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Glycerolysis of Soybean Oil with Crude Glycerol Containing Residual Alkaline Catalysts from Biodiesel Production

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Abstract The glycerolysis reaction of soybean oil was evaluated using crude glycerol obtained from the transesterification of soybean oil with methanol, catalyzed by sodium methoxide and sodium hydroxide, without any purification step other than the methanol removal. Crude glycerol with the lower content of remaining inorganic catalyst produced the highest concentration of monoglycerides (about 42%). The effect of the addition of water on the glycerolysis reaction was analyzed, evidencing a low formation rate of products in the first stages of the reaction due to the transformation of the inorganic catalyst to soaps, which are weaker bases. The sample of crude glycerol that led to the best results was evaluated at several temperatures. It was observed that the reaction with crude glycerol exhibits a lower formation rate of monoglycerides at low temperatures (160 and 180 °C) compared with the reaction with pure glycerol and catalyzed with NaOH. This behavior was explained by the lower activity of the soaps present in the crude glycerol respect to the inorganic base. Above 200 °C the reaction is very fast and the monoglycerides formed are consumed to produce diglycerides.

Keywords Glycerolysis · Crude glycerol · Monoglycerides · Biodiesel · Transesterification

Introduction

In the last decades, biodiesel has emerged as an alternative fuel due to the concerns about global warming and the depletion of fossil fuels. This fuel is generally obtained through alkaline-catalyzed transesterification between vegetable oils and methanol. In addition to the methyl ester mixture, this reaction produces glycerol as a by-product. For every ton of biodiesel around 0.1 ton of crude glycerol is produced. According to the US Energy Department, if the US were to replace only 2% of petroleum diesel by biodiesel then 800 million pounds/year (0.36 metric tons/year) of glycerol would be produced [1]. This exceeds the US glycerol market which is around of 600 million pounds/year (0.27 metric tons/year) [1]. The glycerol surplus can be seen as a threat but also as an opportunity to obtain valuable products from a cheap and versatile reactant.

Crude glycerol from the biodiesel process contains, in addition to the glycerol, the transesterification alkaline catalyst, soaps, oxidation products, methanol, methyl esters, and glycerides. Most of the uses of crude glycerol require the removal, at least, of the alkaline catalyst, through neutralization, and the separation of methanol [2]. However, due to the costs associated with transportation and processing and capital costs, a purification process of the crude glycerol is not always a feasible option for biodiesel producers. On the other hand, economics of biodiesel can be improved if value-added products can be obtained from that by-product. To the best of our knowledge, only two applications can be found in the literature for the crude glycerol containing residual alkaline catalyst from biodiesel process: production of monoglycerides (MG) [3] and as a reaction medium for Heck coupling [4]. The production of MG is an attractive potential application of crude glycerol because the glycerolysis reaction is base

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catalyzed, which suggests the alkaline transesterification catalyst can be reused avoiding its neutralization. MG are important chemicals mainly used in the food industry as emulsifiers, representing about 70% of the synthetic emulsifiers produced [5]. In addition, MG are intermediates in the production of alkyd resins, main component in most commercial oil-based coatings [6].

The general glycerolysis scheme is depicted in Eq. 1, where 2 mol of glycerol (G) react with 1 mol of triglyceride (TG) to produces 3 mol of MG. However, glycerolysis is an equilibrium reaction and diglycerides (DG) can also be produced (Eqs. 2, 3) [7]. According to the mass law, to increase the MG yields the equilibrium has to be displaced to the right, which is generally accomplished by increasing the molar ratio of glycerol to oil and carrying out the process at high temperature [5]. On the other hand, several studies have demonstrated that increasing the miscibility between oil and glycerol, for example through emulsifiers, make it possible to carry out the process under milder conditions [8].

$$\mathrm{TG} + 2\mathrm{G} \rightleftarrows 3\mathrm{MG} \tag{1}$$

$$\mathrm{TG} + \mathrm{G} \rightleftarrows \mathrm{MG} + \mathrm{DG} \tag{2}$$

$$\mathrm{TG} + \mathrm{MG} \rightleftarrows 2\mathrm{DG} \tag{3}$$

The publications related to the direct use of crude glycerol in the production of MG are scarce. For instance, Noureddini et al. [3] reported a continuous process for the glycerolysis of soybean oil using neutral crude glycerol and adding NaOH as the catalyst, obtaining 52 wt% of MG. In that work, variables such as mixing intensity, temperature, reactant flow rates, and stoichiometry were analyzed. The best conditions were 230 °C, 40 mL/min total flow, 25 min, a crude glycerol to soybean oil molar ratio of 2.5:1 and 3,600 rpm. In addition, it was observed that the reaction temperature had a greater influence on the extent of the reaction than mixing. In another recent work the MG production from palm stearin and crude glycerol containing NaOH was optimized. Best conditions were 200 °C, a crude glycerol to palm stearin molar ratio of 2.5:1 and a reaction time of 20 min. Under these conditions the MG yield was 61% [9].

In these previous reports the crude glycerol employed in the assays came from a single transesterification experiment and the effects of catalyst type and its concentration, as well as the presence of other impurities such as water and soaps were not studied. Commercial production of biodiesel is carried out with the catalysts sodium hydroxide and sodium methoxide with concentrations of up to 1%. Therefore, for establishing the applicability of crude glycerol in the MG production it is important to gain insights into the sensibility of the glycerolysis reaction to changes in the composition of that by-product.

In this research the glycerolysis reaction of soybean oil was evaluated using crude glycerol obtained from transesterification reactions with sodium methoxide and sodium hydroxide. The content of MG and DG was monitored as a function of time in order to determine the effect of the concentration of the soaps formed and the remaining inorganic catalyst in the crude glycerol on the formation rate of products. Likewise, the effect of the temperature on the glycerolysis reaction using crude glycerol was studied and compared with similar experiments employing pure glycerol–NaOH. In addition, in order to evaluate the sensibility of the glycerolysis reaction to changes in the composition of raw material through storage, a set of experiments was carried out with the addition of water to the crude glycerol.

Experimental Procedures

Materials

Pure glycerol (99.9%), methanol (≥99.8%), sodium hydroxide (>99%) and sodium methoxide (30 wt% in methanol) were obtained from Sigma–Aldrich. Refined soybean oil (acid value 0.17 mg KOH/g) was purchased from a local supermarket.

Transesterification Reaction

Transesterification reactions were carried out with sodium methoxide and sodium hydroxide because they are the most common industrial catalysts for the process. In industry, sodium methoxide is typically used at concentrations of up to 0.5 wt% [10]. However, in previous experiments it was determined that 1% produces high biodiesel yields [11]. Therefore, two concentrations of sodium methoxide were employed, 0.5 and 1 wt%, with respect to the oil. In order to compare the catalysts on the same molar basis, the concentrations of sodium hydroxide were 0.37 and 0.74 wt%. In a representative experiment, soybean oil (400 g) was mixed with methanol (88 g) and the catalyst (1.482 g of NaOH). The reaction was carried out for 90 min in a round-bottom flask, immersed in an oil bath at 65 °C, equipped with a magnetic stirrer and condenser. The conversion was above 99% and the content of MG in the glycerol phase was 0.29 wt%; DG were not detected. Upon gravity settling, methyl esters and glycerol were separated in a separation funnel. Then, both phases were rotovaporated to remove the excess methanol. No further treatment was done. The samples of methyl ester phase were designated as BM-X or BH-X, where “M” and “H” indicates, respectively, that methoxide or hydroxide was employed as the catalyst and “X” is the weight percentage of catalyst at the beginning of the transesterification. Similarly, the samples of glycerol phase were designated as GM-X or GH-X.

Glycerolysis Reaction

Glycerolysis reactions were carried out in a round-bottom flask immersed in an oil bath equipped with a magnetic stirrer and nitrogen inlet. In a typical experiment, crude glycerol (39.6 g) was mixed with soybean oil (150 g) in a 2.5–1 M ratio of crude glycerol to oil according to Chetpattananondh and Tongurai [9]. The mixture was heated to the reaction temperature and samples were withdrawn for chromatographic analyses. Samples were immersed in an ice container to stop the reaction quickly. In the case of the experiments with pure glycerol, it was mixed with the catalyst and the mixture was stirred until it became homogeneous. Then, the soybean oil was added to the mixture and the reaction was carried out under the same reaction conditions as described above. Because glycerol and alkaline catalysts are hygroscopic substances they can easily absorb water during storage which enables saponification of TG in the early stages of the glycerolysis reaction. Therefore, the effect of the addition of water was studied with the four samples of crude glycerol mixing them with water (10 wt% of crude glycerol) before the glycerolysis reaction and then the same procedure as above was followed. The amount of added water was enough to convert all the catalyst into soaps.

Analysis of Products

The content of methyl esters in biodiesel was analyzed by gas chromatography according to the BS EN14103 method [12]. The determination of free glycerol, MG, and DG in biodiesel was made by the ASTM D 6584-07 method [13]. The concentrations of glycerol, DG and MG in the glycerolysis products were determined by a standardized method [14]. In order to determine the quantity of methyl esters in the crude glycerol, 20–30 mg of sample were taken and dissolved in a solution of isopropanol–tetradecane. Then, the samples were analyzed by GC with a 30 × 0.32 HP-INNOWAX capillary column and a FID detector. The carrier gas was helium. Tetradecane was employed as internal standard for the quantification of products. The quantification of soap and catalyst in the samples was made by titration with HCl using a modified AOCS method Cc 17-79 [15]. The water content was measured by volumetric Karl Fisher Titration (ASTM E 203-01) [16].

Data plotted in all figures correspond to the averages of triplicate experiments with a relative standard deviation lower than 5%. Analysis of variance (ANOVA) was performed to determine the statistical significance of the results.

Results and Discussion

Transesterification Reaction

Compositions of glycerol and methyl ester phases from the transesterification reaction, after methanol removal, are shown in Tables 1 and 2. It can be seen, that high selectivities to methyl esters were obtained in all cases. However, a slightly higher yield of methyl ester was obtained with a higher concentration of the catalysts. According to the results of Vicente et al. [11] the transesterification reaction with 1% sodium methoxide gives high biodiesel yields while minimizing saponification reactions. However, it was observed that a fraction of the catalyst added at the beginning of reaction was transformed to soaps in all cases, although sodium hydroxide was more active toward saponification than sodium methoxide. In theory, the saponification reaction with sodium methoxide is nil, but in the presence of trace amounts of water it produces sodium hydroxide. The presence of water was observed in all the samples of crude glycerol.

The distribution of the components in the two phases is influenced by the hydrophilic or lipophilic character of the products obtained in the transesterification reaction as shown in Tables 1 and 2. Therefore, the catalyst was present almost exclusively in the glycerol phase. On the other hand, a small percentage of MG, which are intermediates in the transesterification reaction, are found in both phases. However, the methyl ester phases were more rich in these components that the respective glycerol phases. The composition of the glycerol and methyl ester phases is also influenced by the presence of soaps because they act as emulsifiers between them. Accordingly, it is observed that increasing the concentration of soaps, the glycerol phases

Table 1 Compositions of the crude methyl ester phases

	Composition (wt%)			
	BM-0.5	BM-1.0	BH-0.37	BH-0.74
Methyl esters	96.20	97.40	96.10	97.70
Glycerol	0.09	0.12	0.11	0.14
MG	0.90	0.77	0.93	0.67
DG	0.00	0.00	0.32	0.00
Soaps[a]	0.04	0.10	0.05	0.07
Catalyst[b]	0.00	0.01	0.01	0.01
Water	0.10	0.08	0.09	0.09
Others[c]	2.68	1.53	2.39	1.33

Numbers denote the catalyst concentration

B methyl ester phase, *M* sodium methoxide, *H* sodium hydroxide

[a] Sodium oleate

[b] Sodium hydroxide

[c] Triglycerides, methanol, inorganic compounds

were richer in MG and methyl esters but less rich in glycerol. Therefore, formation of soaps is detrimental to the biodiesel process due to the reduction in the separation efficiency of glycerol and methyl ester phases.

Glycerolysis Reaction

The statistical significance of the effect of catalyst concentration and catalyst type on the selectivity to MG was evaluated by the analysis of variance (ANOVA) of the MG concentrations once the equilibrium condition was obtained (60 min) as shown in Table 3. Since the *P* values are <0.05, it can be said that the two factors have a statistically significant effect on the MG concentration at the 95.0% confidence level. There was not observed any interaction between the two factors. In addition, according to the variance components analysis (not shown), the catalyst concentration contributes more to the total variation in the MG concentration (54%) than the catalyst type (35%).

The results of the glycerolysis of soybean oil with the four samples of crude glycerol, both with and without water, are compared in Figs. 1, 2, 3 and 4. Regarding the samples that were not treated with water, it is observed that at low catalyst concentrations the formation of MG increased with time until a maximum was reached at 20 min. At high catalyst concentrations, the maximum formation of MG was attained at zero time. On the other hand, it was shown that by increasing the amount of catalyst the concentration of MG diminished due to the formation of DG. These results indicate that the formation rate of MG increased with the catalyst concentration but, at the same time, once formed they were consumed to produce DG according to Eqs. 2 and 3.

Table 2 Compositions of the crude glycerol phases

	Composition (wt%)			
	GM-0.5	GM-1.0	GH-0.37	GH-0.74
Methyl esters	0.04	0.03	0.05	0.23
Glycerol	90.14	86.50	88.07	81.87
MG	0.18	0.16	0.29	0.32
DG	0.00	0.00	0.00	0.00
Soaps[a]	4.45	5.22	7.41	10.87
Catalyst[b]	2.74	5.74	1.73	3.20
Water	2.01	2.21	2.34	2.47
Others[c]	0.44	0.14	0.11	1.04

Numbers denote the catalyst concentration

G glycerol phase, *M* sodium methoxide, *H* sodium hydroxide

[a] Sodium oleate

[b] Sodium hydroxide

[c] Triglycerides, methanol, inorganic compounds

The comparison of methoxides and hydroxides, on the same molar basis, indicates that lower concentrations of MG were observed with the samples of crude glycerol containing sodium methoxide with respect to those containing sodium hydroxide. In addition, in the first case (methoxide catalysts) the MG content diminished from 20 min on, while in the second case (hydroxide catalysts) the MG concentration was more stable through time. This can be attributed to a higher reaction rate of MG to DG caused by the presence of a larger amount of remaining catalyst in the phases containing sodium methoxide, as shown in Table 1. When the catalyst is consumed in saponification reactions is less active for the glycerolysis reaction because soaps are weaker bases than the respective methoxides or hydroxides. However, soaps present in all the samples of crude glycerol may have contributed to the formation of DG, which were in high levels in all samples. Soaps can act as emulsifiers increasing the contact between MG formed previously and TG which favors DG formation (Eq. 3). The effect of emulsifiers on the glycerolysis reaction has been studied by Kaufman and Garti [8]. They reported that sodium stearate at 10 wt% afforded 100% conversion in the methyl stearate glycerolysis, with selectivities to MG and DG of 27.6 and 47.6%, respectively.

The effect of water addition on the glycerolysis with crude glycerol is shown in Figs. 1, 2, 3 and 4 (dashed lines). For the lower catalyst concentrations, the formation rate of MG was very low in the early stages of the reaction. However, after 20 min the water effect was attenuated and

Table 3 Analysis of variance for MG concentration

Source of variation	Sum of squares	Degrees of freedom	Mean square	*F* ratio[a]	*P* value
Main effects					
A: catalyst concentration	83.2133	1	83.2133	30.43	0.0006
B: catalyst type	95.2033	1	95.2033	34.82	0.0004
Interactions					
AB	1.90403	1	1.90403	0.70	0.4282
Residual	21.8747	8	2.73433		
Total	202.195	11			

[a] All *F* ratios are based on the residual mean square error

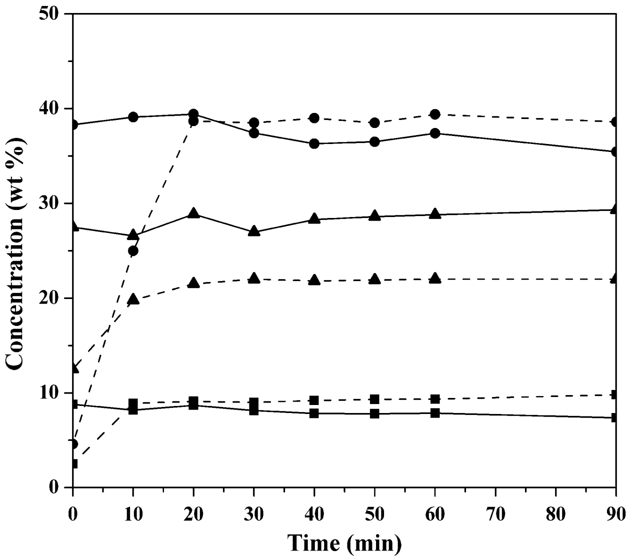

Fig. 1 Concentration of MG. DG and glycerol during glycerolysis of soybean oil with crude glycerol (phase GM-0.5) at 200 °C. *Solid lines* reaction without water, *dashed lines* reaction with water, *filled circles* MG, *filled triangles* DG, *filled squares* glycerol. Glycerol:soybean oil ratio of 2.5:1

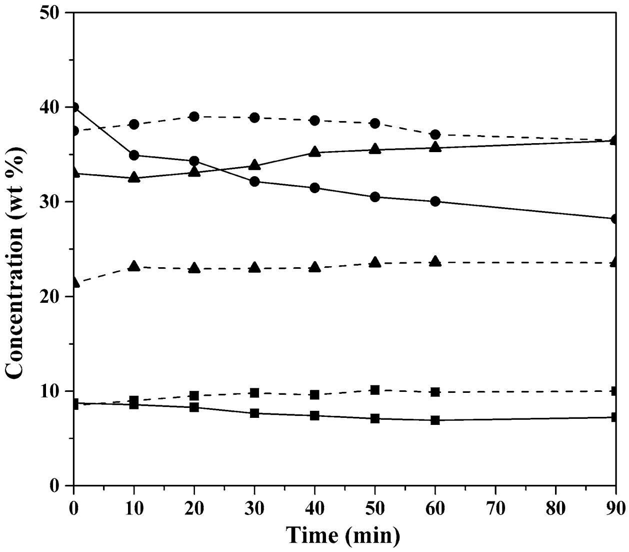

Fig. 2 Concentration of MG. DG. and glycerol during glycerolysis of soybean oil with crude glycerol (phase GM-1.0) at 200 °C. *Solid lines* reaction without water, *dashed lines* reaction with water, *filled circles* MG, *filled triangles* DG, *filled squares* glycerol. Glycerol:soybean oil ratio of 2.5:1

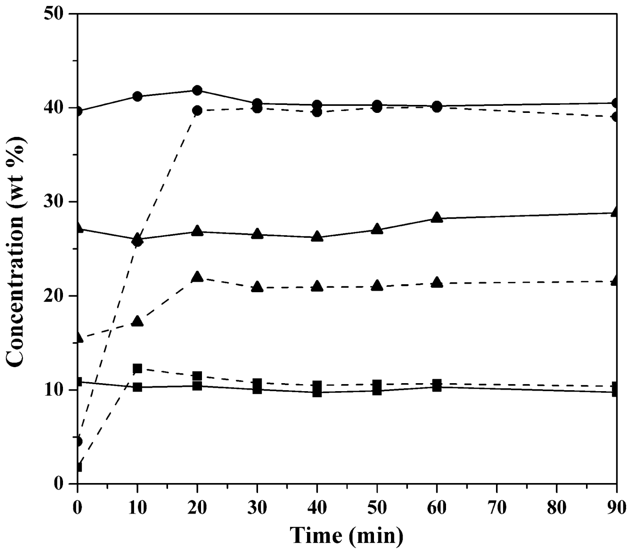

Fig. 3 Concentration of MG. DG and glycerol during glycerolysis of soybean oil with crude glycerol (phase GH-0.37) at 200 °C. *Solid lines* reaction without water, *dashed lines* reaction with water, *filled circles* MG, *filled triangles* DG, *filled squares* glycerol. Glycerol:soybean oil ratio of 2.5:1

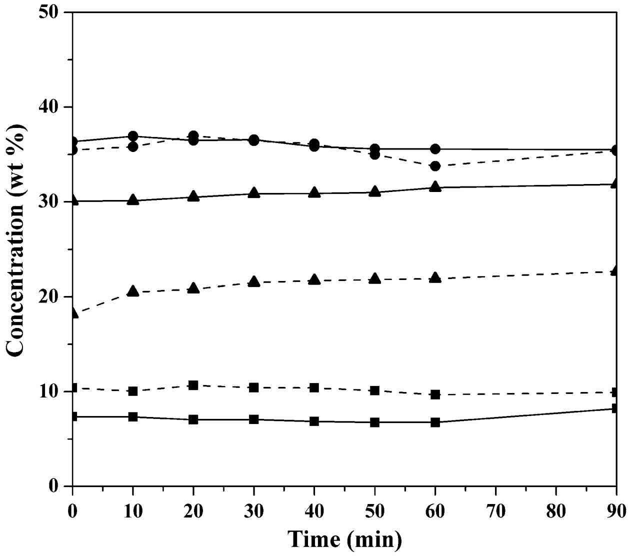

Fig. 4 Concentration of MG. DG and glycerol during glycerolysis of soybean oil with crude glycerol (phase GH-0.74) at 200 °C. *Solid lines* reaction without water, *dashed lines* reaction with water, *filled circles* MG, *filled triangles* DG, *filled squares* glycerol. Glycerol:soybean oil ratio of 2.5:1

similar MG concentrations to the experiment without water addition were obtained. On the other hand, with the highest concentrations of catalyst the highest MG concentration was obtained at zero time. In general, it was observed that once the maximum MG concentration is reached, such value remained almost stable through time. These results can be explained by the transformation of the hydroxides to soaps facilitated by the aqueous medium. As indicated earlier, the soaps are less active catalysts than the respective methoxide and hydroxides and therefore the rates of the reactions 2 and 3 are slower. On the other hand, the lower percentage of DG obtained with the addition of water compared to that one without water addition is remarkable . This suggests that the formation rate of DG can be increased more strongly by the inorganic catalyst than by the soaps derived from them.

The effect of temperature on the MG content was analyzed for the crude glycerol phase that exhibited the best results in the glycerolysis reaction, i.e., the phase GH-0.37, and the results are shown in Fig. 5. First of all, it was observed that the time for reaching the maximum formation of MG diminished with the temperature. Thus, at 220 °C the maximum formation of MG (42%) was reached at zero time but when the temperature was low (160 °C) the reaction was slow and equilibrium was reached at around 40 min. In spite of the high reaction rate of MG obtained at high temperatures, it was observed that their concentration through time decreases rapidly due to DG and TG being formed from them (not shown). For practical purposes, the best conditions for carrying out the glycerolysis reaction seem to be 200 °C and 20 min.

As a comparison basis, the glycerolysis reaction was studied at several temperatures with pure glycerol and NaOH with a concentration equivalent to the total content of alkali (inorganic catalyst and soap) of the phase GH-0.37, as shown in Fig. 6. In general, it is evidenced, such as with the phase GH-0.37 (Fig. 5), that the formation rate of MG increases with temperature until the equilibrium is reached. However, the differences observed among low and high temperatures are small. Even at the lowest temperature the concentration of MG at zero time was around 35% which is not far from the highest value found (41%). The main difference observed between the experiments with crude glycerol and pure glycerol was the lower reaction rates at low temperatures of the former. This is explained by the lower activity of the soaps present in the crude glycerol in comparison with the inorganic catalyst, which was already discussed. At higher temperatures (200 and 220 °C) the results were similar for crude glycerol and pure glycerol because the temperature has a stronger effect on the reaction rate than the type and concentration of the catalyst.

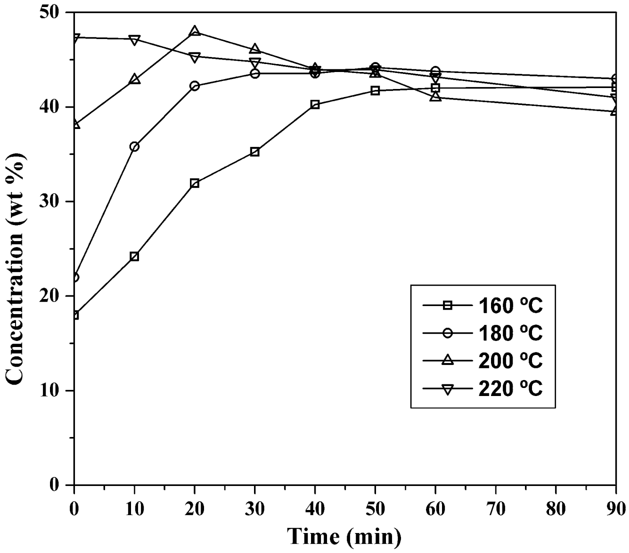

Fig. 5 Effect of the temperature on the MG concentration with the phase GH-0.37. Glycerol:soybean oil ratio of 2.5:1

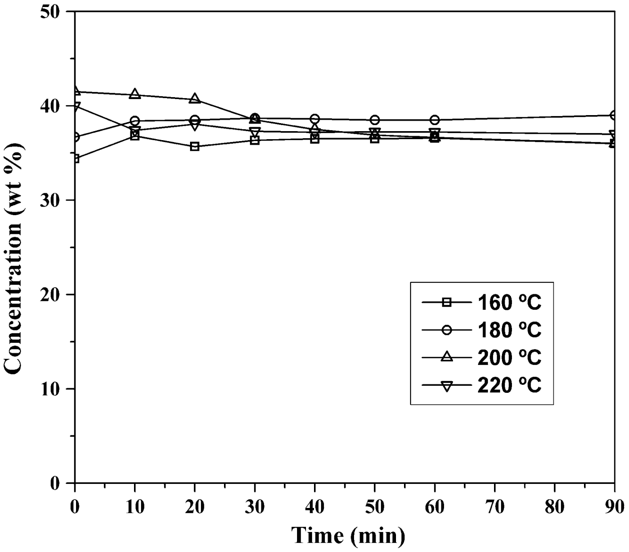

Fig. 6 Effect of the temperature on the MG concentration with pure glycerol and sodium hydroxide (2.7 wt% respect to the crude glycerol). Glycerol:soybean oil ratio of 2.5:1

Conclusion

The composition of crude glycerol obtained from the biodiesel process depends strongly on the concentration and type of alkaline transesterification catalyst. For instance, transesterification reactions catalyzed with NaOH were more prone to soap formation than those catalyzed with CH_3ONa. Reaction rates for the glycerolysis reaction increase with the amount remaining of the inorganic catalyst (NaOH or CH_3ONa) that was used for the biodiesel production, while the MG concentration diminishes due to the DG formation. In addition, transformation of the inorganic catalyst to soaps, due to the addition of water, reduces the glycerolysis reaction rate during the first stages of the reaction at low catalyst concentrations. Therefore, the presence of soaps in the crude glycerol leads to lower reaction rates than those obtained with inorganic catalysts because soaps are weaker bases; this effect is mainly observed at low temperatures.

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