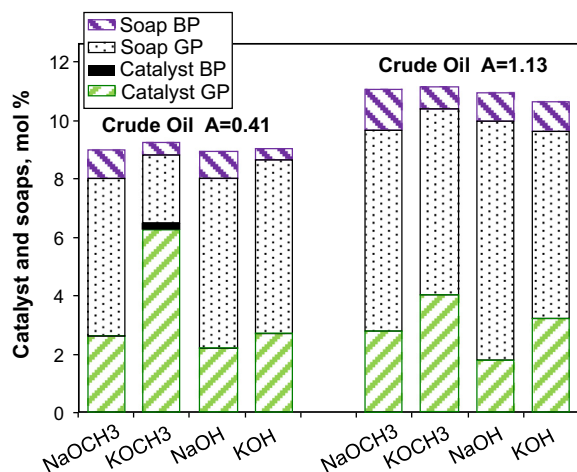
$$NaOCH_3 > KOCH_3 > NaOH > KOH$$
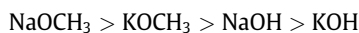
As shown in Eq. (4), the dissolution of hydroxide in methanol leads to the formation of methoxide and water. This reaction is limited by equilibrium. The water formed in this reaction favors the saponification reaction (Eq. (3)), and because of this, the methoxides are more active than the hydroxides, as experimentally observed.

The effect of the catalyst on the saponification reaction was determined by measuring the soaps and catalyst concentration in both phases after the reaction. These concentrations are shown in Table 3. Sodium catalysts formed more soaps than potassium-based catalysts, and on the other hand, the hydroxides are more active towards soaps formation than the methoxides. Table 3 shows that the catalyst that led to lower soap formation was KOCH$_3$. Taking into account the mass of each phase, and the concentrations shown in Table 3, the total amounts of soaps and catalysts in the system were calculated. Results are shown in Fig. 4. Experiments carried out with crude oil with acidity A = 0.41%, showed that the fraction of the catalyst initially loaded in the system that was consumed forming soaps follows the order:

Table 3
Compositions of mono- (M), di- (D), and tri-glycerides (T) at 90 min of reaction with crude oil (A = 0.41%) and catalyst and soaps concentration in biodiesel (BP) and glycerine (GP) phases. Catalysts concentration: 9.0 mol%, methanol: 25 vol%, at 60 °C. BG: bound glycerine.

Catalyst	Composition							
	M (wt%)	D (wt%)	T (wt%)	BG (wt%)	Catalyst (mol%)		Soaps (mol%)	
					BP	GP	BP	GP
$NaOCH_3$	0.66	0.17	0.10	0.20	0	22.9	1.10	46.7
$KOCH_3$	0.74	0.23	0.12	0.23	0.09	50.0	0.47	18.5
NaOH	0.79	0.26	0.21	0.26	0	18.2	1.03	48.7
KOH	0.67	0.28	0.85	0.30	0	17.3	0.47	38.2

Fig. 4. Soap and catalyst distribution in the glycerine and biodiesel phases alter the reaction and decantation. Methanol 25 vol%; catalyst concentration 9.03 mol%, temperature 60 °C.

$$\underset{75\%}{NaOH} > \underset{70\%}{KOH} = \underset{70\%}{NaOCH_3} > \underset{30\%}{KOCH_3}$$

In the case of this raw material (A = 0.41%), 13% of the catalyst initially loaded was consumed to neutralized the free fatty acids. The lowest formation of soaps was obtained in the case of the $KOCH_3$ catalyst. In this case, 70% of the catalysts remained as such after the reaction, while with the other catalysts this percentage was lower than 30%, with a high amount of soaps formed by saponification (Fig. 4).

Even though in the case of KOH and $NaOCH_3$ the fraction of catalysts transformed into soaps were in the order of 70% in both cases, the amount of soaps present in the biodiesel phase was lower in the case of the potassium catalyst. This indicates that there is a difference in the solubility of these salts, being sodium salts more soluble in the biodiesel phase. This agrees with the activity results. If the potassium salts are less soluble in the biodiesel phase and accumulate preferentially in the glycerine phase, its concentration in the phase rich in non-reacted glycerides would be lower, thus affecting the reaction rate. This explains the experimental results previously shown, that indicated that the sodium catalysts are more active than the potassium one for the transesterification reaction.

The soaps concentration in the biodiesel phase is important since it affects the purification stages as above explained, and consequently, catalyst selection has to take into account this effect. The catalytic activity was studied using the four catalysts and the crude oil with acidity A = 1.13%. Table 4 shows the composition reached at a reaction time of 90 min. The best results were obtained with $KOCH_3$, showing $NaOCH_3$ and NaOH very good activity. KOH has lower activity, with the tri-glycerides concentration well above the limit established in the En 14214 standard. The activity order in this case was as follows:

$$KOCH_3 > NaOCH_3 = NaOH > KOH$$

The activity results obtained with the crude oil of acidity 0.41%, indicated that the $NaOCH_3$ was more active than the KOCH3, which is the inverse of the activity order found with the raw material of higher acidity. This is an interesting result, and indicates that the catalyst selection has to take into account the acidity of the raw material. Table 4 shows the catalyst and soaps concentration in both phases obtained with the crude oil (A = 1.13) at the end of the reaction. The soaps formation was higher in the case of the sodium catalysts. Fig. 4 shows soaps and catalyst concentration in both phases, referred to the total mass present in the system, both for the crude oils with acidity 0.41% and 1.13%. In the latter raw material, 30% of the catalyst initially loaded in the system was consumed to neutralize the free fatty acids (Eq. (2)). However, the amount of catalyst transformed into soaps was significantly higher than this amount, according to the following order:

$$\underset{84\%}{NaOH} > \underset{75\%}{NaOCH_3} > \underset{70\%}{KOH} > \underset{64\%}{KOCH_3}$$

These values are higher than those obtained in the case of the raw material with lower acidity, except in the case of the KOH that showed similar values in both cases. Leung and Guo [23] did not measure the amount of soaps in the glycerine phase, but found that there is notable difference in the viscosity. In the case of the glycerine phase obtained with the KOH catalyst, it was liquid, while in the case of the sodium catalyst is was between a paste and a solid, due to the high amount of soaps accumulated in this phase.

Table 4
Compositions of mono- (M), di- (D), and tri-glycerides (T) at 90 min of reaction with crude oil (A = 1.13%) and catalyst and soaps concentration in biodiesel (BP) and glycerine (GP) phases. Catalysts concentration: 11.1 mol%, methanol: 25 vol%, at 60 °C. BG: bound glycerine.

Catalyst	Composition							
	M (wt%)	D (wt%)	T (wt%)	BG (wt%)	Catalyst (mol%)		Soaps (mol%)	
					BP	GP	BP	GP
$NaOCH_3$	0.74	0.23	0.12	0.23	0	21.9	1.62	53.3
$KOCH_3$	0.60	0.17	0.08	0.18	0	31.4	0.89	49.6
NaOH	0.75	0.20	0.16	0.24	0	11.8	1.13	54.4
KOH	0.80	0.21	0.60	0.30	0	20.7	1.21	41.3

Table 5
Compositions after reaction/decantation with crude oil ($A = 1.85\%$). Reaction in one and in two steps. Catalyst: $NaOCH_3$.

Reaction		Composition (wt%)			
		M	D	T	BG
One stage		0.33	0.19	0.15	0.13
Two stages	1°	0.80	3.99	18.9	2.73
	2°	0.37	0.11	0.01	0.11

BG: bound glycerine.

The yield in esters is an indirect measure of the amount of soaps formation. The table presented in the Supplementary data presents yields obtained by different authors [3,15,18]. In all cases the study was carried out with a 6:1 methanol/oil molar ratio and 1 wt% catalyst, at 65 °C. Results are not directly comparable with those shown in this work, since the catalysts concentrations are different. There are differences in the results obtained by different authors, even when using the same catalyst concentration. Yields are lower for the raw material of higher acidity, except in the case of the KOH. In the case of the refined oil, methoxide catalysts led to better yields, while in the other cases the opposite was observed. Nevertheless, in all cases the potassium catalysts had better yields than the sodium one.

This is in agreement with results obtained in this study. Only in the case of the refined oil, $NaOCH_3$ was slightly more active than $KOCH_3$.

It can be concluded that the potassium catalysts are less active towards soaps formation than the sodium catalysts. In the case of neutral or low-acidity raw materials, sodium catalysts have higher activity than the potassium one in the transesterification reaction. On the other hand, in the case of acidity higher than 1%, the $KOCH_3$ was slightly more active than the $NaOCH_3$, result that can be explained by the fact that the latter was consumed in a larger proportion in the saponification reaction, thus decreasing its concentration during the reaction.

Another important conclusion that can be obtained from the data shown in Table 4 and Fig. 4, is that the soaps concentration in the biodiesel phase, obtained with the four catalysts using the crude oil with acidity 1.13%, was above the maximum limit allowed to obtain the product with acidity lower than 0.5 mg KOH/g. Therefore, the use of non-neutralized raw materials does not make it possible to obtain the product with acidity within specification, and consequently, different process strategies are needed, such as using a first neutral washing, as above commented [28].
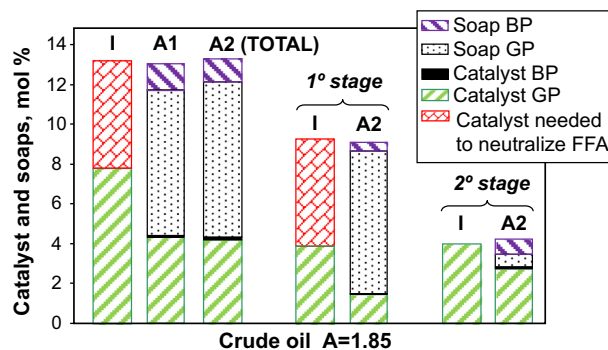
3.1.4. Influence of the reaction strategy

The conversion reached in the case of carrying out the reaction in one stage and the individual values of mono-, di-, and triglycerides are within the limits required in the standards, as above discussed. Table 5 shows the results obtained in both cases, i.e. carrying out the reaction in one and two steps, obtaining a slightly better conversion level in the second case. Nevertheless, it has to be remembered that the total reaction time was higher in the second case, since two reactions steps of 90 min each was used.

Fig. 5. (I) *Initially:* catalyst ($NaOCH_3$) loaded in the reactor: to catalyze and to neutralize FFA; (A) *After reaction and decantation:* soap and catalyst measured in both phases. A1: One stage. A2: Two stages.

Table 6 shows the values of soaps and catalyst concentrations in both phases. In the case of the reaction carried out in two steps, the soaps were largely concentrated in the glycerine phase in the first step, while in the second one, the relative concentration of soap in the biodiesel and glycerine phases increased. This is due to the effect of methanol in increasing the solubility of soaps in the biodiesel phase and also to the fact that the glycerine phase in the second step is proportionally much smaller than in the first one. In the first reaction step, the final methanol concentration was low (1.2 wt%), with a glycerine phase representing 11% of the total weight. In the second step, there was a methanol concentration higher than in the first one (5 wt%), because most of the triglycerides have already been converted thus consuming a smaller fraction of the alcohol. Since the glycerine phase at the end of the second step was only a 4% of the total mass of the system, most of the methanol was concentrated in the biodiesel phase. The catalyst concentration follows a very interesting behavior. At the end of the second step, the catalyst concentration was much higher than in the case of using a single step in the reaction strategy. This suggests that the amount of catalyst loaded in the second step is more efficient due to its accumulation in the biodiesel phase. Therefore there are possibilities of diminishing the total catalyst consumption using this strategy, by decreasing the dosification in the second step. This study is currently being carried out.

Fig. 5 shows the amount of catalyst initially loaded in the system (I), indicating the amounts needed to neutralize the free fatty acids, and the amount that is needed to catalyze the reaction. This figure also shows the amount of soaps and catalysts in each phase, expressed as mol% relative to the whole system. It can be observed that the total amount of soaps and catalyst at the end of the reaction was very similar in both reaction strategies (compare bars labelled as A1 and A2 (TOTAL)). However, there was an important difference between the two steps of the reaction. In the first one, 84% of the catalyst initially loaded in the reactor was transformed into soaps, being 58% due to the neutralization of free fatty acids, and the remaining 26% was due to the saponification reactions. The low catalyst concentration limited the reaction rate during the first stage. On the other hand, after the second reaction step

Table 6
Catalyst and soaps concentrations in biodiesel (BP) and glycerine (GP) phases after reaction/decantation for crude oil ($A = 1.85\%$). Reaction in one and two stages. Catalyst: $NaOCH_3$.

Reaction		Catalyst (mol%)		Soap (mol%)		Phase weight (wt%)[a]	
		BP	GP	BP	GP	BP	GP
One stage		0.04	30.2	1.61	50.6	86	14
Two stage	1°	0.04	13.2	0.45	65.3	89	11
	2°	0.16	74.1	1.20	16.1	96	4

[a] Weight of each phase relative to the total weight, in %.

73% of the catalyst initially loaded was present in the system. Fig. 5 also makes it possible to compare the soaps and catalyst distribution between both phases, as a function of the methanol content in the system. In the first step, according to the conversion values obtained, 73.5% of the methanol was consumed, and consequently there was a low final concentration of methanol. Because of this, the soaps and catalyst are concentrated in the glycerine phase, which is the polar one. In the second step, the methanol present at the end was higher than in the first one, and this increased the concentration of soaps and catalyst in the biodiesel phase.

The important conclusion obtained from these experiments, is that for a total amount of methanol and catalyst, the reaction strategy has little effect on the amount of catalyst consumed to form soaps and, therefore, the process yield is similar in both reaction strategies. However, as above discussed, these results suggest the possibility of improving the catalyst consumption and methanol concentration due to the preferential accumulation of this compounds in the biodiesel phase in the second step.

4. Conclusions

Catalyst selection is a key factor in order to design a biodiesel production process using acid raw materials. Hydroxides are less efficient to catalyze transesterification than methoxides, compared in a molar basis. Potassium catalysts form lower amount of soaps than the sodium one. This is an advantage in order to process acid raw materials. In the case of oils with acidity higher than 1%, $KOCH_3$ is more active than $NaOCH_3$. This is explained by a lower soaps formation by the former. KOH is the less active catalyst independently of the oil acidity.

The oil acidity has a profound impact on the catalyst concentration after some time in reaction. In the case of oil with 0.41% acidity and using $NaOCH_3$ as catalyst, 70% of its initial amount is transformed into soaps, thus reducing the apparent catalytic activity.

Saponification reactions play a major role during transesterification, due to the high fraction of catalyst consumed to form soaps. In order to solve this, a higher amount of catalyst should be loaded, but this will also foster the saponification reaction. The catalyst is concentrated mainly in the glycerine phase, thus increasing the mass transference limitations in this reaction system.

These are important conclusions, since with oils having acidities in the order of 1%, up to 80% of the is consumed due to saponification reactions.

A very interesting result was obtained carrying out the reaction in two steps. The total amount of soaps obtained in this case was exactly the same as that obtained when carrying out the reaction in a one-step strategy. Nevertheless, according to the results obtained in this study, it can be concluded that it is possible to optimize the total catalyst dosification in the case of the two-step reaction strategy, decreasing the total catalyst consumption specifically in the second reaction step. This study is currently being carried out.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2013.08.109.

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