Fuel 92 (2012) 354–359

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Near infrared reflectance spectroscopy and multivariate analysis to monitor reaction products during biodiesel production

Sara Pinzi [a], Fernando Alonso [a], Juan García Olmo [b], M. Pilar Dorado [a,*]

[a] Dep. Physical Chemistry and Applied Thermodinamics, Ed Leonardo da Vinci, Campus de Rabanales, 14071 Cordoba, Spain
[b] NIR/MIR Spectroscopy Unit, Central Service for Research Support (SCAI), University of Cordoba, Campus de Rabanales, 14071 Cordoba, Spain

ARTICLE INFO

Article history:
Received 21 May 2011
Received in revised form 2 July 2011
Accepted 6 July 2011
Available online 21 July 2011

Keywords:
Methyl esters
Vegetable oil
Transesterification
Glyceride
Biodiesel quality

ABSTRACT

In agreement with the principles of green chemistry, near infrared spectroscopy (NIRS) allows multicomponent analysis in a fast and nondestructive way, without requiring complex pre-treatments, being a safe, clean and energy saving technique. In this work, a preliminary study to develop near infrared calibration models to predict methyl esters (ME) yield, monoglycerides (MG), diglycerides (DG), triglycerides (TG), free glycerol (FG) and total glycerol (TotalG) content in biodiesel has been carried out. These parameters are considered key factors to determine biofuel quality, its commercialization and to study and monitor the transesterification reaction. For this purpose, samples of biodiesel produced from three different vegetable oils (maize oil, sunflower oil and olive–pomace oil) were analyzed following the EN14103 and EN14105 European standards as reference methods. NIRS calibration equations were validated with a group of validation samples. The mean spectra showed that the main variability on biodiesel NIR spectra occurred around 1700 and 2300 nm. Moreover, the principal components analysis (PCA) applied to the spectra revealed the grouping of samples according to the type of oils used for biodiesel production. The standard deviation of the prediction (cross validation) errors ($RMSEP_{CV}$) of the calibration models and the standard deviation error (RMSEP) of the validation set resulted similar to the measurement errors (intra lab SEL_r) and repeatability (inter lab SEL_R) of each analyte. Results confirm the accuracy of the developed NIRS models for determination of glycerides content and methyl esters yield in biodiesel.

1. Introduction

In recent years, biofuel research has been directed mainly to explore low cost plant-based fuels, i.e., fatty acid methyl esters (FAME) of seed oils, and in some cases, fats [1]. FAME, also known as biodiesel, is biodegradable and non-toxic, it has low emissions profile and is environmentally friendly [2]. The most common way to produce biodiesel is by transesterification. Methanol is the most common alcohol used and, in this case, the reaction is referred to as methanolysis. This reaction, in turn, consists of three consecutive reversible steps of reactions with the intermediate formation of diglycerides (DG) and monoglycerides (MG). After the reaction, glycerol is separated by settling or centrifuging [3,4].

The content of free glycerol (FG) and its bounded forms as TG, DG and MG are key parameters to define biodiesel quality. After transesterification, free glycerol traces can be easily removed from biodiesel by washing with distilled water. However, a low content of glycerides (in agreement with European biodiesel standard EN14214) can only be achieved by selecting the appropriate reaction reagents (type and concentration) and conditions, or by further distillation of the product [5]. Biodiesel with high content of free glycerol may cause problems during storage and in diesel engine fueling systems, due to glycerol separation. This can lead to injector fouling and high aldehyde emissions. A high content of glycerides, especially triglycerides, may cause the formation of deposits at the injection nozzles and in the valves [5]. As long as the amount of FG and glycerides allowed by the European biodiesel standard EN-14214 are very low, robust and reliable analytical methods for the determination of FG and acylglycerols are highly demanded [6,7].

Several methods, most of them based on gas-chromatography techniques [8,9], are available for the determination of FG, MG, DG and TG in biodiesel. In this sense, Plank and Lorbeer [8] reported a method for the simultaneous determination of glycerol and acylglycerols in biodiesel. This led to the development of standard reference methods such as ASTM D 6584 in USA and EN14105 in European legislations. Darnoko et al. [10] and Arzamendi et al. [11] developed size exclusion chromatography (SEC) methods to monitor glycerides content and FAME yield during biodiesel production. Pinzi et al. [12] developed an ultrasound assisted automatic on-line method for the determination of bounded glycerol

* Corresponding author. Tel.: +34 957 218332; fax: +34 957 218417.
E-mail address: pilar.dorado@uco.es (M.P. Dorado).

0016-2361/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.fuel.2011.07.006

(expressed as the sum of TG, DG and MG) and FG in biodiesel. However, most of these biodiesel analyses are very expensive and time consuming, while near infrared spectroscopy (NIRS) appear to be a cheaper and faster alternative to accomplish biodiesel quality control [13,14].

NIR spectroscopy is a well-established analytical technique based on the absorption of electromagnetic energy in the region from 780 to 2500 nm (12820–4000 cm^{-1}). This type of technique allows multi-component analysis in a fast and non-destructive way, without requiring complex pre-treatments. The implementation of NIRS as an analytical method is in agreement with the principles of green chemistry because 100% of the samples can be reused, so it prevents waste production. This method avoids using solvents, separation agents, or other auxiliary chemicals and it is a safe, clean and energy saving technique [15].

In the NIR region, a component typically absorbs at more than one wavelength. Moreover, absorbance at a given wavelength may have contributions from more than one analyte in chemically complex matrices [15]. Therefore, well-established tools like principal component analysis (PCA) and partial least squares (PLS) have been used for biodiesel classification and quantification purposes. The correlation between the absorption of NIR radiation and the analytical reference data can be improved through the use of specific spectra pre-processing and variable selection methods [16].

In recent papers, the use of NIR in combination with multivariate data analysis for the analysis of biofuels has been reported [13,14,17–24]. Knothe [19,20,22] reported the existence of two ranges in the NIR spectra of soybean oil and its biodiesel, at 4430–4425 cm^{-1} and at 6005 cm^{-1}, respectively, which allow these products to be distinguished. In both regions, the methyl ester displays sharp peaks while the feedstock oil exhibits only shoulders. Furthermore, Baptista et al. [18] reported the development of calibration models for total methyl ester and principal fatty acid content in biodiesel, whereas Felizardo et al. [14] developed calibration models to predict water and methanol traces in biodiesel, besides other quality parameters such as the iodine value, cold filter plugging point, kinematic viscosity at 40 °C and density at 15 °C [23]. Moreover, Dorado et al. [24] determined methanol and glycerol traces in biodiesel using visible spectra and NIRS technique. However, to the best of our knowledge, studies about the use of NIRS besides multivariate data analysis to determine glycerides and glycerol content in biodiesel are inexistent.

According to the principles of green chemistry, this work is focused in the development of an analytical method based on NIRS technology in combination with multivariate data analysis to determine FG, MG, DG, TG and total glycerol in biodiesel. These parameters are considered key factors while establishing biofuel quality, for its commercialization and to study and monitor transesterification reactions.

2. Experimental

2.1. Samples and sample preparation

Fatty acid methyl esters were produced by transesterification of three different vegetable oils (sunflower oil, maize oil and olive–pomace oil) acquired from KOIPESOL (Andujar, Spain) with methanol and KOH as catalyst. The oils fatty acid content is depicted in Table 1. Sample preparation has been described in detail in a previous work [12].

To test biodiesel with different content in esters and glycerides traces, samples were taken at different times during the transesterification (from 30 s of reaction to 2 h). The reaction was stopped cooling down in a cold bath of ethylene glycolate at −10 °C. The residual methanol and water were separated from biodiesel via rotary evaporation at 80 °C during 1 h [25]. Samples were stored at −20 °C [2].

Table 1
Fatty acid composition of different vegetable oils used for biodiesel production. Maize oil (MO), sunflower oil (SFO) and olive–pomace oil (OPO).

Composition (%)	MO	SFO	OPO
Palmitic (C16:0)	13.0	6.9	11.0
Palmitoleic (C16:1)	–	–	0.8
Stearic (C18:0)	2.0	6.0	3.0
Oleic (C18:1)	33.0	26.5	75.2
Linoleic (C18:2)	50.8	66.5	9.5
Linolenic (C18:3)	1.0	–	0.5

2.2. Apparatus and methods

The instrument employed for spectra collection was a Spectrum One NTS FT-NIR spectrophotometer (Perkin Elmer LLC, Shelton, USA) equipped with an integrating sphere module. Samples were analyzed by transflectance using a glass petri dish and a hexagonal reflector with a total transflectance pathlength of approximately 0.5 mm. A diffuse reflecting stainless steel surface placed at the bottom of the cup reflected the radiation back through the sample to the reflectance detector. The spectra were collected using Spectrum Software 5.0.1 (Perkin Elmer LLC, Shelton, USA). Before recording the spectra, samples were thermostated at 24 °C. The reflectance ($\log 1/R$) spectra were collected in duplicate.

On the other hand, samples were analyzed following the EU biodiesel standard [26,27]. The reference methods were performed following the UNE EN14103 standard for the content on methyl esters (yield, wt%) and the UNE EN14105 standard for glycerol and glycerides content determination (wt%). A Varian (Palo Alto, CA, USA) Star 3400 gas chromatograph equipped with a flame ionization detector (FID) was used. The chromatograph was equipped with a Supelco capillary column 12 m × 0.32 mm, film thickness (df) 0.15 μm for triglycerides, diglycerides, monoglycerides, free glycerol and total glycerol determination. A 60 m × 0.25 mm VF-23 ms Varian capillary column (film thickness of 0.25 μm) was used for methyl esters analysis.

2.3. Reference data

Ninety-eight laboratory-scale samples of biodiesel produced from olive–pomace oil (OPO), sunflower (SO) and maize oils (MO) were used for the development of the methods. Among them, 80 samples were chosen for the calibration model of methyl esters (yield) and glycerides content and 17 samples were chosen randomly for the validation step (Table 2). Once the outliers without useful information were removed, the calibration and validation sets were defined. Both sets were independent; thus, the validation set was only used for testing the equations.

For triglycerides determination, a reduced number of samples (75) were used for the calibration and validation steps, because the sensibility of the reference method dramatically decreased for triglycerides content above 4 wt%, due to excessive enlargement of the chromatogram peaks that quantify triglycerides. For this reason, samples with a content of triglycerides higher than 4% were not considered. Table 2 shows information about reference data, calibration and validation sets, in addition to maximum standard error laboratory (SEL). Considering the EU standard (EN14105) as the reference method for glycerides (MG, DG, TG, FG and TotalG) determination, the errors considering precision (intra lab SEL_r) and repeatability (inter lab SEL_R) are expressed as a function of the value of the analyte in the sample. For this reason,