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Chemical Engineering Journal 122 (2006) 31–40

Chemical Engineering Journal

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Monitoring of biodiesel production: Simultaneous analysis of the transesterification products using size-exclusion chromatography

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Received 27 February 2006; accepted 12 May 2006

Abstract

An analytical method based on size-exclusion chromatography allowing to determine simultaneously the total amounts of triglycerides, diglycerides, monoglycerides, fatty acid methyl esters, free glycerol and methanol in samples of the transesterification reaction of sunflower oil with methanol is presented. Only one chromatographic peak was obtained for each kind of compounds, which resulted in an easy and accurate quantitation of these substances. Analyses were carried out at room temperature with samples directly withdrawn from the reactor and subjected only to minimal pretreatments in order to short-stop the reaction. The analytical method was used to monitor the synthesis of biodiesel from sunflower oil and methanol in a series of reactions carried out at 323 K in a mechanically stirred batch tank reactor. The effects of the concentration of homogeneous catalyst (NaOH and KOH) and the methanol/oil molar ratio used on the selectivities to the various products were studied. The influence of two distinct sampling procedures on the experimental results has been also investigated.

Keywords: Biodiesel; Size-exclusion chromatography; Transesterification; Sunflower oil; Methanolysis selectivity

1. Introduction

Biodiesel is by far the most important component of the biofuels sector in the European Union in terms of production, 1.93 million tonnes in 2004 [1]. Growth prospects for the next years are very optimistic due to the impact caused by the Directive 2003/30/EC aiming at promoting the use of biofuels or other renewable fuels to replace diesel or petrol for transport purposes. According to this Directive the Member States should ensure that a minimum proportion of biofuels is placed on their markets, establishing a reference target value of 5.75% biofuels being incorporated on the basis of energy content by the end of the year 2010 [2]. Unfortunately, biofuels are expensive; feedstock costs typically representing 60–80% of total production costs. In the case of biodiesel, its cost is about 50% higher than that of petroleum diesel. Taking into account the current production costs it would take an oil price of about € 70 per barrel to make biofuels competitive with petroleum-derived fuels [3]; we are not far from this barrier (now close to US$ 70 per barrel). Moreover, it is likely that growth in the volume of the business stimulated by an adequate policy and increasing fossil fuel prices will give rise to both economies of scale and innovation that will reduce production costs significantly [4].

Triglycerides found in vegetable oils can be converted by means of a transesterification (alcoholysis) reaction with an excess of methanol (methanolysis) into fatty acid methyl esters, a fuel also known as biodiesel, with chemical and physical properties close to those of diesel fuel which can either be used in a mixture with conventional diesel or as pure biodiesel [5–10]. Animal fats [11], and waste cooking oils [12] also can be used as feedstock for this purpose. Transesterification of triglycerides to biodiesel and glycerol can be catalyzed by bases, acids as well as enzymes (lipases). Homogeneous base catalysts (mainly sodium and potassium hydroxides or methoxides) are the most commonly used due to their high activity and other advantages that make them economically superior over mineral acids and immobilized lipases [8,10]. Nevertheless, a large amount of waste-water is produced to separate the catalyst and wash the products. Therefore, both by environmental and economical reasons there is an increasing interest in the possibility of replacing the homogeneous bases by heterogeneous solid catalysts [13–15].

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doi:10.1016/j.cej.2006.05.009

The present paper deals with the development and application of an analytical method based on size-exclusion chromatography (SEC) in order to determine simultaneously the total amounts of the chemical substances involved in the reaction between vegetable oils and methanol in samples directly withdrawn from the reactor. This is of great interest to monitor the transesterification reaction. Moreover, it should be noted that to satisfy the requirements of biodiesel standards such as the European Standard EN 14214 [16], the quantitation of all individual compounds is not necessary but the quantitation of classes of compounds is (e.g. triglycerides, diglycerides, monoglycerides, total glycerol, etc.) [17]. The chromatographic method developed has been applied to evaluate the conversions and selectivities to the various products in transesterification reactions of edible-grade sunflower oil with methanol using NaOH and KOH as homogeneous catalysts.

Several methods have been developed for analyzing samples obtained by the transesterification of vegetable oils. These include techniques such as thin layer chromatography (TLC), gas chromatography (GC), high performance liquid chromatography (HPLC), gel permeation chromatography (GPC), ^{1}H nuclear magnetic resonance (^{1}H NMR) and near-infrared spectroscopy (NIR). Each method has advantages and drawbacks, so the most suitable one may be different depending on the user necessities and means. Obviously, the analysis quality, cost and duration, including the possible sample pretreatment, are very important aspects to take into account to make the final selection [10,17–20].

2. Experimental procedures

2.1. Transesterification reactions

The experiments were carried out at 323 K and atmospheric pressure in a 1 l jacketed glass batch tank reactor with a drain cock at the bottom. This reactor was fitted with a reflux condenser, a sampling device, a nitrogen inlet, a mechanical stirrer comprising a stainless steel turbine and a thermocouple probe. The reaction temperature was controlled by means of a heated circulating water bath (PolyScience). The experimental set up is depicted in Fig. 1. The sampling device consisted of a polyamide tube (35 cm, 6 mm o.d.) connected to a Perfektum® stainless steel one-way compression-nut stopcock and a 10 ml polypropylene syringe (Norm-Ject®). A recirculation loop comprising a PTFE tube (1.5 m, 1/8 in. o.d.), a diaphragm-type metering pump (ProMinent Gamma/L) and a stainless steel three-way ball valve (Whitey®) was also used for sampling purposes. The flow rate measured for pure water at room temperature as reference was 80 ml/min.

Once the system was purged with pure nitrogen to displace atmospheric air, 300 g of refined edible-grade sunflower oil (Urzante, Navarra, Spain; acid value of 0.07 mg KOH/g measured according to AOCS method [21]) and some methanol (Scharlau, HPLC grade) were initially charged into the reactor and preheated to the reaction temperature. The stirrer speed was set at 370 rpm, which provided satisfactory mixing. Then, the catalyst was rapidly added into the reactor dissolved in the

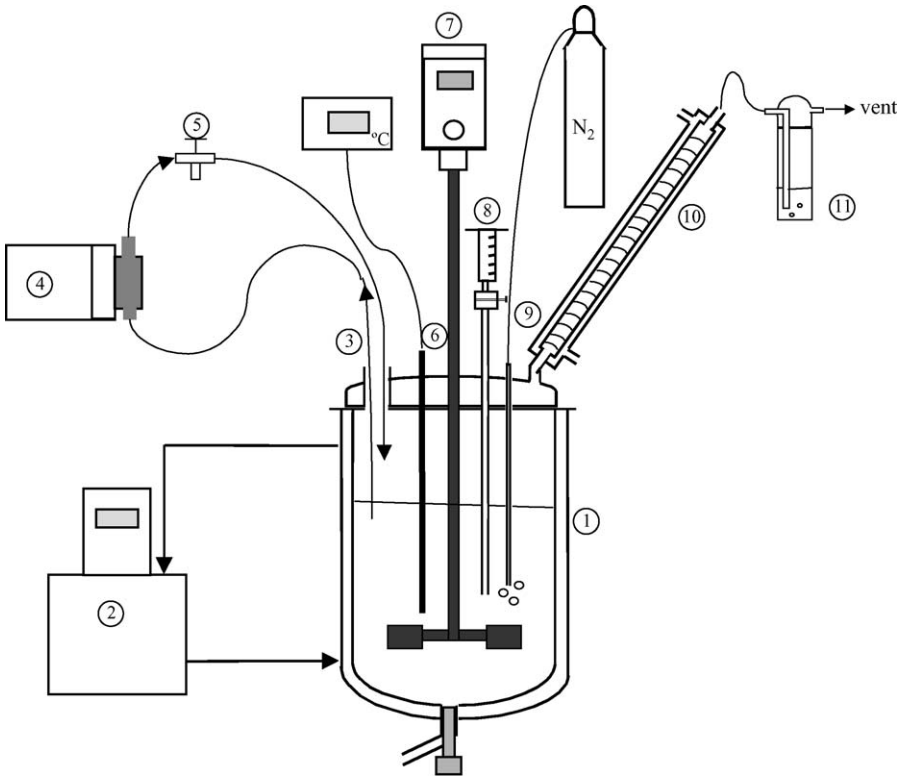

Fig. 1. Drawing of the experimental set up used to perform the transesterification reactions. (1) Jacketed glass batch tank reactor (1 l); (2) circulating water bath; (3) recirculation loop (PTFE); (4) metering pump; (5) stainless steel three-way ball valve; (6) thermocouple probe; (7) mechanical stirrer; (8) polypropylene syringe; (9) nitrogen gas inlet; (10) reflux condenser; (11) glass gas-washing bottle containing methanol.

amount of methanol necessary to give the finally desired alcohol/oil molar ratio. Both NaOH (Aldrich, 99.998%) and KOH (Aldrich, 99.99%) were used as catalysts in amounts ranging from 0.15 to 0.60 g, that is, 0.05–0.20 wt.% referred to the oil mass. The catalyst pellets were ground in an agate mortar prior to be dissolved in methanol at room temperature. Methanol/oil molar ratios considered were the stoichiometric one, 3:1, as well as two other ratios with methanol in excess, 6:1 and 12:1, due to the reversible character of the chemical reactions involved; a molecular weight of 879.5 was assumed for sunflower oil [22]. Samples (1–1.5 g) were withdrawn during the experiments at various intervals and stored in 30 ml sealed glass flasks. The reaction was quenched immediately by addition in each flask of about 0.1 g of a glacial acetic acid (Scharlau, HPLC grade) solution (0.6N) in tetrahydrofuran (Scharlau, HPLC grade) to neutralize the catalysts [23] and cooling and dilution with about 14 g of additional tetrahydrofuran (THF). Samples prepared this way were ready for chemical analysis. Changes in the chemical composition of the samples were not found after several days.

2.2. Chemical analysis and chromatographic instrument

The size-exclusion chromatography (SEC) system consisted of a Waters 510 HPLC pump, a Rheodyne 7725i manual injector, a Waters model 410 differential refractive index (RI) detector, and a Viscotec TriSEC® model 270 dual detector. Data collection and analysis was performed with TriSEC® GPC software. The mobile phase was HPLC grade THF (Scharlau) at various flow rates between 0.6 and 1.2 ml/min. Several configurations of GPC columns connected in series were considered. The columns were 300 mm × 7.8 mm Styragel® HR0.5 and HR2 columns (Waters) of 5 μm particles and 100 and 500 Å single-pore size, respectively. The columns were protected with a Styragel® 30 × 4.6 column guard (Waters). Sample injection volume was 50 μl, and all the analyses were carried out at room temperature.

The following analytical lipid standards were obtained from Larodan Fine Chemicals: monoglycerides mixture MG Mix 21 (monostearin, monoololein, monolinolein, monolinolenin), diglycerides mixture DG Mix 51 (distearin, diolein, dilinolein, dilinolenin), tripalmitin, triolein, trilinolein, methyl palmitate, methyl stearate, methyl oleate and methyl linoleate. Glycerol (99.5+%, Sigma–Aldrich) and HPLC grade methanol (Scharlau) were used as reference standards as well. Identification and calibration of the SEC peaks were performed analyzing mixtures in HPLC grade THF of the above-mentioned standards prepared gravimetrically within a range of concentrations as in the transesterification reactions. Standard calibration curves were obtained for each substance (methanol and free glycerol) or groups of substances (triglycerides, diglycerides, monoglycerides, and fatty acid methyl esters) and used to convert the integrated SEC areas to mass concentrations.

3. Results and discussion

3.1. Method of analysis

Fig. 2 is a representative plot of the SEC chromatograms obtained when analysing a typical transesterification reaction sample with the three configurations of GPC columns checked at an eluant (THF) flow rate of 0.8 ml/min. It can be seen that a chromatographic peak was obtained for each lipid class: triglycerides (sunflower oil), diglycerides and monoglycerides, as well as for the methyl esters (biodiesel); both glycerol and methanol could be analysed also. Methanol was detected as a negative peak because its refractive index is lower than that of the mobile phase (THF) unlike the other compounds involved in the reaction [24]; nevertheless, this was not a problem in order to quantify accurately its concentration in the samples. The very small negative peak preceding the methanol one is due to water resulting from the reaction of NaOH with methanol or free fatty acids.

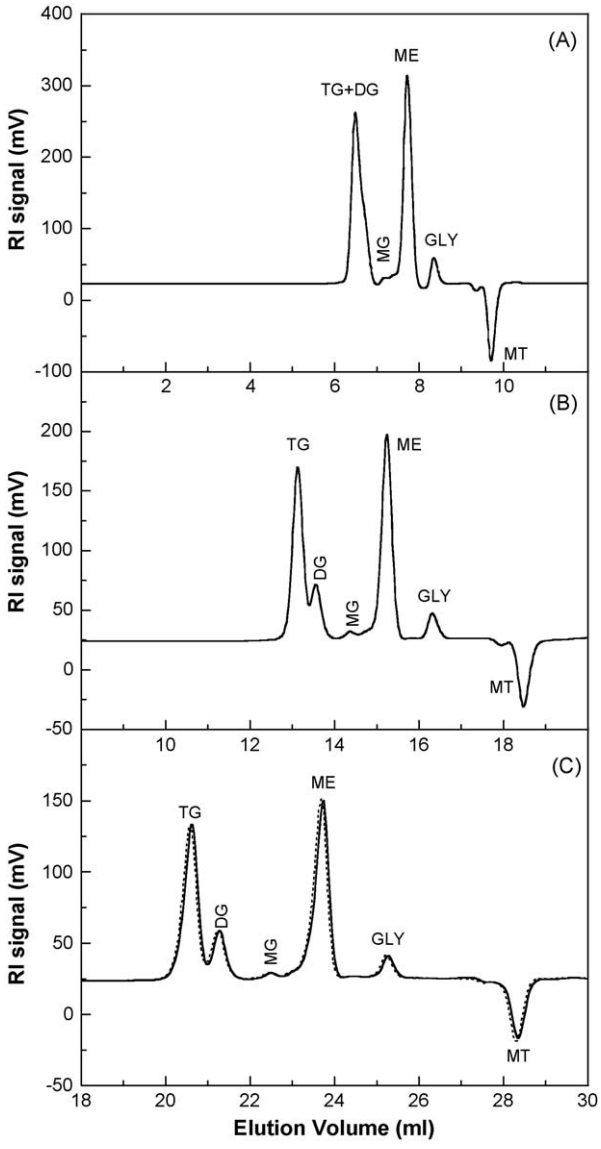

Fig. 2. Representative SEC chromatograms of a typical transesterification reaction sample obtained with the following configurations of columns: (A) an HR0.5 column only; (B) a first HR2 column connected in series to an HR0.5 one; (C) two HR2 and one HR0.5 columns connected in series; the dotted line shows a replicate of the analysis. TG: triglycerides (vegetable oil). DG: diglycerides. MG: monoglycerides. ME: fatty acid methyl esters (biodiesel). GLY: glycerol. MT: methanol.

Separation of the several compounds included in each lipid category by SEC was not possible. This is in accordance with previous studies by Darnoko et al. [20] on palm oil transesterification, Christopoulou and Perkins [25] on fatty acids, mono-, di-, and triglyceride mixtures and Fillières et al. [26] on the ethanolysis of rapeseed oil. SEC is the predominant method used for separating and characterizing substances of high molecular weight. Column packing materials with pores of controlled sizes are used; the degree of retention depends on the size and shape of the solute molecule solvated in the mobile phase relative to the size and geometry of the pores. Small molecules will permeate the smaller pores, intermediate-sized molecules will permeate only part of the pores and be excluded by the remaining ones, and very large molecules will be completely excluded. As a result, the solute molecules elute from the column in the order of decreasing hydrodynamic size (related to the molecular weight). Although column packings do not have a narrow pore size distribution, this is not sufficient to separate all molecular species. This results in a poor discrimination of species of close molecular weight, which are eluted from the column at very close retention times and detected together in a single peak [27].

The process of transesterification of sunflower oil with methanol involves three consecutive reversible reactions, which are accompanied by a significant variation in molecular weight among the several types of substances. Indeed, the first step is the conversion of triglycerides (molecular mass of 873–875) to diglycerides (molecular mass of 612–620), which is followed by the conversion of diglycerides to monoglycerides (molecular mass of 352–356) and finally of monoglycerides to glycerol (molecular mass of 92), yielding one molecule of methyl ester (molecular mass of 292–298) from each acylglycerol at each step [7,19]. This explains the order in which these substances are eluted and detected by SEC (see Fig. 2). As shown in Fig. 2A, a single Styragel® HR0.5 column (100 Å pore size, nominal effective molecular weight range 50–1500) gives poor resolution in the high molecular weight range and does not separate diglycerides from triglycerides; the resolution for monoglycerides is neither satisfactory. When combining the action of this column with one (Fig. 2B) and especially two (Fig. 2C) Styragel® HR2 columns (500 Å pore size, nominal effective molecular weight range 500–20,000) the quality of the separation improves significantly. Also shown in Fig. 2C is a replicate of an analysis to illustrate the good reproducibility of the analytical method. In this work, a configuration consisting of two HR2 columns connected in series to one HR0.5 column was finally adopted, which allowed suitable monitoring and evaluation of the transesterification reaction. This included the quantitation of glycerol and methanol in addition to acylglycerols and methyl esters, which constitutes, to our best knowledge, the first report on the simultaneous analysis by SEC of all the substances involved in the vegetable oils methanolysis reaction [17,20,25].

Fig. 3 shows the effect of the eluant (THF) flow rate on the separation of the solutes when using the selected configuration of columns (two HR2 connected in series to one HR0.5). It can be seen that this variable has negligible effect on the analysis resolution. Of course, retention time decreases as the mobile phase flow rate increases. Nevertheless, in order to avoid excessive solvent consumption, an intermediate flow rate of 0.8 ml/min was adopted. This allows completing an analysis with a reasonable duration of about 35 min. It should be noted that after this period the chromatographic instrument is ready for starting a new analysis since neither the columns temperature nor the eluant flow rate were changed. In contrast, gas chromatographic methods customarily used for this application include more or less sophisticated column temperature programs [17,18,28].

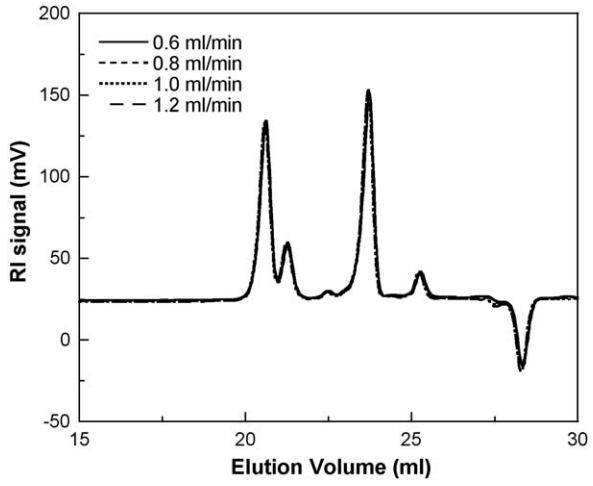

Fig. 3. SEC chromatograms obtained at various mobile phase flow rates. Configuration: two HR2 and one HR0.5 columns connected in series.

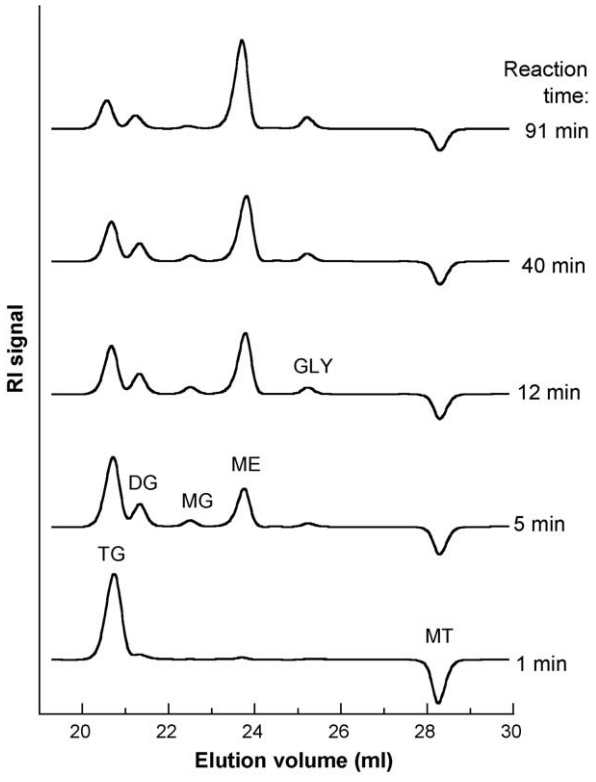

Fig. 4. Evolution with reaction time of the SEC chromatograms of samples of a transesterification reaction under conditions adopted as reference (323 K, 300 g of sunflower oil, 65.5 g of methanol, catalyst: 0.30 g NaOH).

3.2. Monitoring of biodiesel production

The above-described method of analysis has been used to monitor the synthesis of biodiesel from sunflower oil under various reaction conditions.

Fig. 4 depicts the evolution with reaction time of the SEC chromatograms of samples taken from the recirculation loop for a transesterification reaction carried out at standard conditions (323 K, 300 g of sunflower oil, 65.5 g of methanol, catalyst: 0.30 g NaOH) and adopted as reference. Due to the difficulty of analysing exactly the same amount of sample each time, the chromatograms included in Fig. 4 were normalised to take into account this fact. The increase taking place with reaction time of the peak areas corresponding to the reaction end products, fatty acid methyl esters and glycerol, is clearly seen, as well as the concomitant decrease of the reactants peak areas (triglycerides and methanol). It should be noted that methanol is in excess (initial methanol/oil molar ratio of 6:1) compared with the stoichiometric conditions (methanol/oil molar ratio of 3:1), hence the decrease of the methanol peak area is slow in relation to that of the oil.

Quantitation of these data leads to the results included in Fig. 5 showing the evolution with reaction time of the mass of the various compounds. Results are given for samples simultaneously withdrawn from the reactor with a syringe and from the recirculation loop (see scheme in Fig. 1). The inclusion of recirculation loop did not influence the results as evidenced from the comparison of experiments performed with the pump switched on or off. However, thanks to the loop, samples were more homogeneous and representative of the reactor content as well as more easily taken by means of a simple three-way ball valve. Differences between the sampling procedures are found only for the first samples; that is to say for reaction times below about 5 min (points indicated by arrows in Fig. 5). This is due to the high initial viscosity of the reaction mixture, which makes sample extraction with a syringe slow, allowing some phases separation to take place in the tube connected to the syringe. As the reaction progresses and triglycerides are converted in methyl esters the mixture viscosity rapidly decreases and differences between the results obtained with samples withdrawn with the two procedures disappear. Also included in Fig. 5 are the results for a replicate of the reaction, which illustrate the good reproducibility achieved with samples taken from the recirculation loop.

Lines depicted in Fig. 5 allow a comparison between the amounts of fatty acid methyl esters, glycerol and methanol directly measured from SEC analyses of these compounds and the ones calculated from mass balances (dotted lines). It can be seen that a reasonably good accordance exists (within about

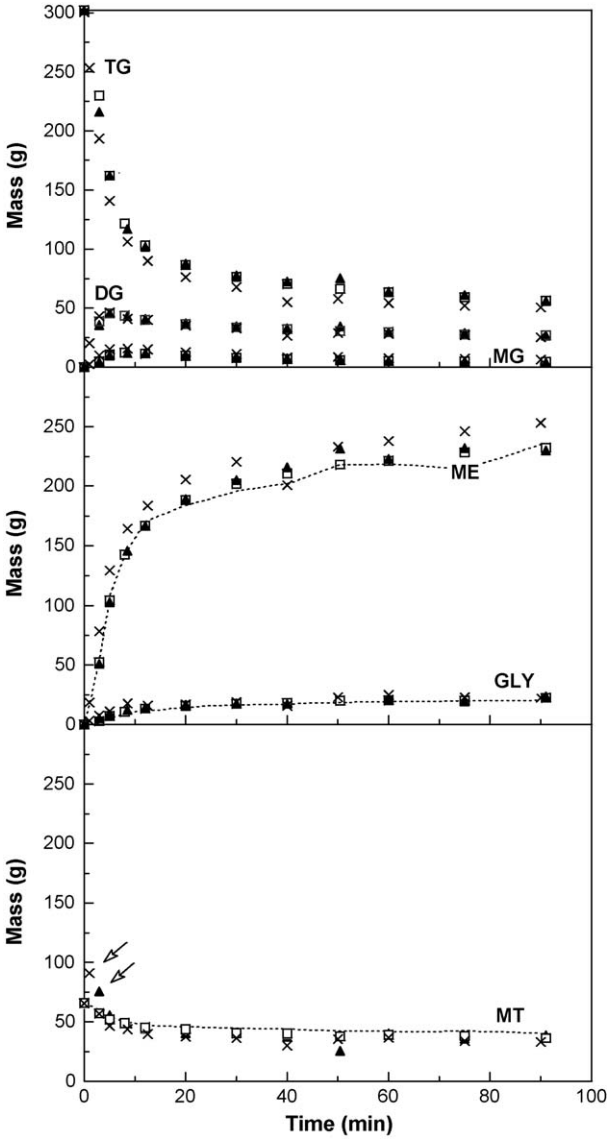

Fig. 5. Transesterification of sunflower oil with methanol carried out under reference conditions (see text). (▲) Results for samples withdrawn from the reactor with a syringe. (□) Results for samples taken from the recirculation loop. (×) Results for a replicate; samples withdrawn from the reactor with a syringe. Dotted lines: results of mass balances for the compounds computed from the amounts of the remaining products. TG: triglycerides (vegetable oil). DG: diglycerides. MG: monoglycerides. ME: fatty acid methyl esters (biodiesel). GLY: glycerol. MT: methanol.

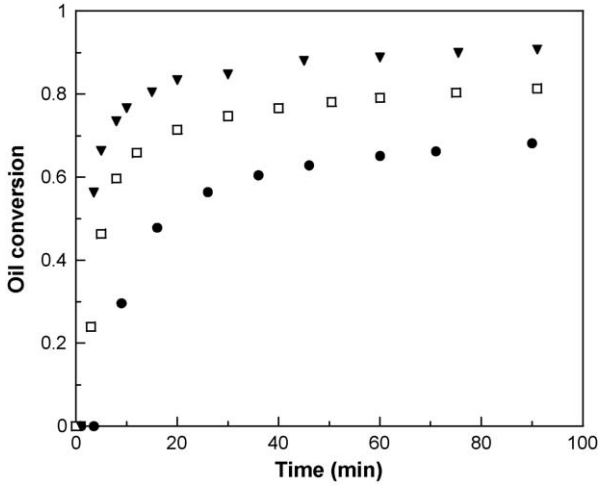

Fig. 6. Evolution with reaction time of the sunflower oil conversion for a series of transesterification reactions carried out at 323 K with 300 g of oil, methanol/oil molar ratio of 6:1 and the following concentrations of NaOH based on the oil mass: 0.05 wt.% (●), 0.10 wt.% (□) and 0.20 wt.% (▼).

5%) which gives confidence in the suitability of the experimental procedure and analytical method used.

3.3. Influence of the catalyst and methanol/oil molar ratio

Amongst the several variables affecting the synthesis of biodiesel, the nature and concentration of the catalyst as well as the alcohol/oil molar ratio are recognized to be of the greatest relevance [29–32]. Other important variables affecting also the methanolysis reaction but not considered in this work are the reaction temperature, water and free fatty acids contents of the oil and the use of organic cosolvents with the aim of improving the methanol–oil miscibility. In this section we illustrate the application of the analytical method developed to the evaluation of the effects of the catalyst (NaOH and KOH) and the methanol/oil molar ratio in the transesterification reaction of sunflower oil.

As concerns the catalysts, there is general agreement that basic compounds are the most active ones. In this regard, sodium and potassium hydroxides are the most commonly used due to their relatively low cost and high solubility in methanol where the hydroxide ions react to form methoxide anions, which are considered the active species [30,31]. The amount of catalyst charged into the reactor is customarily expressed as a percentage of the mass of oil to be transesterified; catalyst concentrations in the 0.4–2 wt.% range are typical in methanolysis reactions, although low concentrations (0.3–0.5 wt.%) have been found to be optimal in some instances [10].

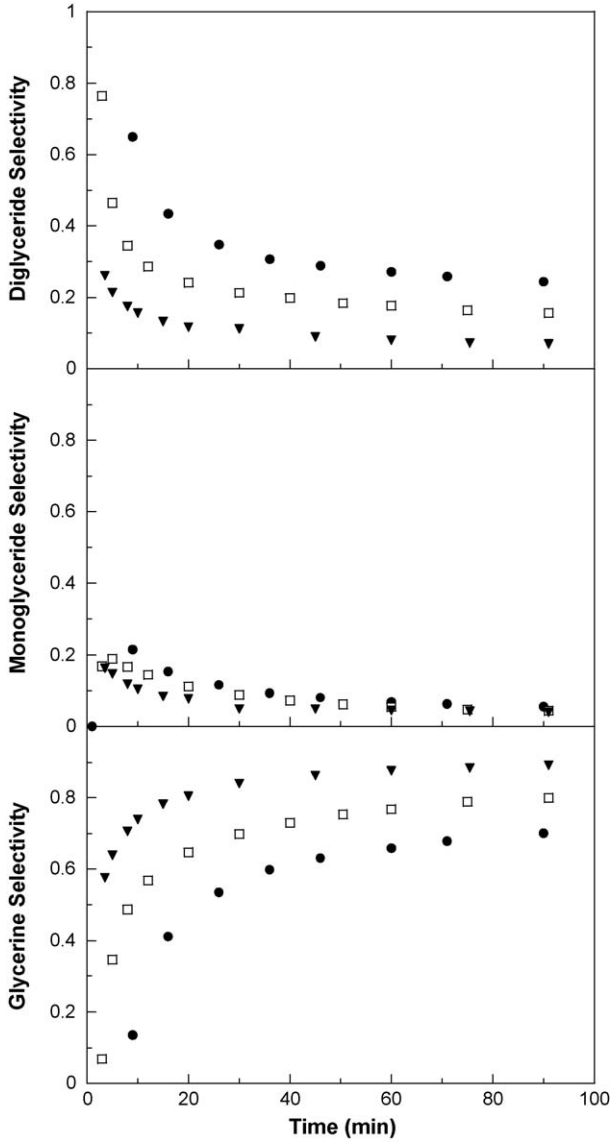

Fig. 7. Evolution with reaction time of the selectivities to diglycerides, monoglycerides and glycerol for a series of transesterification reactions carried out at 323 K with 300 g of oil, methanol/oil molar ratio of 6:1 and the following concentrations of NaOH based on the oil mass: 0.05 wt.% (●), 0.10 wt.% (□) and 0.20 wt.% (▼).

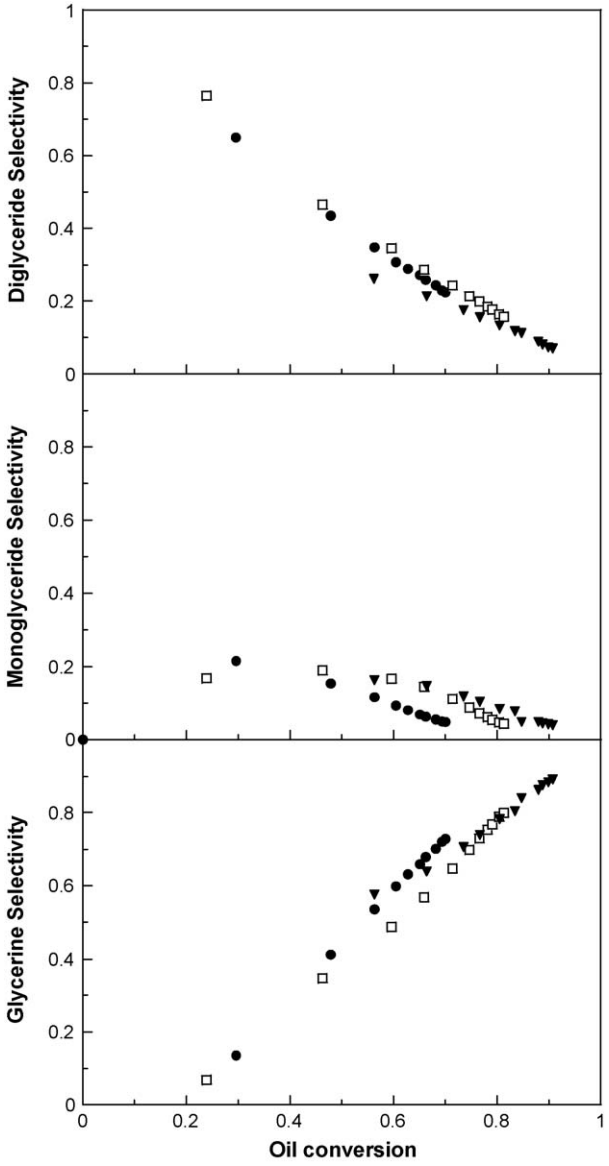

Fig. 8. Selectivities to diglycerides, monoglycerides and glycerol as a function of sunflower oil conversion for a series of transesterification reactions carried out at 323 K with 300 g of oil, methanol/oil molar ratio of 6:1 and the following concentrations of NaOH based on the oil mass: 0.05 wt.% (●), 0.10 wt.% (□) and 0.20 wt.% (▼).

The evolution with reaction time of the sunflower oil conversion and the selectivities to diglycerides, monoglycerides and glycerol for a series of transesterification reactions carried out at 323 K, molar methanol/oil ratio of 6:1 and NaOH concentrations of 0.05, 0.10 and 0.20 wt.% are depicted in Figs. 6 and 7, respectively. Oil conversion and products selectivities were calculated as follows:

$$X_{\mathrm{Oil}} = \frac{N_{\mathrm{TG0}} - N_{\mathrm{TG}}}{N_{\mathrm{TG0}}} \tag{1}$$

where X_{Oil} is the oil conversion at time t, and N_{TG0} and N_{TG} are the moles of oil initially charged into the reactor and remaining at time t, respectively. It was assumed that the oil consists exclusively of triglycerides; as a matter of fact, the SEC chromatograms of the oil showed only one peak corresponding to tryglicerides.

$$S_i = \frac{N_i}{N_{\mathrm{TG0}} - N_{\mathrm{TG}}}, \qquad i = \mathrm{DG, MG, GLY} \tag{2}$$

where S_i is the selectivity to diglycerides (DG), monoglycerides (MG) or glycerol (GLY) at time t, and N_i are the moles of the product for which the selectivity is being calculated contained in the reactor at time t. Because of the molecular weight of glycerol is significantly lower than that of the acylglycerols the error in the glycerol selectivity may be significant. As an alternative to Eq. (2), the glycerol selectivity can be calculated from:

$$S_{\mathrm{GLY}} = 1 - S_{\mathrm{MG}} - S_{\mathrm{DG}} \tag{3}$$

As can be inferred from the results presented in Fig. 6, the transesterification rate is very dependent on the catalyst amount at low catalyst concentrations. After 30 min the oil conversions were about 0.59, 0.75 and 0.87 for NaOH concentrations of 0.05, 0.10 and 0.20 wt.%, respectively. Vicente et al. [30] found a sunflower oil conversion as high as 0.97 after 30 min for a reaction conducted at 333 K, molar methanol/oil ratio of 6:1 and 1 wt.% NaOH. On the other hand, when using only 0.2 wt.% NaOH, Noureddini and Zhu [33] found 0.8 conversion of soybean oil at 323 K and methanol/oil ratio of 6:1, in line with our results.

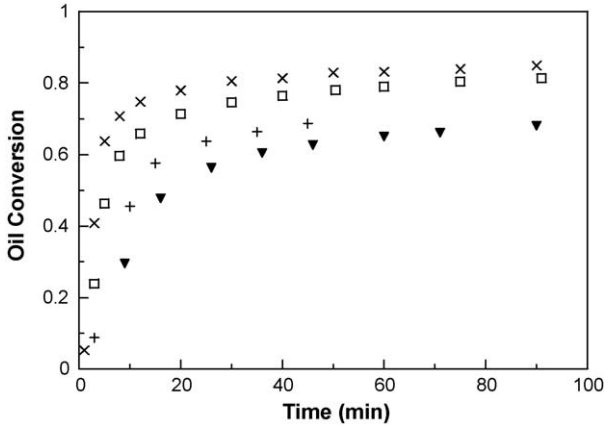

Fig. 9. Evolution with reaction time of the sunflower oil conversion for a series of transesterification reactions carried out at 323 K with 300 g of oil, methanol/oil molar ratio of 6:1 and the following concentrations of NaOH: 0.05 wt.% (▼) and 0.10 wt.% (□) and KOH: 0.07 wt.% (×) and 0.14 wt.% (+) based on the oil mass.

Base-catalyzed methanolysis is an addition–elimination reaction involving the nucleophilic attack of the methoxide anion on a carbon atom of the carbonyl groups of acylglycerols resulting in the displacement of the oxygen atom of glycerol and the formation of a methyl ester. As the methoxide anion results from the reaction of methanol with the hydroxide ions, the concentration of methoxide ions increases as the amount of NaOH charged into the reactor increases as well, thus explaining the results shown in Fig. 6. Moreover, kinetic rate constants seem to increase with an increase in the concentration of homogeneous alkali catalysts [5].

As regards the reaction selectivity, it can be seen from Fig. 7 that the results are consistent with a reaction scheme of three consecutive reactions with diglycerides and monoglycerides acting

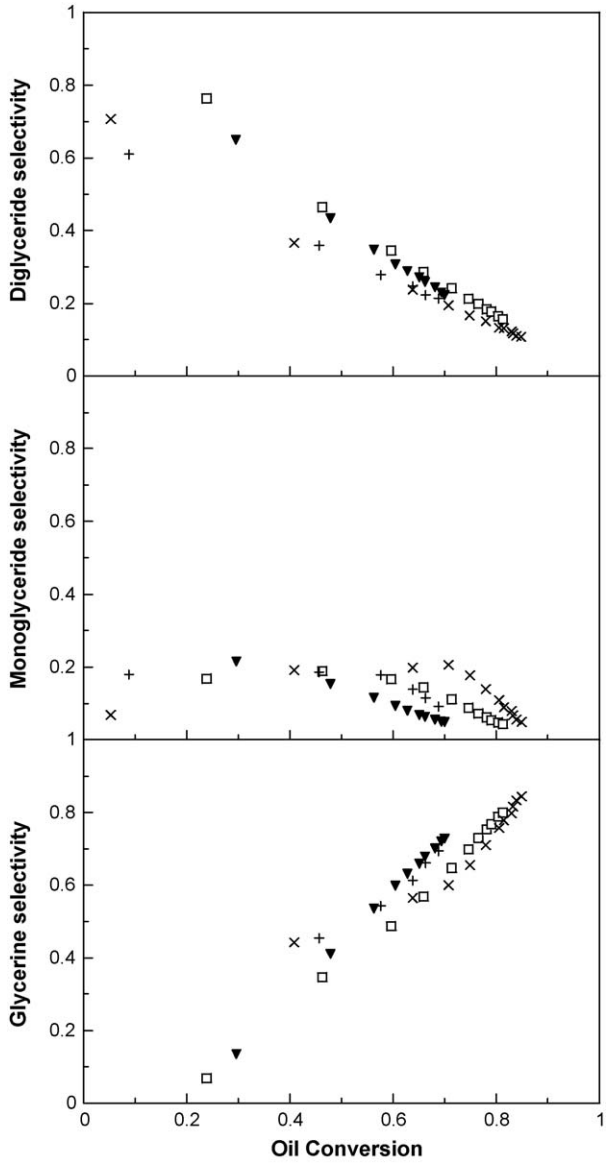

Fig. 10. Selectivities to diglycerides, monoglycerides and glycerol as a function of sunflower oil conversion for a series of transesterification reactions carried out at 323 K with 300 g of oil, methanol/oil molar ratio of 6:1 and the following concentrations of NaOH: 0.05 wt.% (▼) and 0.10 wt.% (□) and KOH: 0.07 wt.% (×) and 0.14 wt.% (+) based on the oil mass.

as intermediates and glycerol as end product [33,34]. This is perhaps more clearly shown in Fig. 8 where the products selectivities are plotted against the oil conversion instead of reaction time. Indeed, for very low oil conversions the diglycerides selectivity tends to 1 whereas those of monoglycerides and glycerol are close to 0. As the reaction advances the diglycerides selectivity continuously decreases, that of monoglycerides passes through a maximum of about 0.2 and the glycerol selectivity increases to reach a value close to 1 by the end of the reaction. The low monoglycerides concentrations found indicate that the conversion of monoglycerides into glycerol proceeds much faster than the previous steps. It can be seen as well that the concentration of homogeneous NaOH catalyst does not influence significantly the evolution with time of the selectivities to the various reaction products.

The performance of NaOH and KOH as catalysts for the methanolysis reaction of sunflower oil is compared in Fig. 9. The KOH concentrations referred to oil mass were adjusted taking into account the molecular weights in order to be the same on a molar basis as those of NaOH. As it can be seen, the reactions conducted with KOH were slightly faster than those catalyzed by NaOH. This is in accordance with previous results, such as those of Vicente et al. [32] for the transesterification of sunflower oil with 1 wt.% NaOH and 1.5 wt.% KOH at 338 K and methanol/oil molar ratio of 6:1. However, great differences between KOH and NaOH were found by Dorado et al. [12] in the methanolysis of waste olive oil at 298 K and methanol/oil molar ratio of 4:1. In this case, the oil conversion was above 0.9 after 30 min when using 1.26 wt.% KOH whereas no methyl esters were formed with NaOH at the same concentration. As used cooking oils are characterized by relatively high free fatty acids contents, a higher resistance of KOH to these compounds compared to that of NaOH could be suggested as one of the reasons contributing to the better performance of potassium hydroxide. We used refined sunflower oil with very low free fatty acids content, resulting in a more similar behaviour of the catalysts.

As concerns the selectivity of the reaction, the results shown in Fig. 10 indicate that there are no significant differences between NaOH and KOH. Nevertheless, the decrease of the diglycerides selectivity is faster in presence of KOH, which seems to be in accordance with the higher activity of this catalyst.

The effect of the methanol/oil molar ratio in the transesterification reaction of sunflower oil at 323 K with 0.10 wt.% NaOH is presented in Fig. 11. It can be seen that the shape of the oil conversion versus reaction time curves changes markedly with the methanol/oil ratio. There is a positive effect of the alcohol excess on the oil conversion for reaction times only well above 20 min. Afterwards, the oil conversion increases with the methanol/oil molar ratio. For example, after 90 min the oil conversion is 0.76 for the stoichiometric methanol/oil ratio (3:1), 0.83 for a ratio of 6:1 and increases up to 0.93 for a 12:1 ratio. This is as was to

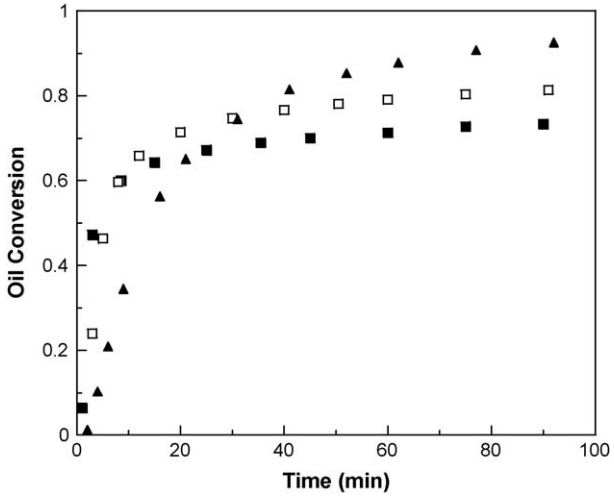

Fig. 11. Evolution with reaction time of the sunflower oil conversion for a series of transesterification reactions carried out at 323 K with 300 g of oil, 0.10 wt.% NaOH and the following methanol/oil molar ratios: 3:1 (■), 6:1 (□) and 12:1 (▲).

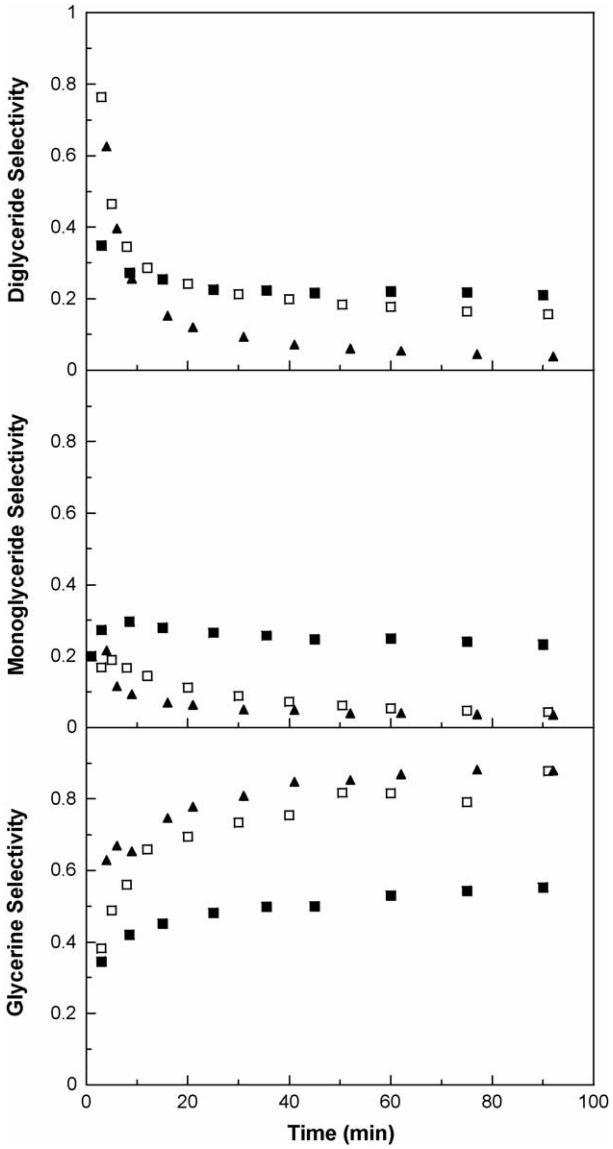

Fig. 12. Evolution with reaction time of the selectivities to diglycerides, monoglycerides and glycerol for a series of transesterification reactions carried out at 323 K with 300 g of oil, 0.10 wt.% NaOH and the following methanol/oil molar ratios: 3:1 (■), 6:1 (□) and 12:1 (▲).

be expected for reversible reactions since the alcohol in excess helps to shift the forward reactions leading to improve the conversion of triglycerides. However, for short reaction times, our results indicate that the methanolysis rate decreases as the alcohol excess increases. This would be compatible with a dilution effect; in this regard, it should be noted that these reactions were conducted with the same amount of catalysts, 0.10 wt.% referred to the oil mass, which was kept constant. Therefore, in this series of reactions the catalyst concentration decreases with the methanol/oil ratio. Another important factor that has to be considered is the two-phase nature of the methanolysis reaction. According to Boocock et al. [31,35], as the homogeneous catalysts is exclusively in the methanol phase where the solubility of the oil is low, the reaction becomes mass transfer limited in spite of using vigorous stirring. Moreover, diglycerides and monoglycerides are formed in the methanol phase, so it is more likely that they react with the alcohol in excess than they diffuse to the oil-rich phase; as a result, second-order kinetics is not followed. Therefore, although the concentration of alcohol is higher as the methanol/oil ratio increases, that of oil in the methanol phase may even decrease when the reaction is started, which would explain the trend observed for the initial rates.

This view is reinforced by the evolution with reaction time of the products selectivities shown in Fig. 12. Indeed, the selectivities to diglycerides and monoglycerides decrease much faster in the reaction performed with the highest methanol/oil ratio. As explained above, this is a consequence of the two-phase nature of the reaction and the fact that the NaOH catalyst is located in the methanol phase where the mono- and diacylglycerols are formed and further easily react to methyl esters. These results also illustrate the inconvenience of using stoichiometric transesterification conditions since the selectivities to both diglycerides and monoglycerides reach almost stationary values of about 0.25, thus leading to a biodiesel composition, which does not fulfil the adopted standards [16].

4. Summary and conclusions

In this work, an analytical method based on size exclusion chromatography has been presented that allows the simultaneous determination of the total amounts of the several compounds involved in the methanolysis reaction of sunflower oil, including methanol and glycerol. The method is simple, robust, relatively fast, may be conducted at room temperature and gives accurate and reproducible results. Moreover, samples directly withdrawn from the reactor and subjected only to minimal treatments in order to short-stop the reaction are ready for its analysis with this method. Nevertheless, the high cost of the SEC columns may be a drawback. Results for samples simultaneously withdrawn from the reactor with a syringe and from a recirculation loop have been compared. Because of the high initial viscosity of the reaction mixture, samples taken from the loop were more homogeneous and representative of the reactor content. Differences between the sampling procedures were found only for reaction times below about 5 min.

The analytical method developed has been used to monitor the synthesis of biodiesel from sunflower oil and evaluate the effects of the catalyst (NaOH and KOH) concentration and the methanol/oil molar ratio. At low catalyst concentrations the methanolysis rate rapidly increased with the amount of NaOH. On the other hand, the evolution of the products selectivities with reaction time was not affected by the catalyst concentration. A slightly better performance of KOH compared to NaOH has been found. As regards the methanol/oil molar ratio, whereas the long-term oil conversion increases with the excess of methanol, as expected for the effect on the equilibrium conversion, the initial methanolysis rates decreased. This can be interpreted as a consequence of the two-phase nature of the reaction and the fact that the homogeneous catalyst is exclusively in the methanol phase.

Acknowledgement

The Education Department of the Navarre Government (Dirección General de Universidades y Política Lingüística) is gratefully acknowledged for its financial support (I. Campo fellowship).

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