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Monitoring of the methanolysis reaction for biodiesel production by off-line and on-line refractive index and speed of sound measurements

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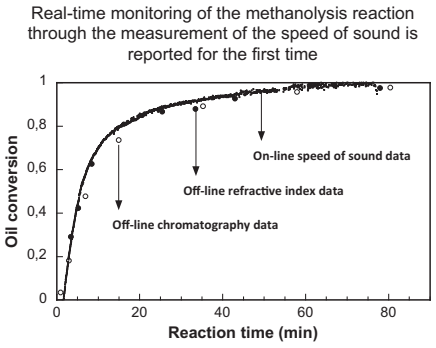
HIGHLIGHTS

- The refractive index of the alcoholic phase is very sensitive to the oil conversion.
- The speed of propagation of sound in the reaction mixture is sensitive as well.
- Both physical properties increase with the oil conversion mainly due to the glycerol.
- Good linear relationships have been found under wide ranges of operating conditions.
- Real-time monitoring using the speed of sound is feasible and first reported here.

GRAPHICAL ABSTRACT



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ABSTRACT

Two techniques based on the measurements of the refractive index (n_D) of the alcoholic phase at 20 °C ($n^{20}_{D,AL}$) and the speed of propagation of sound (u_s) in the reaction mixture are presented for monitoring the methanolysis of vegetable oils. Application of these techniques for the real-time monitoring of the synthesis of biodiesel is described for the first time. Size exclusion chromatography has been used as reference method. Both $n^{20}_{D,AL}$ and u_s increase linearly with the oil conversion due to the contribution of the glycerol formed. Good correlations have been found whose coefficients depend on the initial methanol/oil ratio and in the case of u_s also on the temperature Due to flow instabilities in the refractometer chamber, monitoring based on n_D has been possible only off-line whereas the measurement of u_s allowed an effective, fast, accurate and cheap real-time monitoring of the process.

1. Introduction

According to recent energy outlooks, if the current growth of 1.6% per year continues, as expected from the growing economies of the developing countries and increasing population, this would require the worldwide energy production to double in about 40 years [1]. In order to meet this impressive demand with acceptable environmental costs it is crucial that the role of renewable energy sources increases remarkably. Whereas the contribution of e.g. wind and solar energies to the power generation sector are increasing at good pace, it is expected that the decarbonization of the transportation sector depends more in the short and medium term on the biofuels, electricity and hydrogen [2].

In the European Union (EU), bioenergy plays a very important role regarding renewable energy policies, accounting for more than half of projected renewable energy output in 2020. Finding resource-efficient combinations of biomass sources, conversion

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technologies and energy end uses is of the outmost importance in order to prevent new environmental issues such as the negative effects on the greenhouse gases (GHG) balance and ecosystem impacts connected to indirect land use change [3]. At present, first-generation biodiesel and bioethanol are the only commercially-available bioenergy-based options for the transportation sector. Their consumption in the EU 27 amounted in 2012 to 11.41 and 2.87 Mtoe for biodiesel and bioethanol, respectively, with a combined growth of 2.9% between 2011 and 2012 [4].

Biodiesel is a biofuel for use in direct injection compression ignition engines that can be produced from different kinds of oleaginous crops, animal fats, algal oil and waste oils. It is a mixture of the fatty acid alkyl esters obtained by transesterification, most frequently with methanol, of the triglycerides that constitute the oils and fats [5–8].

Part of the success in the introduction of biodiesel into the market has been due to efficient standardization because of the great variety of feedstocks that can be used for its manufacture that make necessary to establish and meet specific standards [9]. A number of analytical procedures have been developed to assess the quality of biodiesel fuel [9–12]. On the other hand, suitable methods for monitoring the production of biodiesel are necessary to avoid operational problems and guarantee the quality of the final product through dedicated process control systems [10].

Regarding the analytical procedures for the quality control of biodiesel, the chromatographic ones have been the characterization techniques most intensively developed due to their very high sensitivity and ability to detect low contents of possible contaminants [10,13]. Particularly, gas chromatography (GC) is the basis of most of the methods included in the national standards, and methods are available with this technique for the complete analysis of total alkyl esters, glycerides (monoglycerides, diglycerides and triglycerides), as well as free glycerol in biodiesel obtained using methanol or ethanol in the transesterification processes, also called methanolysis and ethanolysis, respectively. A complete characterization of the individual compounds can be carried out by reversed-phase high performance liquid chromatography (HPLC) working in both gradient elution with ultraviolet detection [14] and isocratic elution with refractive index detection [15]. GC- and HPLC-based methods often involve laborious, time-consuming procedures (e.g. sample derivatization in the case of GC analyses) that are not well suited for reaction monitoring. Simpler and faster methods have been developed using gel permeation-size exclusion chromatographies (GPC-SEC) that allow the simultaneous analysis of the main categories of compounds (fatty acids alkyl esters, glycerides, and glycerol) but no the individual characterization (e.g. methyl stearate, methyl linoleate, methyl palmitate, etc.) within each category [16–18]. Even simpler and cheaper methods exist based on thin layer chromatography (TLC) for the determination of the main categories of compounds present in the transesterification reaction, as well as free fatty acids (FFAs) and glycerol [19]. Anyway, all chromatographic techniques require sampling from the reactor and then off-line analysis of the sample, so they do not allow real time monitoring of the transesterification process.

Since the first results reported by Knothe for biodiesel produced from soybean oil [20,21], an increasing interest exists in the spectroscopic techniques, mainly on the ones based on Fourier-transformed infrared spectroscopy (FTIR) [13], for the monitoring of the transesterification reaction and the assessment of the biodiesel quality. The underlying reasons of this interest are the operational ease, rapidity, accuracy and reliability of the measurements, as well as the possibility of easy adaptation of the techniques for on-line monitoring (e.g. using fiber-optic probes in the case of FTIR spectroscopy). However, the similarity between the FTIR spectra of the triglycerides and the transesterification products introduces some analytical difficulties. On the other hand, multicomponent analysis is possible by FTIR spectroscopy, so methodologies such as principal component and multivariate analyses are routinely applied nowadays. Both, the near-IR (NIR, 12820–4000 cm^{-1}) and mid-IR (MIR, 4000–700 cm^{-1}) spectral regions have been considered for monitoring the synthesis of biodiesel and assessing its quality. In the case of NIR spectroscopy, it is possible to simultaneously analyze the fatty acids alkyl esters, glycerides, and free glycerol for the methanolysis and ethanolysis of vegetable oils [22,23]. This technique has been successfully applied to the on-line monitoring of transesterification reactions using NIR probes working in reflection or transflectance modes [23]. As for MIR spectroscopy, it has been used in both transmission and attenuated total reflectance (ATR) modes for the monitoring of methanolysis and ethanolysis reactions, although glycerides cannot be analyzed individually with these techniques [16]. On-line monitoring by means of ATR-FTIR is also possible using cylindrical internal reflectance cells [24]. Among the vibrational spectroscopic techniques, Fourier-transformed Raman spectroscopy (FT-Raman) has been applied to monitor the ethanolysis of vegetable oils through the quantitation of the fatty acid ethyl esters concentration by uni- and multivariate analyses [25]. Other optical spectroscopies such as the visible and UV–visible ones allow determining traces of alcohol and glycerol in biodiesel [26] and the monitoring of the transesterification reaction through the analysis of the produced glycerol [27,28]. Finally, it is well-known for long time that ^1H nuclear magnetic resonance (^1H NMR) spectroscopy can be utilized to monitor the transesterification of vegetable oils through the quantitation of the fatty acid alky esters. At present, the development of high-resolution ^1H NMR allows a more complete characterization, including FFAs and glycerides. Furthermore, unilateral ^1H NMR has been recently described as a fast, portable and cheap technique for the on-line monitoring of biodiesel synthesis [29].

It can be concluded from the preceding brief review that a great interest exists in the characterization of biodiesel and in the monitoring of the methanolysis and ethanolysis reactions. Relatively few of the chemical techniques, most notably NIR and ATR-FTIR spectroscopies, may be used for the real-time monitoring of these processes. But this monitoring is required for suitable control of the industrial biodiesel production as well as for fundamental studies on the reaction kinetics, reactor design, catalysts development, etc.

With the aim of contributing to the field of biodiesel synthesis monitoring, the main objective of this work is to investigate the usefulness of techniques based on the change of the refractive index and the speed of propagation of sound during the course of the methanolysis reaction, with emphasis on real-time applications. SEC is used as reference method. While there are previous reports on the use of the refractive index, to our knowledge, the application of the speed of sound measurements in this field is reported in this work for the first time.

2. Experimental procedures

2.1. Transesterification reactions

The transesterification reactions were carried out at atmospheric pressure in an experimental setup similar to the one described in a previous work [17]. It consists of a mechanically stirred jacketed glass tank reactor of 1 l. Stirring speed was set at 400 rpm according to the results of a series of preliminary experiments that allowed to establish that this speed was high enough to minimize the effects of mass transfer limitations. The reactor was fitted with a reflux condenser, a thermocouple probe and a thermostatic circulating bath (HUBER UNISTAT 340 W) that was used to control the reaction temperature within the 30–60 °C range. Re-