

Process Design for Biodiesel Production with Crude Soybean Oils: Methanol Recovery from the Reacting System

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ABSTRACT: Biodiesel production has widely spread out throughout the world, with facilities in a wide range of capacities, from a few liters to more than a million liters per day. The process design is strongly related to the size of the production plant and the quality of the raw material. However, each alternative has advantages and disadvantages that have to be carefully evaluated. Methanol elimination by evaporation from the biodiesel phase or from both phases present after the reaction leads to a reversion of the reaction because of the shift of equilibrium toward the reactants. In this work, this process stage is studied, i.e., methanol evaporation before glycerine and biodiesel phase separation, and the effects that different homogeneous catalysts have on this operation. Through a decrease of the methanol concentration in the system, the soaps and other impurities present in the biodiesel are transferred to the glycerine phase because of a decrease in the solubility in the biodiesel phase. The operation time should be short to avoid an increase in the monoglyceride concentration formed by the reverse reaction between methyl ester and glycerine. This process is especially suitable for small installations that use nonneutralized oils as raw materials.

1. INTRODUCTION

Biodiesel is a renewable fuel obtained by transesterification of vegetable oils or animal fats. These raw materials have as a major component the triacylglycerols (~95%) and have others compounds in different proportions such as free fatty acids (FFAs), mono- and diacylglycerols, phospholipids, and non-saponifiable materials. The most common technology used to obtain biodiesel is transesterification of triacylglycerides with methanol using a basic catalyst such as sodium or potassium methoxides and hydroxides.

There are many publications in the literature related to biodiesel, studying different raw materials,^{1–6} the kinetics of the reaction,^{7–9} heterogeneous catalysts,^{10–13} the use of ethanol instead of methanol,^{5,6,14–16} or different technologies to carry out the reaction, such as under supercritical conditions,^{17–19} ultrasonic treatment,^{19–21} and enzymatic catalysis.^{10,19,22} In these cases, the main focus of the study was the reaction step. Only in a few situations have the problems associated with the other steps of the process been addressed. Mendow et al.²³ studied the purification of methyl and ethyl esters and proposed the use of a first neutral washing to avoid soap hydrolysis, which leads to high acidity in the final product.

The studies addressed different raw materials with a given catalyst,^{2,3} or a different catalyst with a given raw material.^{6,24–26} Only a few works compared different catalysts and raw materials.^{27,28} However, in all of these cases, the catalysts have been compared at the same weight percentage, instead of using the same molar concentration, which is needed in order to compare the intrinsic activity of homogeneous catalysts with different molecular weights.

The yield loss has been attributed to the saponification reactions; however, soap formation with different catalysts has not been quantified. In a few cases, the amount of soaps present in the glycerine phase was determined^{24,29–31} but without measuring soaps in the biodiesel phase. This property defines the acidity of the final product because when the biodiesel is

neutralized with an acid solution, soap hydrolysis leads to the formation of FFAs, raising the biodiesel acidity.

Recently, the effect of different catalysts (hydroxides and methoxides of sodium and potassium) on the transesterification reaction has been studied, using the same molar concentration.³² In addition, the saponification reactions that take place in parallel to the transesterification reaction had been quantified, measuring the amount of soaps and catalysts in both the glycerine and biodiesel phases.

It is important to study the effect of the catalysts also in the operations downstream of the reactor. In medium- and small-sized production plants, it is very common to use crude oils as raw materials, containing phospholipids and FFAs. In these cases, the design of the purification process is more complex than that in the case of refined raw materials.

In conventional processes, after the reaction the biodiesel and glycerine phases are separated. Afterward, either the biodiesel is neutralized with an aqueous acid solution (or purified with ion-exchange resins) or the methanol is evaporated from the biodiesel before washing. In the latter case, depending upon the soap content in the biodiesel phase, gel formation may occur. This has been a problem detected in several plants in operation. Figure 1 shows an example of gelification in a biodiesel sample from which methanol was eliminated after separation from the glycerine phase. Sample 1 corresponds to the biodiesel before methanol evaporation, and samples 2–4 have a decreasing amount of methanol. This phenomenon occurs because, as methanol is being eliminated, the soaps together with the free glycerine (FG) become insoluble in the biodiesel phase, forming a gel. Consequently, in the plants that use this process strategy, careful control of methanol evaporation from the biodiesel

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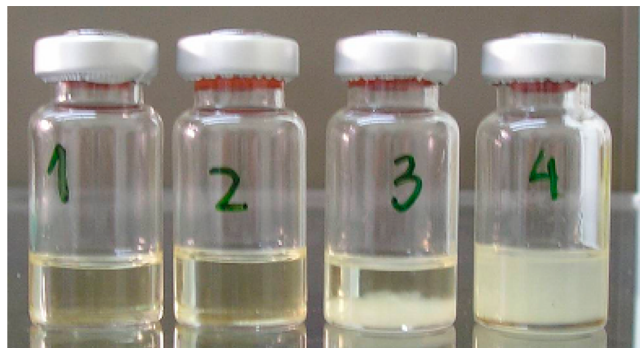


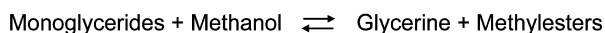
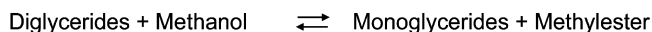
Figure 1. Samples of biodiesel taken during evaporation of methanol from a nonpurified biodiesel phase. The methanol concentration decreases from samples 1 to 4.

phase is needed, mainly in those cases in which crude oils are used, producing high soap concentrations in the biodiesel phase. In plants using this strategy, gel formation was in several cases so intense that it was necessary to open the evaporators to remove the gel.

In this work, a different process sequence was studied in order to avoid this problem of gel formation when methanol was eliminated from the biodiesel phase. This alternative process is based on the elimination of methanol right after the reaction, before phase separation. The objective is to decrease the polarity of the biodiesel-rich phase, thus favoring accumulation of the polar impurities (soaps, FG, and catalyst) in the glycerine phase. This sequence also makes it possible to recover methanol from both phases, with a negligible amount of water.

However, when methanol is eliminated from the system having a composition very close to the equilibrium one, the reverse transesterification reactions can occur, depending on the amount of methanol evaporated. The direct transesterification reactions are shown in Scheme 1. At the end of the reaction, the tri-, di-, and monoglyceride concentrations are very low, while the glycerine and methyl ester concentrations are high.

Scheme 1. Transesterification Reactions



Taking this into account, methanol evaporation from the system after the reaction was studied, in order to quantify the reversion of the transesterification reaction in different conditions. The effect of different catalysts on this system was also addressed. The objective is to understand the system and develop the process, avoiding a reversion leading to mono-, di-, and triglyceride concentrations out of specifications.

2. EXPERIMENTAL SECTION

2.1. Materials. The raw materials used in this study were refined soybean oil with an acidity of 0.01% (expressed as grams of oleic acid per 100 g of oil) and crude soybean oils with acidities of 0.41% and 1.13%. The three raw materials were dried before use by bubbling nitrogen at 80 °C, obtaining oils with a water content in the range of 400–500 ppm.

The alcohol used in the transesterification reaction was methanol PA (Cicarelli), containing 300 ppm of water.

Four different catalysts were studied: sodium hydroxide (Cicarelli PA), potassium hydroxide (Cicarelli PA), and sodium methoxide and potassium methoxide solutions, both dissolved in methanol with concentrations of 30 and 32 wt %, respectively (Evonik-Degussa).

2.2. Transesterification Reaction. The reaction was carried out in a batch glass reactor, working at atmospheric pressure, under reflux conditions. The reactor was immersed in a thermostatic bath at 60 °C, under vigorous stirring (600 rpm), using a magnetic stirrer. The methanol concentration loaded in the reactor was 25 vol %, referred to the volume of oil (25 mL of methanol/100 mL of oil). This amount corresponds to a 100% excess relative to the stoichiometric value, and it is a typical value of dosification at the industrial level.

The catalysts were mixed with methanol and transferred to the reactor once the oil was at the reaction temperature. The catalysts were loaded at a concentration normally used in commercial applications, e.g., for sodium methoxide, 15 kg/ton of oil. Throughout this study, and in order to compare the different catalysts, the concentration is expressed as mole percent, defined as (mol of catalyst/100 kg of oil + methanol). The reference value of the concentration used for all of the catalysts is 7.83 mol %. In order to neutralize the FFAs contained in the oil, an extra amount of catalysts was added, equivalent to the moles of FFAs contained in the raw material. In the case of the oils with acidities of 0.41% and 1.13%, the amounts added to neutralize the FFAs were 1.2 and 3.3 mol %, respectively.

2.3. Methanol Evaporation: Reaction Reversion. After 90 min of transesterification reaction, the system was allowed to settle for 10 min in order to take the first sample for analysis. This moment is referred to throughout the text as the end of the reaction. Afterward, a vacuum was gradually applied, evaporating the methanol, which was collected in a refrigerated vessel. Evaporation was carried out at different temperatures, 60 and 70 °C, following two procedures. In one of them, methanol was evaporated during 30 min, and in the other one, evaporation was carried out in three steps of 10 min each, allowing the sample to settle for 10 min after each step. In this way, the evolution of soaps and methanol in the biodiesel phase, as well as the mono-, di-, and triglyceride compositions, was followed.

In all cases, evaporation was started at atmospheric pressure, increasing the vacuum as fast as possible but avoiding a boilover.

2.4. Samples Analyses. The compositions of the biodiesel and glycerine phases were determined after 10 min of decantation, after either the reaction or the evaporation steps. The analyses and techniques followed in each case are summarized in Table 1.

Table 1. Analysis Carried Out on Biodiesel and Glycerine Samples

| sample | analysis | method |
|----------------------|--|--------------------------------------|
| biodiesel phase (BP) | methanol | UNE-EN 14110 (methanol >1 wt %) |
| | soaps and catalyst | IRAM 5599 |
| | free and TG, mono-, di-, and triglycerides | ASTM D 6584 UNE-EN 14105 |
| glycerine phase (GP) | methanol | UNE-EN 14110 (methanol in glycerine) |
| | water | UNE-EN ISO 12937, Karl Fisher |
| | soaps and catalyst | IRAM 5599 |

The total glycerine (TG) content is one of the most important parameters in defining the biodiesel quality. It represents the sum of FG and bound glycerine (BG). The latter corresponds to the glycerine that is forming the unconverted mono-, di-, and triglycerides in the final product.

3. RESULTS AND DISCUSSION

Figure 2 shows the part of the biodiesel production process under evaluation in this study. The focus of this investigation is to analyze the changes that take place in the biphasic system during methanol evaporation (evaporator in Figure 2). After the

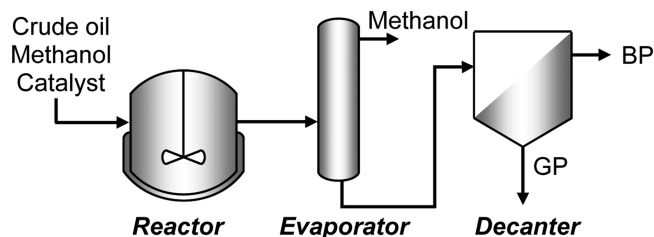


Figure 2. Scheme of the modified process.

phases are separated, the biodiesel must be further purified, by neutralization, washing, and drying.

3.1. Reaction Step. 3.1.1. Influence of the Raw Material.

At the end of the reaction, i.e., after the reaction and 10 min of settling, the concentrations of mono-, di-, and triglycerides, as well as the corresponding value of BG, were determined. The concentrations determined after the reaction and 10 min of settling are presented in Table 2, corresponding to an

Table 2. Composition of the Biodiesel Phase as a Function of the Evaporation Time, after Reaction with Different Raw Materials, 25 vol % Methanol, and NaOCH₃ as Catalysts

| raw material | evaporation time (min) | composition (wt %) ^a | | | |
|-----------------------|------------------------|---------------------------------|------|------|-----------|
| | | M | D | T | BG |
| refined oil, A = 0.01 | 0 | 0.39 | 0.09 | 0.07 | 0.12 |
| | 30 | 0.71 | 0.14 | 0.06 | 0.21 |
| crude oil, A = 0.41 | 0 | 0.65 | 0.17 | 0.10 | 0.20 |
| | 30 | 0.87 | 0.20 | 0.08 | 0.25 |
| crude oil, A = 1.13 | 0 | 0.74 | 0.23 | 0.12 | 0.23 |
| | 30 | 1.05 | 0.24 | 0.05 | 0.31 |
| limits EN 14214 | | ≤0.8 | ≤0.2 | ≤0.2 | TG ≤ 0.25 |

^aM = monoglycerides, D = diglycerides, T = triglycerides, BG = bound glycerine, and TG = total glycerine.

evaporation time of 0 min. It can be observed that, for experiments carried out with different raw materials (refined and crude oils) with methanol and sodium methoxide as catalysts, the conversion was high in all cases. In the case of the refined oil, the concentrations of mono-, di-, and triglycerides were well below the maximum limits established in the EN 14214 standard. However, this conversion slightly decreased as the oil acidity increased.

In the reactor, not only does the transesterification reaction occur, but also the neutralization and saponification reactions take place. In these latter reactions, the catalyst is consumed, forming soaps.^{31,32} The concentration of soaps in the biodiesel phase before evaporation is shown in Figure 3 for experiments carried out with raw materials having different initial acidities (evaporation time 0 min). It can be observed that, as the oil acidity increased, the amount of soaps formed because of neutralization of the FFAs that remain in the biodiesel phase also increased. As mentioned above, this is due to catalyst consumption by the neutralization and saponification reactions, and because of this, a lower conversion level was obtained, as shown in Table 2. The neutralization and saponification reactions occur faster than the transesterification reaction, and because of this, catalyst consumption occurs mainly at the beginning of the reaction, and the acidity in the reactor is zero

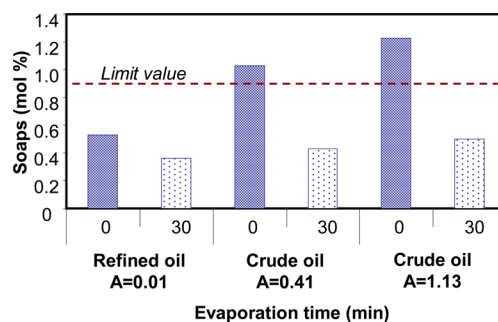


Figure 3. Soap concentrations in the biodiesel phase after the reaction and after 30 min of methanol evaporation, for different raw materials. Catalyst: NaCH₃O.

after a few minutes of operation. However, as was recently demonstrated,³² as the acidity increases, the amount of catalyst consumed due to the neutralization and saponification reactions increases in a more significant way. This is due to the water formed in the neutralization that in an alkaline media leads to saponification. For example, it was experimentally determined that, for an oil with acidity of 1.13%, the amount of catalyst consumed was 75% of the initial amount, being 30% of the amount that was consumed because of neutralization. It means that a large extra amount of catalyst was consumed because of the saponification that occurred due to the water formed in the neutralization.

After decantation, the biodiesel phase must be purified. Typically, the first operation of the purification is neutralization of the catalyst present in the biodiesel phase with an aqueous acid solution, such as citric, hydrochloric, sulfuric, or phosphoric acid. In this step, the soaps are hydrolyzed, forming FFAs that are soluble in the biodiesel phase, thus remaining in the final product and increasing the acidity. The acidity index established in the international standards is 0.50 mg of KOH/g of sample. This concentration corresponds to 0.89 mol % of FFA in the biodiesel. Therefore, because 1 mol of FFA is formed by hydrolysis of 1 mol of soaps, the concentration of this impurity in the crude biodiesel right before the neutralization, i.e., after decantation, must be lower than 0.89 mol % in order to meet the standard specification regarding the acidity. This reference value is shown in Figure 3 as a dotted line.

The experiments carried out with the refined soybean oil showed a lower soap concentration, with a value on the order of 0.5 mol % after the reaction step. This value allowed the purification step (neutralization, washing, and drying) to be performed without problems because the soap limit concentration, in order to have an acidity in the biodiesel within specifications, is 0.89 mol %. In the case of the crude oils, the soap concentration was higher than the reference value, and consequently in a conventional process, the biodiesel would be out of specification in the acidity parameter.

3.1.2. Influence of the Catalyst. Table 3 shows the compositions obtained after the reaction, i.e., before the beginning of methanol evaporation (time 0), for experiments carried out with the crude soybean oil of acidity 0.41% and different catalysts. The conversion was good with the four catalysts studied. However, the sodium catalysts had better activity than the potassium ones, and on the other hand, methoxides were more active than hydroxides. The TG obtained with both hydroxides was out of specification.

The concentration of soaps in the biodiesel phase before evaporation is shown in Figure 4B for experiments carried out

Table 3. Composition of the Biodiesel Phase as a Function of the Evaporation Time, after the Reaction with Crude Soybean Oil, of Acidity 0.41%, 25 vol % Methanol, and 9 mol % Catalysts

| catalyst | evaporation time (min) | composition (wt %) ^a | | | |
|--------------------|------------------------|---------------------------------|------|------|-----------|
| | | M | D | T | BG |
| NaOCH ₃ | 0 | 0.66 | 0.17 | 0.10 | 0.20 |
| | 10 | 0.54 | 0.13 | 0.07 | 0.16 |
| | 20 | 0.74 | 0.17 | 0.06 | 0.22 |
| | 30 | 0.85 | 0.19 | 0.09 | 0.25 |
| KOCH ₃ | 0 | 0.74 | 0.23 | 0.12 | 0.23 |
| | 10 | 0.71 | 0.18 | 0.08 | 0.22 |
| | 20 | 0.84 | 0.18 | 0.08 | 0.25 |
| | 30 | 1.04 | 0.20 | 0.09 | 0.30 |
| NaOH | 0 | 0.79 | 0.26 | 0.21 | 0.26 |
| | 10 | 0.63 | 0.23 | 0.16 | 0.21 |
| | 20 | 0.76 | 0.24 | 0.17 | 0.25 |
| | 30 | 0.97 | 0.24 | 0.16 | 0.30 |
| KOH | 0 | 0.67 | 0.28 | 0.85 | 0.30 |
| | 10 | 0.65 | 0.31 | 0.73 | 0.29 |
| | 20 | 0.86 | 0.32 | 0.79 | 0.35 |
| | 30 | 1.08 | 0.37 | 0.79 | 0.41 |
| limits EN 14214 | | ≤0.8 | ≤0.2 | ≤0.2 | TG ≤ 0.25 |

^aM = monoglycerides, D = diglycerides, T = triglycerides, BG = bound glycerine, and TG = total glycerine.

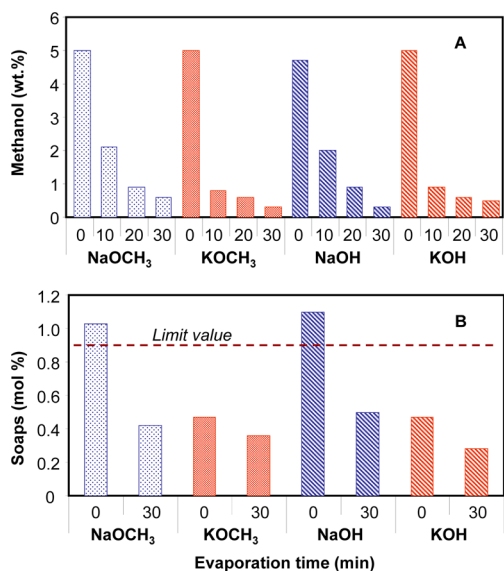


Figure 4. Biodiesel phase composition as a function of methanol evaporation time. Reaction with oil of acidity 0.41%, 25 vol % methanol, and 9 mol % catalyst: (A) methanol concentration; (B) soap concentration.

with the crude oil with acidity 0.41%. Potassium catalysts formed a lower amount of soaps than sodium catalysts, which is an advantage when using nonrefined raw materials. It is important to highlight that, in the case of sodium catalysts, the soap concentration is higher than the reference value (dotted line). Similar results were obtained with the crude oil with acidity 1.13%, although in this case, the soap concentration in the biodiesel phase at the end of the reaction was above the maximum value allowed in order to have a final acidity within specifications (Figure 5A). For this reason, in these cases, i.e.,

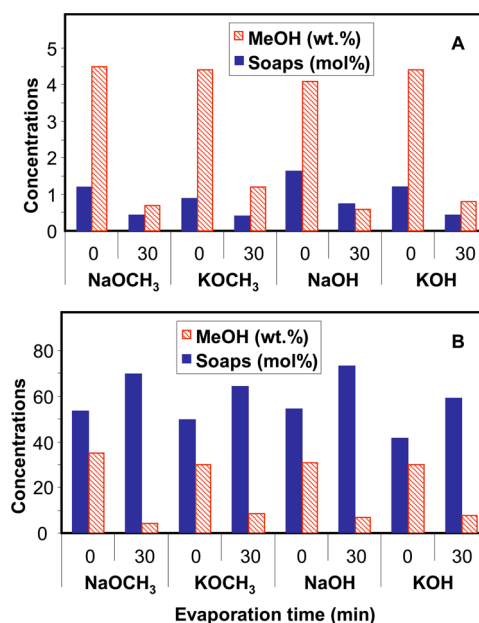


Figure 5. Composition of biodiesel (A) and glycerine (B) phases, before and after methanol evaporation. Reaction with oil of acidity 1.13%, 25 vol % methanol, and 11.1 mol % catalyst.

when using nonneutralized crude oils, it is necessary to modify the purification sequence, for example, introducing the methanol evaporation step before phase separation and biodiesel neutralization, in order to favor the transference of soaps and catalyst to the glycerine phase.

3.2. Methanol Evaporation. **3.2.1. Effect of the Initial Oil Acidity.** Table 2 shows the composition of the biodiesel phase obtained in the reaction with refined and crude soybean oils with different acidity levels, before and after the methanol evaporation step. In these experiments, the methanol concentration was measured after 30 min of evaporation at 60 °C. It can be observed that the mono- and diglyceride concentrations were higher at the end of the evaporation, with the increase in the monoglyceride concentration being higher than that in the case of the diglycerides. It is interesting to highlight that the triglyceride concentration had a further decrease during this operation. Therefore, these results show that methanol evaporation, even at 60 °C, may increase the mono- and diglyceride concentrations, leading to a biodiesel out of specifications, even in cases in which the conversion right after the reaction step was at an appropriate level.

On the other hand, as shown in Figure 3, after methanol evaporation, the soap concentration in the biodiesel phase was significantly reduced, decreasing to 0.43 and 0.50 mol % for the oils with acidities 0.41 and 1.13%, respectively. Therefore, this operation made it possible to reduce the soaps in the biodiesel to levels at which, after neutralization, the acidity would be within specifications.

3.2.2. Effect of the Methanol Evaporation Conditions. Table 3 shows the composition of the biodiesel phase obtained in the reaction with crude soybean oil of acidity 0.41%, after methanol evaporation during three consecutive intervals of 10 min each. It can be observed that, during the first evaporation step of 10 min, the glyceride composition decreased in all experiments, i.e., with all of the catalysts used in this study. Therefore, at the beginning of the evaporation, the net reaction rate of the transesterification was still in the forward direction,

even though the absolute value would be smaller because of the lower methanol concentration. The methanol concentrations determined in these experiments are shown in Figures 4A and 6

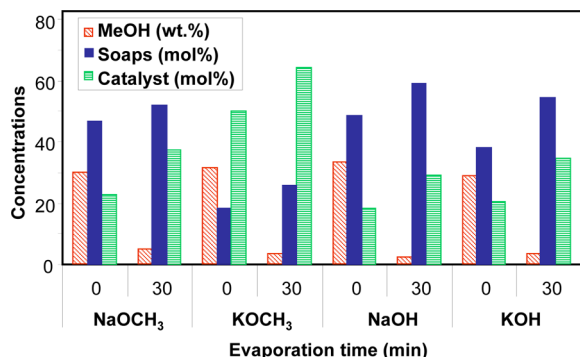


Figure 6. Composition of the glycerine phase before and after methanol evaporation. Reaction with oil of acidity 0.41%, 25 vol % methanol, and 9 mol % catalyst.

for the biodiesel and glycerine phases, respectively. The amount of methanol present in the glycerine phase after the reaction represents more than half of the total amount of alcohol in the system.

In small- and medium-sized facilities, glycerine is not treated, thus decreasing the overall process efficiency due to methanol loss in this phase. The strategy proposed in this work makes it possible to recover a high proportion of the alcohol. Practically 90% of the methanol present in the system after the reaction with the crude oil of acidity 0.41% was recovered, as shown in Figures 4A and 6. Parts A and B of Figure 5 show the methanol concentrations in the biodiesel and glycerine phases, respectively, in the case of experiments carried out with crude oil with acidity 1.13%. These results are similar to those previously shown for the oil with acidity 0.41%.

At the end of the reaction, the methanol concentration in the biodiesel phase was approximately 5 wt % (Figure 4A). After 10 min of evaporation, this concentration significantly decreased.

Table 3 shows that, after 20 min of evaporation, with the four catalysts the concentration of monoglycerides increased although in different quantities. The monoglyceride concentration at 20 min of evaporation was out of specification with both potassium catalysts, and at 30 min, it was out of specification with the four catalysts. It is interesting to observe that the triglyceride concentration was practically not affected by this operation.

3.2.3. Effect of the Catalyst. In the case of experiments carried out with the crude oil with acidity 0.41%, after 10 min of evaporation, it was possible to remove 80% of the methanol in the case of the potassium catalysts, without having a reaction reversion (Figure 4A and Table 3). On the other hand, in the case of sodium catalysts, the fraction of methanol evaporated was approximately 40%. This difference is due to the fact that the vacuum was gradually applied in order to avoid foam formation with a boilover. Because of this, the rate at which the vacuum was increased was limited by the foam formed in each case. It is very interesting to observe that sodium catalysts led to a higher amount of soaps formed during the reaction, as shown in Figure 4B. Therefore, the vacuum was increased at a slower rate in the case of sodium catalysts compared to the potassium ones because of a more intensive foam formation with the former. Consequently, after 10 min of evaporation, a higher amount of methanol was removed in the case of potassium catalysts. This issue is important regarding the design of the evaporators because higher space should be left above the liquid level to avoid the boilover in the case of high soap content in the biodiesel phase. Also, it can be observed in Table 3 that the monoglyceride concentration obtained at 10 min of evaporation was very similar to the initial one in the case of potassium catalysts, while there was an appreciable reduction in the case of sodium catalysts. This is due to the lower level of methanol reached in the case of the former catalysts.

As the methanol content in the biodiesel phase decreased, the soap concentration also decreased (Figures 4B and 5A), making it possible to obtain the final product with a correct acidity after the neutralization, washing, and drying steps. This is particularly important for sodium catalysts, which formed higher amounts of soaps, and also in the case of acid raw materials with more than 1% acidity. The evaporation of methanol made it possible to decrease the soap concentration well below the maximum limit needed to obtain a low enough final acidity.

3.2.4. Effect of the Methanol Concentration in the Impurity Distribution. One of the most important advantages of the process strategy discussed in this work is that the soap and catalysts are preferentially concentrated in the glycerine phase when methanol is removed from the reacting system. Figure 6 shows the methanol, soap, and catalyst concentrations in the glycerine phase before and after methanol evaporation. There was an increase in the concentrations of catalyst and soap in the glycerine phase after methanol was evaporated.

In this work, the FG was also determined in the biodiesel phase during the methanol evaporation operation. At the end of the reaction, the methanol concentration in the biodiesel phase

Table 4. Composition of the Biodiesel Phase as a Function of the Evaporation Times and Temperatures, after the Reaction with Refined Oil, 25 vol % Methanol, and 7.8 mol % Catalysts (NaOCH₃)

| evaporation temperature (°C) | evaporation time (min) | monoglyceride concentration increase (%) | composition (wt %) ^a | | | |
|------------------------------|------------------------|--|---------------------------------|------|------|------|
| | | | M | D | T | BG |
| 60 | 0 | | 0.63 | 0.20 | 0.17 | 0.21 |
| | 10 | 5.3 | 0.66 | 0.21 | 0.09 | 0.21 |
| | 20 | 8.8 | 0.68 | 0.23 | 0.08 | 0.22 |
| | 30 | 16.4 | 0.73 | 0.26 | 0.06 | 0.23 |
| 70 | 0 | | 0.54 | 0.18 | 0.11 | 0.18 |
| | 10 | 8.2 | 0.58 | 0.17 | 0.07 | 0.18 |
| | 20 | 18.4 | 0.64 | 0.21 | 0.06 | 0.20 |
| | 30 | 36.7 | 0.74 | 0.23 | 0.05 | 0.23 |

^aM = monoglycerides, D = diglycerides, T = triglycerides, and BG = bound glycerine.

was approximately 5 wt % and the FG was around 0.4 wt % in all cases. At the end of evaporation, the glycerine concentration decreased 2-fold (approximately to 0.2 wt %). As methanol was removed from the system, the FG solubility in the biodiesel decreased according to the phase equilibrium diagram (methyl ester/methanol/glycerol) reported by Zhou et al.³³ and Andreatta et al.³⁴ It is important to highlight that the FG concentration in the final biodiesel must be below 0.02 wt % in order to meet the specifications of the EN 14214 standard. As mentioned above, the concentration of FG in the biodiesel phase after the reaction, and even after methanol evaporation, was above this limit. After the purification steps, not included in this study, the FG concentration decreases well below the value of 0.02 wt %.

3.2.5. Effect of the Evaporation Temperature. Table 4 shows the glyceride composition in the biodiesel phase after each consecutive evaporation step, at 60 and 70 °C. In both cases, a more important increase in the monoglyceride concentrations, compared to the diglyceride concentration, was observed. However, in the case of evaporation at 70 °C, the increase in the monoglyceride concentration was significantly higher than that at 60 °C. After 30 min of evaporation, the monoglyceride concentration increased 36.7% and 16.4% at 70 and 60 °C, respectively, compared to the value before methanol elimination. In these experiments, the amount of methanol eliminated in each step was very similar between the two temperatures (final value of approximately 2 wt %), thus making it possible to clearly observe the effect of this variable. There is a strong effect of the evaporation temperature in the rate of the reverse reaction.

3.2.6. Effect of the Methanol Concentration. Figure 7 summarizes the results of the monoglyceride concentration

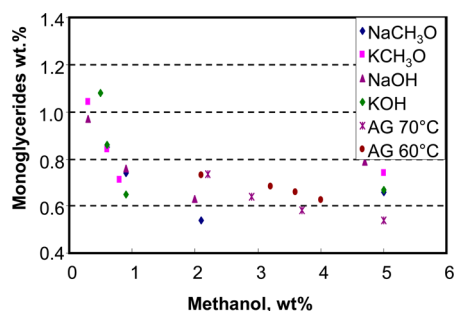


Figure 7. Monoglycerides concentration as a function of the methanol concentration in the biodiesel phase, during the methanol evaporation stage.

obtained during the methanol evaporation operation. Results correspond to experiments presented in Tables 3 and 4. It is very interesting that even though different raw materials and catalysts are included in this figure, as well as data obtained at an evaporation temperature of 70 °C, the results indicate that when the methanol concentration is approximately 1 wt %, the reverse reaction between methyl ester and glycerine starts accelerating, increasing the monoglyceride concentration at a faster rate, reaching concentrations above the limit of 0.8 wt %.

4. CONCLUSIONS

Methanol evaporation from the reacting system before phase separation makes it possible to recover the alcohol in order for it to be used in the production process.

The most important advantage is the decrease in the solubility of soaps, catalysts, and FG in the biodiesel phase, and consequently these impurities are transferred to the glycerine phase. This is particularly useful in the processes that operate with nonneutralized oils; moreover, if the catalysts used are sodium hydroxides and methoxides. This operation makes it possible to decrease the soap concentration to a level low enough, in order to obtain the biodiesel with acidity below the maximum limit.

In order to avoid a significant reaction reversion forming glycerides out of specification, very important variables are the time and temperature of evaporation and the level of demethanolization. At 60 °C, 20 min of evaporation and a methanol concentration in the order of 1 wt % are approximate limits to take into account to design this operation. In summary, it is possible to carry out this process strategy but properly designing the methanol evaporation stage, selecting the lowest possible evaporation temperature, and selecting a target value of the final methanol concentration in the biodiesel phase of approximately 1 wt %.

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Notes

The authors declare no competing financial interest.

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