Research article

Biodiesel production by transesterification in two steps: Kinetic effect or shift in the equilibrium conversion?

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ABSTRACT

In continuous biodiesel production plants, practically all technologies carry out the transesterification in two steps, feeding methanol and catalyst in each of them. The glycerine phase is separated after the first one. The explanation normally given to justify this procedure is that the glycerine separation after the first step shifts the equilibrium towards products, thus increasing the conversion. The reacting mixture is a system with partial miscibility, being the compositions of the biodiesel and glycerine phases different depending upon the global composition of methanol, catalyst, soaps, water, etc. The results presented in this work make it possible to conclude that the most important cause of the conversion improvement when performing the reaction in two steps is a change in the catalyst and methanol distribution between the biodiesel and glycerine phases. The separation of the glycerine phase leads to a positive impact on the kinetic of the second reaction step, since it allows that both the catalyst and the methanol concentrate in the biodiesel phase. This is due to the small quantity of glycerine phase present in the system in the second reaction step. Therefore, the higher concentrations of catalyst and methanol in the biodiesel phase significantly increase the rate of transesterification and decrease the mass transfer limitations.

1. Introduction

Biodiesel is commonly obtained by transesterification of vegetable oils and animal fats with methanol and basic homogeneous catalysis, being sodium methoxide the most common catalyst used in this process. Sodium hydroxide is less frequently used because upon dissolution of this salt in methanol, water is formed and this leads to lower process yields due to saponification reactions, which occur in the presence of water. These catalysts have as a major drawback the formation of soaps due to free fatty acids neutralization and also due to the saponification reaction of the ester group. Soaps formation is highly undesirable, because on one hand it consumes the catalyst and this affect the conversion level, which has to be very high to meet the quality parameters regarding mono-, di- and triacylglycerides content in the final product [1]. On the other hand, the presence of soaps favors the formation of emulsions, thus complicating the biodiesel purification steps. In addition, when the biodiesel phase is neutralized after the reaction, soaps are hydrolyzed forming free fatty acids soluble in biodiesel, leading to an increase in the acidity of the final product.

The reaction mixture is a complex multicomponent system, containing compounds with very different polarity, and because of this, during the reaction phase separation takes place. As the reaction proceeds, the amounts of methyl esters (biodiesel) and glycerine increase, having a low mutual solubility. The reacting system contains two phases. The biodiesel-rich phase (BP) and the glycerine-rich phase (GP) have compositions that depend on the global concentration of the different compounds present in the system, such as methanol, catalyst, soaps, water, etc.

In continuous processes, all the technologies carry out the transesterification reaction in at least two steps, dosing methanol and catalyst in each of them, and separating the glycerine after the first step. The explanation given to this operation is that the equilibrium is shifted towards the products when removing the glycerine, thus improving the conversion, as stated in the Le Chatelier's principle [2–4].

In this work this concept is discussed, and it is shown that in fact, this operation leads to a highly positive impact on the kinetics of the second step of the reacting system, not having any effect on the equilibrium conversion.

There are few publications in which the transesterification reaction using methanol is carried out in two steps [5–7], and some of them are

theoretical models [2,8]. Nevertheless, in none of these studies a precise characterization of the system regarding soaps, catalyst and methanol distribution was related to the amount of glycerine present in the system. As will be shown in this paper, this is a key aspect of the analysis. Moreover, in the three experimental studies that carried out the reaction in two steps [5,7], NaOH or KOH have been used as catalysts, in spite of the fact that sodium methoxide is the preferred option in the industry. In a previous work, we have studied the transesterification of soybean oil using ethanol and sodium methoxide as catalyst, in two steps. In this case, the objective was to determine the optimum conditions regarding the dosification of ethanol and catalyst, and the effect of temperature on the soybean oil conversion [9]. B. Likozar et al. carried out a very complex modelling of this reacting system, including the chemical equilibrium, reaction kinetics and mass transfer, taking into account the detailed fatty acid profile of the vegetable oil used in the reaction, with different alcohols [10–12]. In these studies the catalysts were KOH and NaOH, and the experiments and modelling were carried out either in a batch reactor in one step [10,11], or in a continuous tubular reactor, also with one step [12]. It was assumed that the catalyst is only in the methanol (or glycerine) phase, and the catalyst consumption due to the fatty acid neutralization is not included in the modelling.

In this work the transesterification reaction of crude soybean oil in one and two steps is addressed, using similar amounts of catalyst and methanol than those used at industrial level. According to our experience in providing technological assistance to many biodiesel producers, including plants with proven technologies such as Lurgi, De Smet, Westfalia, Crown, and other local technologies in Argentina, the total amount of catalyst dossed to the reactors is in the range 14–24 kg of sodium methoxide solution (30 wt%) per ton of oil, with a typical value of 16–18 kg sodium methoxide solution per ton of oil. The amount of methanol loaded to the system is approximately 20 wt% (referred to the oil).

This study is focused not only in obtaining information regarding the effect of different process variables on the performance of the transesterification in two-steps, but mainly to discuss and understand the reasons that justify the results obtained with this reaction strategy. Therefore, there are two main objectives in this work. The key issue that is the main and more important objective is to determine whether the positive impact of removing the glycerine phase after the first reaction step is due to an increase in the equilibrium conversion, or to an increase in the reaction kinetics. Besides the detailed analysis of both phases (BP and GP) in the reacting system, the equilibrium composition was also addressed in order to better understand its behaviour. The distribution of the components between both phases in the presence of different amounts of glycerine and methanol were analysed, and the system behaviour is discussed both from the kinetics and thermodynamics points of view. The other objective, with practical consequences, is to determine the best conditions to carry out the reaction, using one or two reactions steps with different dosifications of methanol and catalyst in each of them.

2. Experimental

2.1. Transesterification reaction in one and two steps

2.1.1. Reaction in one step

The reaction was carried out in a glass batch reactor, in a water bath at 60 °C, working under reflux conditions. The reaction mixture was maintained under vigorous stirring using a magnetic stirrer at 500 rpm. Degummed soybean oil with an acidity of 0.48% (g of oleic acid/100 g of oil) was used in all the experiments. The acidity was measured according to the ASTM D-974 [13]. Sodium methoxide ($NaOCH_3$) in methanol solution (30 wt%) was used as catalyst. The total amount of methanol (M) loaded to the reacting system was 25%v/v referred to the oil (VO).

The reaction in one step was carried out using three different catalyst concentrations: 0.66, 0.61 and 0.52 wt% (g of $NaOCH_3$/100 g of oil), which is the order of concentrations used at industrial level, as above mentioned. It has to be kept in mind that the oil used in this study had an acidity of 0.48%, and therefore an amount equivalent to 0.092 wt% of catalyst was needed to neutralize the free fatty acids present in the oil. This means that in the case of using a catalyst concentration of 0.66 wt%, this amount (0.092 wt%) is consumed in the neutralization of the FFA, and the remaining 0.568 wt% really acts as catalyst. The reaction was carried out during 120 min. As mentioned in the Introduction section, a typical concentration of catalyst (sodium methoxide in methanol, 30 wt%) used at industrial level with proven technologies and neutralized oils is approximately 16 kg/ton of oil, which corresponds to 0.48 wt% (g catalyst/100 g vegetable oil). Since and additional amount of 0.092 wt% of catalyst is needed to neutralize the free fatty acids present in the oil, the catalyst concentration loaded to the reactor should be 0.572 wt%. Taking into account this reference value, the three concentrations mentioned above (0.66, 0.61, and 0.52 wt%) were selected to address the effect of catalyst concentration around a typical industrial value.

2.1.2. Reaction in two steps

In the case of the reaction carried out in two steps, the amount of sodium methoxide loaded as catalyst that remains in the system after the FFA neutralization (i.e., the total amount loaded to the reactor minus 0.092 wt% used to neutralize the free fatty acids) was divided in two equal parts and loaded in each reaction step. In the first reaction step the extra amount of sodium methoxide (0.092 wt%) was loaded in order to neutralize the free fatty acids of the vegetable oil, and therefore it was consumed forming soaps (see Eq. (6) below). Experiments in two reactions steps were carried out using different amounts of catalyst. Each reaction step had a duration of 60 min. The total amount of methanol loaded to the system (25%v/v referred to the oil) was divided in two parts and loaded in the first and second reaction steps respectively, as follows: (i) 12.5% and 12.5%; (ii) 10% and 15%; (iii) 15% and 10%.

Throughout this study, in order to facilitate the discussion, the catalyst concentration is expressed also as mol% (moles of $NaOCH_3$ / (100 kg of oil + methanol)) [1]. In this scale, the total amount of catalyst loaded to the reactor equivalent to 0.61 wt% was 9.23 mol%, corresponding 1.4 mol% to the amount added to neutralize the free fatty acids.

This scale has the advantage of making it possible a direct comparison of the catalyst consumed and the soaps formed, having these two compounds very different molecular weights (54 and 304 g/mol respectively). It has to be taking into account that each mole of catalyst consumed during the saponification reaction, leads to the formation of 1 mol of soap.

Table 1 summarizes the reaction experiments presented in this work.

After the first reaction step, phase separation was carried out by gravitational decantation during 10 min. This short decantation time was adopted in order to better observe the effects of the process variables in the distribution of catalyst and soaps between the two phases. The mass of each phase was determined and samples were taken in order to measure its composition. The glycerine rich phase was discarded and the biodiesel rich phase was used in the second reaction step, adding the methanol and catalyst amounts specified in Table 1. After the second reaction step the phases were separated as in the first step, measuring the mass of each phase and its composition. Scheme 1 shows an example of the procedure followed in these experiments carried out in two steps (Experiment B of Table 1).

In the biodiesel phase the unconverted glycerides concentrations were measured (mono- (MAG), di- (DAG), and triacylglycerides (TAG)) by gas chromatography according to the ASTM D-6584 standard [14], which is essentially the same as the UNE-EN 14105 [15]. The limits established in the UNE-EN 14214 [16] for these three components are

Table 1
Methanol and catalyst concentration in the reaction experiments in one and two steps.

Experiment	Step	Methanol mL/100 mL oil	Catalyst concentration	
			Wt%[a]	Mol%[b]
A		25.0	0.66	10.10
B	1	15.0	0.35	5.72
	2	10.0	0.26	4.38
C		25.0	0.52	7.91
D	1	15.0	0.35	5.72
	2	10.0	0.13	2.19
E	1	12.5	0.35	5.83
	2	12.5	0.26	4.30
F	1	10.0	0.35	5.95
	2	15.0	0.26	4.21
G	1	15.0	0.35	5.72
	2	10.0	0.19	3.29
I	1	15.0	0.35	5.72
	2	10.0	0.06	1.10
J	1	12.5	0.35	5.83
	2	12.5	0.19	3.22
K	1	12.5	0.35	5.85
	2	12.5	0.12	2.15
L		25.0	0.61	9.23

[a] wt%: g of catalyst/100 g oil.
[b] mol%: mol of catalyst/100 kg (oil + methanol).

as follows: MAG < 0.7 wt%, DAG < 0.2 wt%, TAG < 0.2 wt%. The catalyst and soaps concentrations are not directly specified in the quality standards. However, these values are important in order to correctly design the process and to understand the physical chemistry of this system. In particular, this information is relevant when using vegetable oils containing free fatty acids, as is the case of the oil used in this study. The procedure used to determine catalyst and soaps in the biodiesel and glycerine phases was described by J. Van Gerpen et al. [17]. Soaps analysis is based on the procedure described in AOCS Cc17-95 [18].

2.2. Phase-equilibrium experiments

The phase equilibrium was studied preparing mixtures of pure biodiesel (FAME) and pure glycerine with compositions similar to those found at the end of the reaction in the following situations:

- 100% conversion, which is equivalent or similar to the system in the case in which the reaction is carried out in one step. According to the stoichiometry of the reaction, the mixture FAME-Glycerine for 100% conversion of glycerides contains 9.4 wt% of glycerine.
- 85% conversion, which is similar to the first reaction step, in the two-steps reaction strategy. The mixture FAME-Glycerine for this situation contains 8 wt% glycerine.
- 15% conversion, which is similar to the system after the second

Table 2
Methanol and catalyst concentration in the phase equilibrium experiments.

Experiment	LABEL	Methanol[a]	Catalyst concentration	
			wt%[b]	mol%[c]
M	100/0	1	0.54	8.7
N	100/10	10	0.59	8.7
O	100/20	20	0.65	8.7
P	85/0	1	0.53	8.7
Q	85/10	10	0.58	8.7
R	85/20	20	0.64	8.7
S	15/0	1	0.50	8.7
T	15/10	10	0.55	8.7
U	15/20	20	0.61	8.7

[a] mL/100 mL (biodiesel + glycerine).
[b] wt%: g of catalyst/100 g oil.
[c] mol%: mol of catalyst/100 kg (oil + methanol).

reaction step. The mixture FAME-Glycerine for this conversion contains 1.4 wt% glycerine.

In all cases, the same total concentration of catalyst was added (8.7 mol%), and three different methanol concentrations were used. In the transesterification reaction, methanol is loaded both as a part of the catalyst since it is diluted in methanol, and as pure methanol. Taking into account both contributions, the concentrations of methanol used in these experiments were 1, 10 and 20% (mL methanol/100 mL (biodiesel + glycerine). In these experiments, there are no glycerides present in the system and therefore the reaction cannot occur, being possible to evaluate the composition of the different species in each phase in equilibrium. Table 2 summarizes the experiments carried out to study the phase equilibrium. The labels included in this table have two numbers, e.g. 100/10. The first number indicates the conversion of triglyceride needed to obtain the composition of the mixture biodiesel/ glycerine, in this case 100%. The second number represents the methanol concentration in the system.

The mixtures thus prepared were put in sealed flasks and vigorously agitated, and then left at 60 °C during 40 h. Afterwards, aliquots of each phase were taken, and the mass of each phase determined. The concentrations of methanol, soaps and catalyst were measured. Methanol concentration was determined as indicated in the UNE-EN 14110 standard [19], using the GC analysis by the head-space procedure. Calibrations curves for the glycerine and biodiesel phases were determined for the different ranges of methanol concentrations used in this work.

3. Results and discussion

Selected experiments of reactions carried out in one and two steps have been replicated in order to have information regarding the repeatability of the results under analysis. It has been found that in the
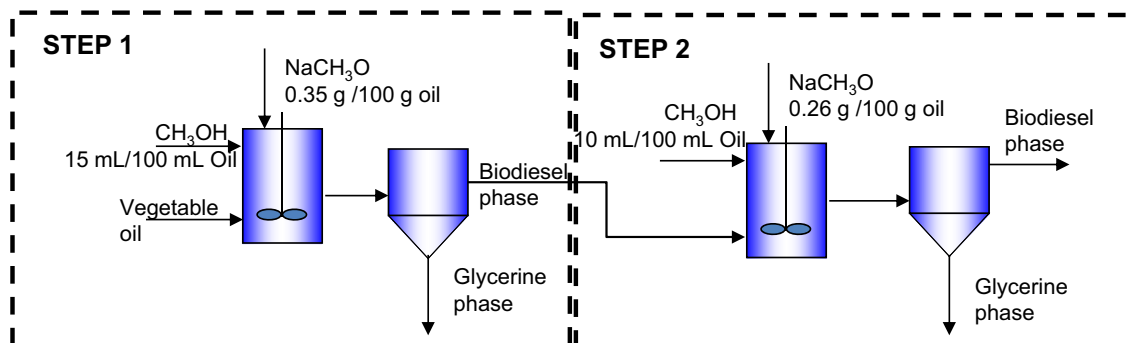
Scheme 1. Scheme of the process followed in experiment B (Table 1).

experiments carried out in one step, the final concentration of MAG, DAG and TAG do not differ in > 10% between two runs. In the case of the experiments with the reaction carried out in two steps, these concentrations do not differ in > 15%.

3.1. Reacting system

Several reactions take place in the transesterification reactor, as follows:

$$TAG + MeOH \rightleftarrows DAG + FAME \tag{1}$$

$$DAG + MeOH \rightleftarrows MAG + FAME \tag{2}$$

$$MAG + MeOH \rightleftarrows G + FAME \tag{3}$$

$$MeO^- + H_2O \rightleftarrows OH^- + MeOH \tag{4}$$

$$FAME + NaOH \rightleftarrows Soap + MeOH \tag{5}$$

$$FFA + NaMeO \rightleftarrows Soap + MeOH \tag{6}$$

MAG, DAG, TAG: mono-, di- and triacylglycerides respectively; FAME: fatty acid methyl esters, G: glycerine; MeO^-: methoxide; MeOH: methanol; FFA: free fatty acids; NaMeO: sodium methoxide.

Water is present in the system as an impurity of methanol, sodium methoxide and soybean oil. The saponification reaction consumes an ester that may be the FAME as indicated in Eq. (5), or MAG, DAG and TAG. This reaction occurs only in the presence of water.

In addition to these chemical reactions, other processes present in the system are the distributions between the two phases of all the components, for example in the case of the glycerine, as follows:

$$G)_{BP} \rightleftarrows G)_{GP} \tag{7}$$

Mass transfer between phases controls the rate of the process at the beginning of the reaction [20,21] since methanol has low miscibility with the vegetable oil, and also in the case of low Reynolds numbers due to a deficient agitation [20]. After few minutes of reaction with an appropriate turbulence in the system, the drops of the disperse phase reach a small value, approximately 0.3 mm [21]. Since the reaction rate rapidly approached the equilibrium conversion, after 10–15 min of reaction it is slow and the chemical kinetics controls the overall reaction rate [20]. This means that the distribution of methanol, sodium methoxide, glycerine, and the other components of the system between the two phases (Eq. (7) for glycerine and similar for the other compounds) can be considered in equilibrium.

3.2. Effect of the reaction strategy

In the case of the reaction carried out using 25%v/v of methanol and the amount of catalyst typically used in the industry, the conversion obtained was very good both when the reaction was carried out in one step during 120 min, and in two steps of 60 min each. These results are shown in Table 3, experiments A and B respectively. The conversion level is evaluated taking into account the amount of acylglycerides present in the product, such as mono-, di- and triacylglycerides (MAG, DAG, TAG). The sum of these three compositions represents the non-converted fraction of glycerides (NC). It can be observed in Table 3 that in both experiments (A and B) the maximum limits established in the quality standards are met using either reaction strategy.

In order to optimize the quantity of catalyst loaded to the reactor, additional experiments were carried out using half the amount of NaOCH₃ in the second reaction step, compared to that used in experiment B (Table 3). This experiment is included in Table 3 as experiment D. In this experiment, the reaction had two steps and the conversion obtained was very good, obtaining a product that meets the specifications regarding the conversion level. However, if the same total amount of catalyst is used in a reaction in one step, the amount of unconverted triglycerides is very high (experiment C). This is a very interesting

Table 3
Acylglycerides concentration and total non-converted glycerides obtained in experiments A, B, C and D (described in Table 1).

Compositions	Experiment			
	A	B	C	D
	1 step	2 steps	1 step	2 steps
Methanol (%v/v)	25	1st 15	25	1st 15
		2nd 10		2nd 10
NaOCH₃ (mol%)	10.1	1st 5.72	7.91	1st 5.72
		2nd 4.38		2nd 2.19
MAG (wt%)	0.32	0.34	0.48	0.50
DAG (wt%)	0.15	0.11	0.28	0.15
TAG (wt%)	0.04	0.00	0.94	0.01
NC (wt%)	0.51	0.45	1.7	0.66

result, and generally, it is explained using the Le Chatelier's principle. Since one product, in this case glycerine, is extracted from the system after the first reaction step, it is considered that there is a shift of equilibrium towards the products in reactions 1, 2, and 3 [2–4,22]. However, the data and discussion presented below suggests that the reason of the better conversion when carrying out the reaction in two steps, as compared to one step, is a change in the distribution of catalyst and methanol between the glycerine and biodiesel phases leading to a faster reaction rate, rather than shifting the equilibrium composition.

3.3. Effect of methanol dosification

Table 4 shows results obtained using different distributions of methanol between the first and the second steps, maintaining constant the total amounts of methanol and catalyst loaded to the system referred to the oil. As above explained, in the first step it was loaded the amount of sodium methoxide needed as catalyst plus the amount needed to neutralize the free fatty acids. The amount of sodium methoxide used as catalyst was equal in both reaction steps (g catalyst/100 g of oil). However, since different amounts of methanol were used in these experiments in each reaction step, the concentrations of catalyst referred to the total mass of oil and methanol (mol%) are slightly different among them, as shown in Table 1.

In the three experiments (B, E, F) the amount of non-converted glycerides is very low, and the biodiesel obtained is within the specifications regarding the content of mono-, di- and triacylglycerides compounds. Nevertheless, the best result was obtained using the highest proportion of methanol in the first step (i.e. 15%v/v) and the lowest in the second one (i.e. 10%v/v) (experiment B, Table 4). Even though the final conversion is very good in the three alternatives of methanol distributions, there are major changes in the conversion in the first step, being the highest in the case of using 15%v/v of methanol in the first step, and 10%v/v in the second (experiment B). The consequence of this is that in the second reaction step a smaller amount of glycerine is formed, and therefore the catalyst and the methanol concentrations in the biodiesel phase will be higher in experiment B as

Table 4
Results obtained in the experiments with the reaction in two-steps using different proportions of methanol in each step. Experiments B, E, and F (described in Table 1.

	Experiment	Methanol %v/v	NaOCH₃ mol%	MAG wt%	DAG wt%	TAG wt%	NC wt%
1st step	B	15.0	5.72	1.40	2.90	11.23	15.53
	E	12.5	5.83	2.04	4.86	20.40	27.30
	F	10.0	5.95	2.02	5.16	35.67	42.85
2nd step	B	10.0	4.38	0.34	0.11	0.00	0.45
	E	12.5	4.30	0.34	0.15	0.00	0.49
	F	15.0	4.21	0.43	0.18	0.15	0.76

compared to E and F, as will be shown below. This leads to higher final conversions. This issue is addressed in the following sections. These results are important not only to understand the physicochemistry of this system, but also regarding the process design at industrial level. According to these results, it is highly convenient to dosify more methanol in the first reactor and a lower amount in the second one. In fact, the key is to have a relatively high conversion in the first reactor, e.g. 85%, in order to form a small amount of glycerine in the second step.

The higher methanol content in the first step (experiment B) not only favors the advancement of the reaction but also leads to lower viscosity of both phases and to a different distribution of the components of the system, between the biodiesel and the glycerine phases, as shown in the following paragraphs. This has an impact in the process design and performance, particularly in the settling step. The methanol concentration in the system has influence on one hand, on the diffusion rate of the components due to the change of the viscosity, and on the other hand, it modifies the equilibrium compositions leading to higher concentration of impurities (methanol, catalyst) in the biodiesel phase [23,24]. In continuous systems, a faster settling rate makes it possible to obtain the biodiesel phase in a level of purity closer to that corresponding to the equilibrium. In the experiments carried out in this work, the settling was carried out at the reaction temperature for 10 min. Fig. 1 shows the results obtained at the end of the first step in experiments B, E, and F, in which the methanol was loaded in different proportions in each step, but maintaining constant its total amount. The lower viscosity of both phases in experiment B, leads to a system in which the soaps and the catalyst are concentrated preferentially in the glycerine phase. In addition to this effect, the conversion in the first step of experiment B (using 15%v/v of methanol) is significantly higher than in experiments E and F in which 12.5 and 10%v/v of methanol were used, respectively. Therefore, there is a formation of a glycerine phase larger in the former case, thus extracting more impurities than in the other two experiments. Note that in experiment B (15%v/v methanol in the first step), the soaps and catalyst concentration in the glycerine phase are larger than in the other two similar experiments (E and F).

In the first reaction step a fraction of catalyst is consumed by the neutralization and saponification reactions, leading to the formation of soaps. After settling, the soaps are concentrated in the glycerine phase due to its high polarity [1]. This makes it possible to remove the free fatty acids originally present in the vegetable oil, as soaps in the glycerine phase. Fig. 1 shows that in experiments B, E and F, the soaps are formed mainly during the first reaction step, and a much smaller amount was formed during the second step.
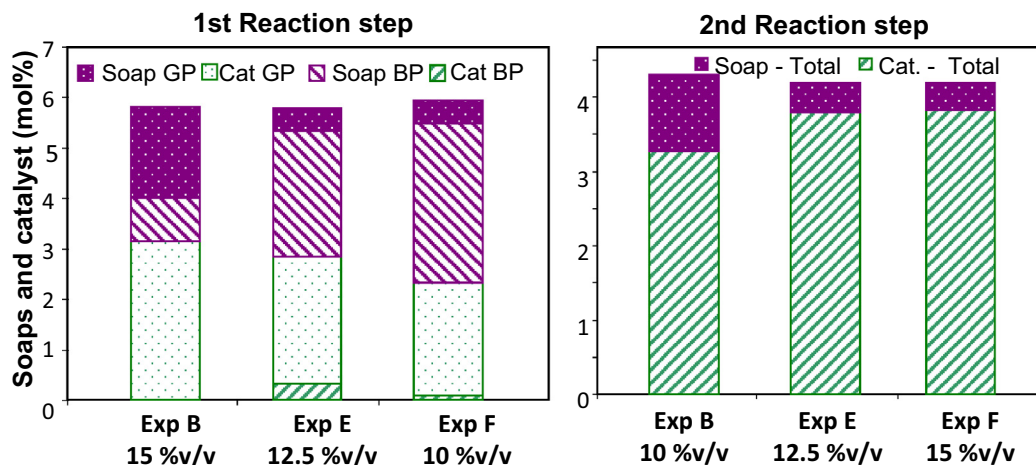
Table 5
Compositions of mono-, di-, and triacylglycerides in two-steps reactions, changing the dosification of catalyst in the second step.

	C_{MeOH} %v/v	C_{cat} mol%	MAG wt%	DAG wt%	TAG wt%	NC wt%
1st step	15	5.72	1.69	3.40	11.79	16.88
2nd step	10 (Exp. B)	4.38	0.34	0.11	0.00	0.45
	10 (Exp. G)	3.29	0.43	0.14	0.03	0.60
	10 (Exp. D)	2.19	0.50	0.15	0.01	0.66
	10 (Exp. I)	1.10	0.66	0.52	1.77	2.95

3.4. Effect of catalyst loading in the second step

The catalyst concentration in the second step was modified in order to study its impact in the concentration of unconverted glycerides with the objective of improving also the process efficiency. Using 12.5%v/v of methanol in both steps, and a concentration of 0.35 wt% (5.83 mol%) of catalyst in the first one, three concentrations of catalyst in the second step were used: 0.26 wt%, 0.19 wt% and 0.12 wt% (4.30, 3.22, and 2.15 mol% respectively), listed in Table 1 as experiments E, J, and K. Another set of experiments was carried out using a concentration of methanol of 15%v/v in the first step and 10%v/v in the second. Four different concentrations of catalyst in the second step were used: 0.26, 0.19, 0.13, 0.06 wt% (4.38, 3.29, 2.19, and 1.10 mol% respectively, presented in Table 1 as experiments B, G, D, and I). The most important difference between these two sets of experiments is that after the first step the amount of non-converted glycerides is much smaller when using the higher dosification of methanol, being 16.88 wt% when using 15%v/v of methanol (Table 5), and 27.65 wt% when using 10%v/v of methanol (Table 6). Therefore, the amount of glycerine that will be formed in the second reaction step is much higher in the experiments carried out using the lowest methanol concentration in the first step.

Fig. 2 shows the total amount of unconverted glycerides as a function of the catalyst concentration in the second step. It can be observed that in order to obtain high conversion levels, less catalyst is needed in the second step when using lower amount of methanol in this second step, and corresponds to the case in which the glycerine phase is smaller, thus making it possible to the catalyst and methanol to concentrate in the biodiesel phase. In addition, the conversion is more insensitive to the catalyst concentration in the second step at the lowest methanol concentration, what makes it possible to reduce the catalyst consumption in the process.

The compositions obtained in these experiments are shown in Tables 5 and 6.

Fig. 1. Soaps and catalyst concentrations in the glycerine phase (GP) and biodiesel phase (BP), in experiments B, E and F, carried out using different distribution of methanol between the first and second reaction steps.

Table 6
Compositions of mono-, di-, and triglycerides in two-steps reactions, changing the dosification of catalyst in the second step.

	C_{MeOH} %v/v	C_{cat} mol%	MAG wt%	DAG wt%	TAG wt%	NC wt%
1st step	12.5	5.83	2.51	4.65	20.49	27.65
2nd step	12.5 (Exp. E)	4.30	0.34	0.15	0	0.49
	12.5 (Exp. J)	3.22	0.44	0.18	0.13	0.75
	12.5 (Exp. K)	2.15	0.61	0.56	2.10	3.27
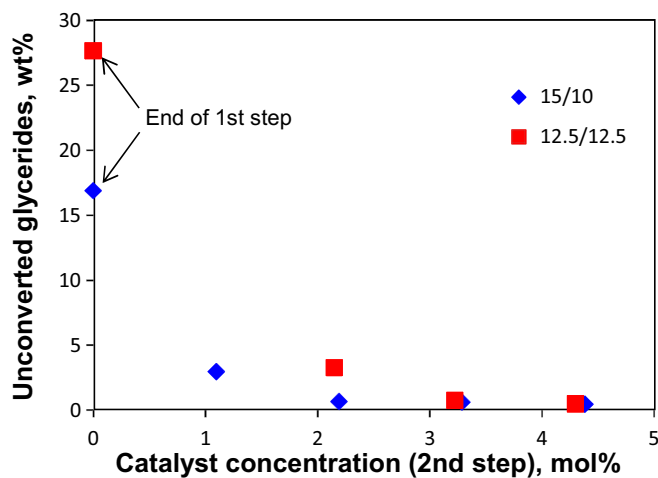
Fig. 2. Non converted acylglycerides at the end of the first step, and at the end of the second steps, using different catalyst dosifications. Experiments E, J, K: 12.5% methanol in both steps (■), experiments B, G, I, D: 15% methanol in the first step, 10% in the second (◆).

3.5. Effect of glycerine phase removal

An experiment was carried out using the dosifications of experiment B, first step (Table 4) during 60 min. Under the same conditions, the experiment was run during 7 min, then the mixture was settled and the glycerine phase removed. After this operation, the biodiesel phase was put back in the reactor at the reaction temperature, taking samples to follow the advancement of the reaction. As shown in Fig. 3, the removal of the glycerine phase leads to a sharp decrease in the reaction rate. This is a conclusive evidence that the glycerine removal is not an important factor as compared to the methanol and catalyst removal that are present in the glycerine phase. In other words, removing practically all the product (glycerine) from the reactor, does not lead to a shift in the equilibrium conversion towards the products.

3.6. Phase equilibrium

In these experiments, mixtures of glycerine and biodiesel were prepared using a proportion of glycerine equivalent to 100%, 85% and 15% of triglycerides conversion. This experimental design makes it possible to simulate the end of the process in the case of a reaction carried out in a single step (100% conversion), and at the end of the first and second steps (85% and 15% conversion respectively), in the case of a two-steps reaction strategy. In these mixtures, methanol was added in different amounts, and catalyst in a fixed proportion, as presented in Table 2. Fig. 4 shows the concentrations of soaps and catalyst in both phases. Results obtained in the experiments carried out with the glycerine corresponding to 100% conversion and to 85% conversion are very similar. The concentration of soaps and catalyst are presented in the scale of mol%, that as above explained makes it possible to do a direct comparison between the catalyst consumed and the soaps formed during the reaction.
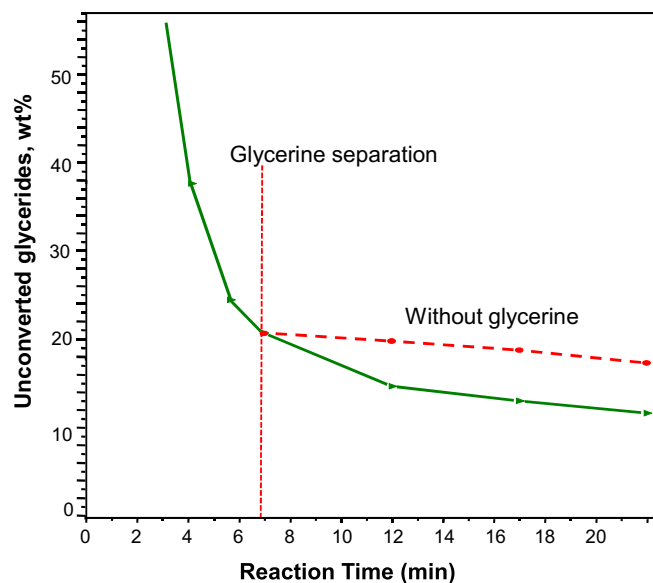

Fig. 3. Effect of glycerine removal in the conversion. Reaction conditions as in experiment B, 1st step.

In the experiments with high level of glycerine (equivalent to 85% conversion) no catalyst was found in the biodiesel phase, no matter the concentration of methanol used in the system. Since the glycerine phase has high polarity and is present in a large amount, all the catalyst was concentrated in this phase. This explains why in the case of the reaction carried out in one step, the final conversion was not enough to obtain biodiesel within specifications (Table 3, experiment C). This is because the catalyst is concentrated in the glycerine phase while the unreacted glycerides are concentrated in the biodiesel phase, and therefore the reaction kinetics is not favored. On the other hand, when the amount of glycerine is equivalent to 15% conversion, i.e. similar to that obtained in the second reaction step, it is possible to determine the presence of catalyst in the biodiesel phase (Fig. 4, experiments 15/10, 15/20), thus improving the reaction kinetics, and increasing the final conversion as can be observed in Table 3 (experiment D). This is a key observation because it explains the better conversion obtained in a system in which a two-step strategy is used, even though the total amount of catalyst loaded to the system is the same as that used in one-step obtaining lower conversion (experiment C in Table 3).

As above described, in each biodiesel-glycerine mixture (equivalent to 100%, 85% and 15% conversion) three different concentrations of methanol were used, being 1%, 10% and 20% referred to the mixture. For each level of glycerine, as the methanol content increases, the amount of soaps in the biodiesel phase increases (Fig. 4). In the system with lower amount of glycerine (equivalent to 15% conversion) the concentration of soaps and catalyst in the biodiesel is significantly higher than in the case of higher amount of glycerine.

In the case of the system that represents the second reaction step (glycerine equivalent to 15% conversion) it was not possible to measure the amount of soaps and catalysts in the glycerine phase in two cases: experiments 15/0 and 15/20, and because of this are indicated in Fig. 4 with question marks (??). In the experiment 15/0, since no methanol was added in addition to that contained in the solution with the sodium methoxide, a gel was formed in the bottom of the reactor due to the high level of soaps contained in this phase. The important consequence of this concentration of impurities in the glycerine phase is that the biodiesel phase contains very small amount of soaps. On the other hand, when using a high methanol concentration (experiment 15/20) a high solubility of the polar compounds in the biodiesel phase is observed leading to a system in which the biodiesel phase is practically the only phase present in the system. The mass of glycerine phase present in the
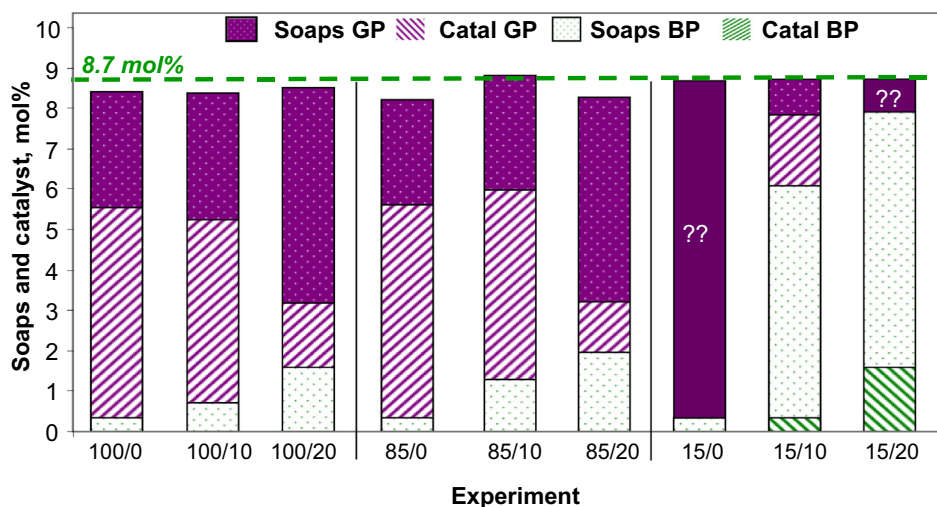
Fig. 4. Phase equilibrium experiments. Catalyst and soaps concentrations in biodiesel (BP) and glycerine (GP) phases. Experimental details: see Section 2.2.

system in this case is only 1.3% of the total mass of the reacting system, not being possible to determine its composition. This is also a key observation regarding the process design, and indicates that the conversion in the first step should not be too high, because in this case, no glycerine phase will be formed in the second step. Therefore, all the impurities, particularly the soaps, will be concentrated in the biodiesel phase increasing its acidity in the neutralization step during the biodiesel purification.

In the case of the experiment 15/10, it is an intermediate situation between the two experiments 15/0 and 15/20, and is very similar to the situation found in the second reaction step in which 10% methanol was added. Fig. 4 shows that in the case of the system 15/10 the availability of catalyst in the biodiesel phase is higher than in the case of the system 85/10. It means that during the second reaction step the concentration of catalyst is higher in the biodiesel phase than during the first step, with the consequent increase in the reaction rate at a given methanol and catalyst concentrations. Because of this more efficient use of the catalyst when the reaction is carried out in two steps, the final conversion is better than in the case of one step reaction (Table 3, experiments C and D).

In addition to high concentrations of soaps and catalyst, the glycerine phase contains important amounts of methanol, as can be inferred taking into account the different polarity of the components of this system, and the ternary diagrams already reported [25,26]. As the glycerine is formed due to the advancement of the reaction, the catalyst accumulates in this phase as shown in Fig. 4. In order to quantify the distribution of methanol between the two phases in the presence of catalyst and soaps, its concentration was measured in the experiments shown in Fig. 4.

The concentration of methanol in the biodiesel phase is shown in Fig. 5, as a function of the glycerine content in the reacting mixture. Three different levels of methanol concentration were used: 1%, 10% and 20% of methanol referred to the (biodiesel + glycerine) mixture. The first case corresponds to the situation in which no methanol other than that contained in the catalyst solution was added. It can be observed that the methanol concentration in the biodiesel phase decreases as the glycerine content in the system increases. This behaviour has a strong effect in the kinetics of the reaction. For example, in the system in which 20%v/v of methanol was added, which is similar to the amount used when the reaction is carried out in one step, the concentration of methanol in the biodiesel phase drop to 10.5 wt% when the glycerine concentration in the system is only 1.4 wt% (see Fig. 5). As the glycerine global concentration increases to 8 wt% and 9.4 wt%, which are quantities equivalents to 85% and 100% conversion respectively, the methanol concentration in the biodiesel phase further
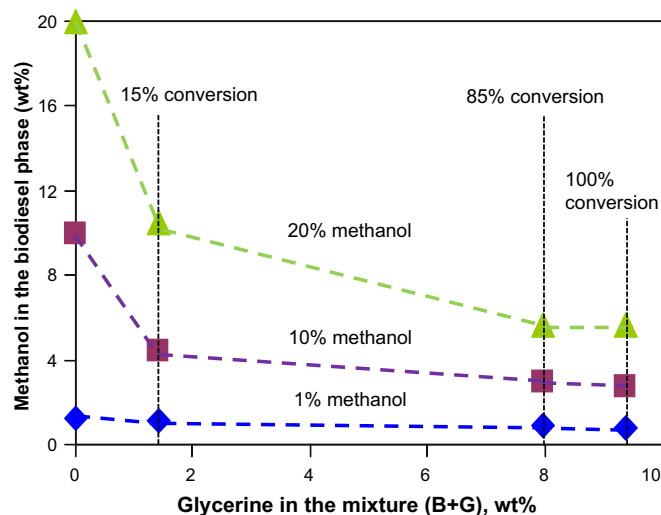

Fig. 5. Phase equilibria experiments. Methanol concentration in the biodiesel phase at different contents of glycerine in the system. Experimental details: see Section 2.2.

decreases to 5.7 wt% and 5.6 wt% respectively. This is almost one fourth of the global concentration of methanol in the system, and therefore, highly inefficient regarding the reaction rate. Therefore, in the case in which the reaction is carried out in two steps, the catalyst and the methanol are more concentrated in the biodiesel phase during the second step, thus improving the kinetics of the system. This is in agreement with an observation highlighted by B. Likozar et al. [10]. They found that at very short reaction time (e.g. 1 min) the conversion obtained with methanol is lower than with other alcohols, such as ethanol, isopropanol, butanol, and terbutanol, and ascribed this behaviour to the fact that in the case of methanol the alcohol is in a different phase than the oil, while in the other cases there is only one phase thus improving the kinetics. However, at longer reaction times and at equilibrium the conversion obtained with methanol is higher than with the other alcohols [10].

As mentioned above, it was normally attributed the better conversion obtained in two steps than in one step, to the fact that when the glycerine phase is removed, the equilibrium shifts towards the products. Nevertheless, this reacting system is formed by two phases. When phase equilibrium is reached, situation that occurs at high conversions, the chemical potential of each compound is equal in both phases. For

example, for the glycerine the physicochemical equilibrium is represented by the following equation:

$$\mu_G)_{GP} = \mu_G)_{BP}$$

When the glycerine phase is removed, the chemical potential of the glycerine present in the biodiesel phase is not modified, and therefore the chemical equilibrium is not perturbed and it is not possible to have a shift in the compositions of the system towards the products of the reactions 1, 2 and 3. In other words, removing the glycerine phase does not affect the glycerine composition in the biodiesel phase, nor its chemical potential. Consequently, the idea of having a displacement of the reaction 3 and consequently reactions 2 and 1 towards the products is wrong.

Results shown in Fig. 5 indicate that when the amount of glycerine in the reacting system is high, e.g. the amount that corresponds to 85% conversion or higher, the concentration of methanol in the biodiesel phase practically does not depend on this amount. For example, the methanol concentration in the biodiesel phase is 5.7 wt% and 5.6 wt% in the presence of glycerine amounts equivalents to 85% and 100% conversion respectively. These results explain the process strategy adopted in several commercial technologies, in which the glycerine phase formed in the second reactor, is recycled to the first one. In this way, there is an increase in the global concentrations of methanol and catalyst and consequently an improvement in the conversion in the first step. In order to avoid the problem of a high dissolution of soaps in the biodiesel phase in the second step, which could lead to problems in the quality of the final biodiesel, the global concentration of methanol in the second step should not be too high. In summary, in order to optimize the process from the point of view of methanol and catalyst consumption, a higher proportion of methanol should be loaded to the first reactor, while the higher proportion of catalyst should be loaded in the second one, recycling the glycerine phase from the second reaction step, to the first one. In this way, it is possible to obtain a good conversion in the first step, obtaining a phase of glycerine in the second step that concentrates the soaps.

4. Conclusions

In this study it is shown that in order to optimize the consumption of methanol and catalyst, it is important to properly distribute these components between the first and second reaction steps. A key issue related to the reaction rate and therefore the final triglycerides conversion, is the amount of glycerine present in the system. When the glycerine content is low, the methanol and the catalyst have high concentration in the biodiesel phase, thus improving the kinetic of the transesterification reaction. Therefore, it is important to have a relatively high conversion in the first step, then removing the glycerine and finally carrying out a second step, which has higher efficiency due to the higher concentration of reactants and catalyst in the same phase. For this reason, using the same total dosification of methanol and catalyst, the reaction carry out in two steps has better conversion levels than in one step. The removal of glycerine after the first reaction step has an impact on the kinetics of the reaction due to the change in the distribution of methanol and catalyst, but this operation does not shift the equilibrium towards the products, simply because it does not modify the glycerine's chemical potential or the composition of glycerine in the biodiesel phase.

Acknowledgements

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