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Article

Separation of the Glycerol-Biodiesel Phases in an Ethyl Transesterification Synthetic Route Using Water

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Biodiesel is obtained by the transesterification of vegetable oil (or fat) and alcohol, with methanol being the most used alcohol. Methanol can be replaced by ethanol; however, this alcohol acts as a surfactant in the reaction mixture, promoting a stable dispersion of the glycerol in biodiesel, which hinders the separation of the glycerol-biodiesel phases. In this study, it was found that the addition of 1% v/v water relative to the total volume of the reaction mixture expedites the separation of the phases by interrupting the emulsifying action of ethanol with an immediate separation of glycerol from biodiesel. The characterization of the produced biodiesels was performed using hydrogen nuclear magnetic resonance (^{1}H NMR) and gas chromatography (GC). ^{1}H NMR indicated a 96.9% conversion of triglycerides to biodiesel. The fatty acid compositions of the synthesized ethyl and methyl biodiesels determined using GC are essentially the same.

Keywords: biodiesel, transesterification, ethanol, methanol, water, phase separation

Introduction

Fossil fuels are non-renewable energy resources and can be depleted. In the transportation sector, there is a great demand for petrol diesel, a polluting fuel that causes serious environmental problems. Therefore, the use of environmentally friendly sources of energy is required to supply anthropic needs.

Biodiesel appears in this scenario as an alternative fuel, which can be used in diesel motors without modifications of the engine because it exhibits properties similar to those of petrol diesel.[1,2] Because biodiesel is obtained from renewable raw materials, it is biodegradable and non-toxic. Biodiesel has a high flash point, indicating that it is safe to store and handle, and it causes less environmental impact regarding the emission of pollutants.[3,4]

Biodiesel is produced through the transesterification reaction of oils or fats using a short chain alcohol in the presence of a catalyst. The product of this reaction is a mixture of fatty acids, acids, alkyl esters (biodiesel) and glycerol as a byproduct.[5,6]

Methanol is the most used alcohol in the transesterification reaction. Methanol is highly reactive and generates satisfactory yields at lower temperatures and reaction times compared with other alcohols.[5,6] However,

methanol presents the disadvantage of higher toxicity compared with ethanol. In the case of Brazil, which has a high production rate of ethanol from sugarcane, methanol is imported, presenting a disadvantage under certain political and economic conditions.[7]

In Brazil, ethanol is an interesting alternative to methanol because a high scale production of this alcohol currently exists, and a significant increase in the production of sugarcane, the raw material, *per* area is expected. Additionally, the use of the bagasse and the straw of the sugarcane to produce ethanol has been significantly increasing.[8]

In addition to its lower toxicity, ethanol also endows biodiesel with the status of a product essentially obtained from biomass; methanol is commonly produced from mineral petrol. Ethyl biodiesel exhibits higher lubricity and a higher cetane number compared with the methanol derivative, implying lower ignition time and less wear of the metal surfaces.[9]

However, as the synthesis progresses through the transesterification reaction, ethanol promotes a more stable dispersion between the ethyl esters and glycerol, impeding the phase separation and thus increasing the time required for the production process and lowering the quality of the obtained biodiesel.[6]

There have been certain proposals in the literature to facilitate the separation between the two phases when using

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ethanol. For example, one method proposes performing the reaction using a 20:80% m/m mixture of methanol:ethanol, adding analytical grade glycerol after the reaction is complete, centrifuging the reaction mixture and allowing a long period for the decantation process to occur.[9,10]

Other author has reported that the glycerol dispersed in the biodiesel-ethanol mixture causes the displacement of the reaction towards the formation of triglycerides and alcohol, decreasing the yield of fatty acid monoesters.[11]

In this context, this study presents a new proposal for the synthesis and purification of ethyl biodiesel, focusing on the separation of the glycerol-biodiesel phases, which is a problematic portion of the production process.

Experimental

Materials

For the synthesis of methyl or ethyl biodiesel, soy oil purchased in the local market was used. The methyl route was performed using absolute methanol (Synth, Brazil, Diadema-SP), and the ethyl route was achieved with absolute ethanol (Synth, Brazil, Diadema-SP). In both of the routes, a solution of 30% m/m sodium methoxide in methanol was used as the catalyst (Vetec, Brazil, Rio de Janeiro-RJ).

Synthesis procedure: ethyl route

The ethyl route was performed in two steps. Initially, 591 g of ethanol and 5.7 g of 30% m/m sodium methoxide solution in methanol was added to 985 g of the oil. The relative quantities of the ethanol and the catalyst solution relative to the weight of oil were 60% and 0.58% m/m, respectively.

The mixture was shaken at 900 rpm at 60 °C under reflux for 1 h. The mixture was transferred to a separatory funnel, and approximately 1.5 mL (1% v/v) of water at 60 °C was added. Then, the mixture was gently agitated. After a few seconds, phase separation occurred, and the inferior phase was removed. The superior phase was transferred to the reaction flask. An additional 148 g of ethanol was added along with 1.4 g of the catalyst solution. This second step of the reaction was performed in the same manner as the first. The percentages of the additional ethanol and the catalyst solution relative to the initial weight of the oil were 15% m/m and 0.15% m/m, respectively.

The biodiesel was washed with five portions of 50 mL of water at 60 °C, followed by decantation to remove the water and impurities. The biodiesel was dried at 100 °C for 1 h and then purified by percolation in a column with the cation exchange resin AMBERLITE BD10DRY. Approximately

180 g of the resin *per* liter of biodiesel was used, and the flow rate was approximately 4 mL min⁻¹.

Synthesis procedure: methyl route

The methyl route was performed under the same conditions as the ethyl route, and the quantities used were 980 g of soy oil, 157 g of methanol and 5.49 g of the catalyst solution. The percentages of the additional methanol and the catalyst solution relative to the initial weight of oil were 16% m/m and 0.56% m/m, respectively.

After the first reaction step was complete, the mixture was transferred to a separatory funnel in which the separation of the two phases occurred spontaneously without the addition of water. The glycerol was removed, and the second step was performed after the addition of an additional 39 g of methanol and 1.4 g of the catalyst solution. This second step of the reaction was performed in the same manner as the first. The percentages of the additional methanol and the catalyst solution relative to the initial weight of oil were 4% m/m and 0.14% m/m, respectively.

Analytical method: total water

The total water content in the biodiesel was determined according to EN ISO 12937[12] using Karl Fischer coulometric titration (Metrohm model 831).

Analytical method: oxidative stability

The induction period, which expresses the oxidative stability, was determined through the EN 14112[13] method using a Metrohm Rancimat model 873.

Analytical method: iodine number

The iodine number was determined according to EN 14111,[14] titrating with an 809 Titrando Metrohm using a Pt Titrode glass electrode and an automatic sampler Metrohm 814 USB Sample Processor.

Analytical method: hydrogen nuclear magnetic resonance (¹H NMR)

To evaluate the conversion of triacylglycerols (TAGs) to mono alkyl esters, ¹H NMR spectra were obtained after the first step, after the second step and after the final purification of the biodiesel with the cationic resin. To obtain the spectra, an aliquot of 20 μL was dissolved in 600 μL of CDCl$_3$ containing tetramethylsilane (TMS) as an internal reference. The spectra were obtained in a NMR Bruker Avance III 500 MHz under the following conditions: spectral window −4.00 to 16.00 ppm; spectra with 32,768 points; 11.75 μs at 90° pulse; 5 s delay; and 16 scans.

Analytical method: gas chromatography (GC)

The fatty acid compositions of the soy oil used for the experiments and the produced biodiesels were determined using GC. A Perkin Elmer Clarus 600 was used under the following conditions: FID detector; Agilent column ("crossbond", 50% cyanopropylphenyl and 50% dimethylpolysiloxane) 30 m long, 0.25 mm internal diameter, 0.25 μm film thickness; helium (gas carrier) flow rate 1 mL min^{-1}; split injection 1:40; injection volume 0.4 μL; injector temperature 250 °C; detector temperature 250 °C; initial temperature of the oven 100 °C; and 5 °C min^{-1} heating rate up to 230 °C, with a 20 min hold at 230 °C.[15]

For the oil sample, chromatographic analysis was performed as previously described using the method of saponification and esterification of fatty acids developed by Metcalfeet *et al.*[16] and Hartman and Lago.[17]

The identification of the esters was performed according to the retention times of the previously analyzed standard substances. The quantitation was obtained through the normalization of the area of each chromatographic peak.

Analytical method: acid number

The acid number was determined following the method proposed by Aricetti *et al.*[18] To perform the titration, a Metrohm Titrando 809 was used with a Metrohm Solvotrode electrode (electrolyte-saturated LiCl in ethanol) and an automatic sampler Metrohm 814 USB Sample Processor.

Analytical method: density

Slightly less than 5 mL of the sample was added to a calibrated 5 mL volumetric flask of known weight. The flask with the samples was thermostated in a water bath at 20.0 ± 0.1 °C for 10 min. Then, the flask was brought to volume at this temperature. The flask was dried with paper towels and weighed. The density was calculated based on the mass/volume relationship.

Results and Discussion

The alcohols used in the transesterification reaction (methanol and ethanol in the present study) act not only as reagents but also as surfactants because they are soluble in glycerol (polar phase) and in biodiesel (non-polar phase). The carbon chain of the alcohol molecule is responsible for its solubility in biodiesel, whereas the hydroxyl group exhibits affinity for the glycerol.[19] When the interfacial tension between two liquids is reduced to a sufficiently low value due to the presence of a surfactant, the emulsification of these liquids occurs. According to Traube's rule, for a homologous series of surfactants, the concentration of the surfactant required to produce an identical decrease in the

superficial tension decreases by a factor of three for each additional CH$_2$ group.[19]

Ethanol contains an additional CH$_2$ group in its molecule compared with methanol. Therefore, ethanol is a more efficient surfactant and causes the emulsification of the glycerol-biodiesel mixture, indicating that separation of the phases will be more difficult. This situation presents a problem in the production of ethyl biodiesel because it results in a long wait for the decantation process and it provokes the retention of glycerol in the biodiesel, indicating that the concentrations of this byproduct can reach higher concentrations than that allowed by regulatory agencies.[20]

The fact that the addition of a low quantity of water (1% m/m) provokes a rapid separation of the two phases can be understood by the formation of hydrogen bonds between ethanol and water that are energetically more favorable than the van der Waals interactions between ethanol and biodiesel.

The ^{1}H NMR spectra of the soy oil and the reaction mixtures after the transesterification steps, after separation of the phases, and after drying and purification with the cationic resin are presented in Figure 1 for ethyl and methyl biodiesels.

The conversion of the triacylglycerides to mono alkyl esters is clearly observed in the ^{1}H NMR spectra by the disappearance of the double duplets at 4.30 and 4.15 ppm, which are related to the glycerol CH$_2$ groups, and by the appearance of the quartet at 4.12 ppm, which is related to the ethyl CH$_2$ group (in the case of the ethyl derivative). The conversion is also noted by the appearance of the singlet at 3.66 ppm related to the CH$_3$ of the methyl biodiesel. The signal at 3.72 ppm observed in the spectrum in Figure 1b of the ethyl biodiesel is related to the CH$_2$ group of the ethanol. In the spectra of the methyl biodiesel, the signal at 3.49 ppm is related to methanol, which is a reagent in the transesterification reaction. Figure 1 shows that the drying procedure in the oven at 100 °C removes the remaining alcohol (ethanol or methanol). Purification through the resin removes the eventual alcohol molecules that are yet present in the biodiesel and removes substantial quantities of residual water, as observed by Karl Fischer analyses and by the absence of the signal at 1.56 ppm in the ^{1}H NMR spectra, which is characteristic of water.[21]

The conversion percentages (% mol/mol) for the ethyl and methyl biodiesel were calculated from equations 1 and 2.[22,23]

$$\%C_{ME} = 100\,(2\,I_{CH_3}/3\,I\alpha_{CH_2}) \tag{1}$$
$$\%C_{EE} = 100\,(I_{TAG\,+\,EE} - I_{TAG})/I\alpha_{CH_2} \tag{2}$$

where: $\%C_{ME}$ = percentage of conversion from soy oil to methyl biodiesel; $\%C_{EE}$ = percentage of conversion from
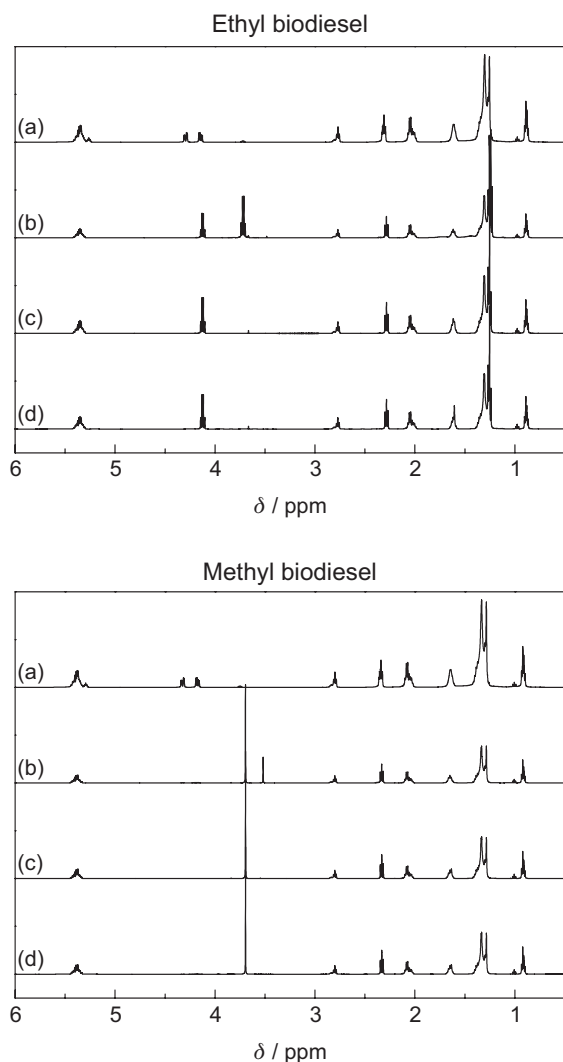
Ethyl biodiesel

Methyl biodiesel

Figure 1. ^{1}H NMR spectra: (a) soy oil; (b) of the reaction mixture after the first step of the reaction and the phase separation; (c) of the reaction mixture after the second step of the reaction, the phase separation and 1 h of drying in the oven at 100 °C; (d) of the final biodiesel after purification with the cationic resin.

soy oil in ethyl biodiesel; I_{CH3} = integral of the signal at 3.66 ppm representing the CH_3 of the methoxy group in the methyl ester; $I_{\alpha CH2}$ = integral of the signal at 2.27 ppm representing the αCH_2 of the ester, which is present in TAG and in biodiesel; $I_{TAG + EE}$ = integral of the signal at 4.12 ppm that considers the CH_2 hydrogens of the ethyl group and two of the hydrogens of the CH_2 groups of the glycerol of the residual TAG; and I_{TAG} = integral of the signal at 4.30 ppm that considers two of the hydrogens of the CH_2 of the residual TAG glycerol; the intensity of the signal is equal to the signal that is superposed at 4.15 ppm.

The obtained conversion percentages of the transesterification reactions are presented in Table 1.

Table 1. Conversion rate percentages of soy oil in biodiesel obtained using the ^{1}H NMR spectra

Conversion rate of the soy oil in biodiesel / % (mol/mol)		
After reaction step	Ethyl biodiesel	Methyl biodiesel
1	95.5 ± 0.7	91.0 ± 0.3
2	96.5 ± 0.4	96.3 ± 0.3
After purification with the resin	96.9 ± 0.4	97.7 ± 0.4

The fatty acid compositions of the soy oil and the produced biodiesels are shown in Table 2.

Table 3 shows the obtained values for certain physical and chemical properties of the synthesized biodiesels.

Importantly, when water was added for the separation of the glycerol and biodiesel phases, no soap formation was observed, the formation of which would result in a lower yield and a lower quality of the obtained product.[24-26]

The fatty acid compositions of the soy oil and the formed biodiesel are similar (Table 2), indicating the non-occurrence of side reactions as, for example, thermal

Table 2. Fatty acid compositions of the soy oil and the produced ethyl and methyl biodiesels

Fatty acid	Symbol[a]	Soy oil / % (m/m)	Ethyl biodiesel / % (m/m)	Methyl biodiesel / % (m/m)
Hexadecanoic	C16:0	11.01 ± 0.01	11.01 ± 0.02	10.98 ± 0.02
Cis-hexadecanoic-9-enoic	C16:1	0.09 ± 0.01	0.09 ± 0.01	0.09 ± 0.01
Heptadecanoic	C17:0	0.07 ± 0.01	0.08 ± 0.01	0.09 ± 0.01
Cis-heptadec-9-enoic	C17:1	0.05 ± 0.01	0.05 ± 0.01	0.05 ± 0.01
Octadecanoic	C18:0	3.25 ± 0.03	4.30 ± 0.01	3.27 ± 0.01
Cis-octadec-9-enoic	C18:1	23.28 ± 0.01	23.12 ± 0.09	23.33 ± 0.05
Cis,cis-octadec-9,12-dienoic	C18:2	54.58 ± 0.02	53.98 ± 0.07	54.67 ± 0.08
Trans,trans-octadec-9,12-dienoic	C18:2*t*[b]	0.11 ± 0.01	0.10 ± 0.01	0.11 ± 0.01
All-*cis*-octadec-9,12,15-trienoic	C18:3	6.66 ± 0.01	6.43 ± 0.02	6.57 ± 0.02
Icosanoic	C20:0	0.32 ± 0.01	0.30 ± 0.01	0.30 ± 0.01
Cis-icos-9-enoic	C20:1	0.20 ± 0.01	0.18 ± 0.01	0.19 ± 0.01
Docosanoic	C22:0	0.38 ± 0.01	0.35 ± 0.01	0.34 ± 0.01

[a]Cx:y, where: x = number of carbon atoms; y = number of carbon to carbon double bonds; [b]*trans* isomer.

Table 3. Values of certain physical and chemical properties of the synthesized biodiesels

Property	Unit	Method	Limit[17]	Ethyl biodiesel	Methyl biodiesel
Water content	mg kg^{-1}	EN ISO 12937	≤ 500	195 ± 5	249 ± 4
Oxidative stability at 110 °C	h	EN 14112	≥ 8	6.0 ± 0.2	6.0 ± 0.2
Iodine number	g (100 g)$^{-1}$	EN 14111	≤ 120	122 ± 1	136.2 ± 0.7
Linolenic acid ester	% m/m	EN 14103	≤ 12	6.43 ± 0.02	6.57 ± 0.02
Acid number	mg KOH g^{-1}	Reference 15	≤ 0.5	0.11 ± 0.02	0.0711 ± 0.0005
Viscosity at 40 °C	mm^2 s^{-1}	EN ISO 3104	3.5-5.0	4.35 ± 0.03	4.122 ± 0.007
Density at 20 °C	kg m^{-3}	Described in Experimental section	860-900	870 ± 3	878 ± 2

degradation, oxidation, saponification, etc. Additionally, the two types of synthesized biodiesels exhibited similar properties, with values that were in accordance with the specifications of the regulatory agencies.

Conclusions

The separation of the glycerol and biodiesel phases is a critical point in the synthetic production of ethyl biodiesel through the transesterification reaction because a stable emulsion is formed. In the present study, it was shown that the addition of water (1% v/v relative to the total volume of the reaction mixture) clearly accelerates the separation of the two phases, increasing the rate of the decantation process and greatly facilitating the overall process.

Although there was concern that the addition of water could cause soap formation, none was observed. The high rate of conversion of the soy oil to ethyl biodiesel (96.9% mol/mol) is similar to the rate of conversion in the case of the methyl derivative (97.7% mol/mol), and the fatty acid compositions of the two products are similar. Additionally, the physical and chemical properties of the ethyl and methyl derivatives are equivalent and are within the limits established by the regulatory agencies.

Acknowledgments

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