



## Conventional and fast gas chromatography analysis of biodiesel blends using an ionic liquid stationary phase

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### ARTICLE INFO

#### Article history:

Received 24 July 2009

Received in revised form 20 October 2009

Accepted 23 October 2009

Available online 30 October 2009

#### Keywords:

Ionic liquids  
Fatty acid methyl esters  
Fast gas chromatography  
Biodiesel blends

### ABSTRACT

The present research is focused on the GC-FID determination of fatty acid methyl esters (FAMES) in diesel blends, by means of an ionic liquid stationary phase, characterized by a dicationic 1,9-di(3-vinylimidazolium)nonane bis(trifluoromethyl)sulfonylimidate structure (SLB-IL100). The high polarity of the ionic liquid stationary phase allowed the separation of the FAMES, from the less-retained hydrocarbons, thus avoiding the requirement of a hydrocarbon LC pre-separation. The results derived from the analyses of a soybean FAMES B20 sample, carried out on an SLB-IL100 conventional column (30 m × 0.25 mm i.d. × 0.20 mm  $d_f$ ), were compared with those attained on a polyethylene glycol column, of equivalent dimensions. Conventional and fast GC methods, for the analysis of FAMES in diesel blends, were developed on an SLB-IL100 30 m × 0.25 mm i.d. × 0.20  $\mu$ m  $d_f$  and on an SLB-IL100 12 m × 0.10 mm i.d. × 0.08  $\mu$ m  $d_f$  column, respectively. The optimized IL methods were subjected to validation: retention time and peak area intra-day precision ( $n = 5$ ) were good, with CV % values lower than 0.08% and 4.9%, respectively. With regards to the quantitation of FAMES in biodiesel blends, a five points calibration curve was constructed, using C<sub>17:0</sub> as internal standard.

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### 1. Introduction

Biodiesel, defined as a mixture of fatty acid methyl or ethyl esters and processed from biological materials such as vegetable oils (e.g. soybean, rapeseed, sunflower, palm and coconut), recycled cooking oils, animal fats and plant and waste products [1,2], represents one of the most significant alternatives to conventional petrodiesel fuel. Alternative and renewable fuels have recently received increased attention due to: (I) the predicted shortage in oil supplies and consequent rise in oil price; (II) the effects associated with ambient air pollution, that has led to the introduction of more stringent environmental regulations worldwide [3].

Biodiesel can be used pure or mixed with petroleum distillates to attain blends defined with the abbreviation BX, where X stands for the biodiesel percentage (v/v). Biodiesel is characterized by diesel like properties, does not contain hazardous constituents such as sulfur, nitrogen and polycyclic aromatic compounds and can be exploited for industrial processes and transportation engines.

The most widely used blend at present is commonly known as B20, containing 20% biodiesel.

The qualitative and quantitative determination of fatty acid methyl esters in these mixtures is achieved to discover inaccurate volume blending or addition of oils with an excessive content of polyunsaturated fatty acids (PUFAs). It has been reported that an increased content of PUFAs leads to a decrease in the oxidative stability of biodiesel [4,5]. Biodiesel blends are highly complex and contain, besides FAMES, saturated and aromatic hydrocarbons contained in petroleum. Several spectroscopic and chromatographic techniques have been employed for the analysis of biodiesel blends, including IR [6], HPLC [7–9], <sup>1</sup>H NMR [10] and comprehensive two-dimensional gas chromatography [11–13].

The determination of the content of biodiesel in diesel fuel oil is carried out, according to the ASTM D 7371 procedure, by means of IR spectroscopy [14]: this method is applicable only to biodiesel, in the form of fatty acid methyl esters, with a concentration between 1% and 20%.

According to the UNI EN 14331 procedure [15], the elucidation of the FAME profile in diesel blends is carried out, after an LC pre-separation step, by using a Carbowax-type conventional GC column. This method is applicable to FAMES of vegetable or animal origin, with a chain length between C<sub>14</sub> and C<sub>24</sub>, and has been exploited for the analysis of FAMES with a concentration up to 5% (v/v) in middle distillates. The complexity of the procedure, as well as the cost of sample preparation has stimulated the development of easier, less expensive and less time consuming methods.

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The aim of the present study is the development of a method for the qualitative and quantitative analysis of biodiesel blends, suitable for FAMES concentrations higher than 5% (v/v). An SLB-IL100 GC column was employed, characterized by a highly polar room temperature ionic liquid (IL) stationary phase [dicationic 1,9-di(3-vinyl-imidazolium)nonane bis(trifluoromethyl)sulfonylimidate].

Room temperature ionic liquids represent a class of organic non-molecular solvents that are liquid at 20 °C [16], and are usually formed of an organic cation containing N or P (*i.e.*, alkyl imidazolium, phosphonium), counterbalanced by an anion of organic or inorganic nature. Ionic liquids have been widely employed in several chemistry fields, such as solvents in organic synthesis and catalysis [16], as liquid matrices in matrix-assisted laser desorption/ionization mass spectrometry [17,18], as buffer additives in capillary electrophoresis [19] and as GC stationary phases [20–23]. Specific IL properties such as low volatility, high thermal stability, excellent selectivity towards specific chemical classes and good wetting abilities on the inner wall of fused silica capillaries, make this class of compounds suitable as GC stationary phase. Consequently, several ionic liquids have been evaluated as stationary phases in the GC field [24,25]. Several ionic liquids have been evaluated using the linear solvation energy model [26,27,29,31,32], because these phases can undergo multiple interactions. In order to increase their thermal stability and, hence, their suitability for GC analysis, ILs have recently been subjected to cross-linking [26]. Applications in the GC field include the analysis of polyaromatic hydrocarbons (PAH) [26,27], essential oils [28], chlorinated pesticides [26], fatty acid methyl esters [26,29,30], and flavours and fragrances [29,31]; IL stationary phases have also been used in comprehensive two-dimensional GC [33] and tuned pressure dual-column GC [34].

During the initial phase of the present research, the suitability of the IL phase, in the analysis of a standard FAME solution, was evaluated, then the IL polarity was determined through McReynolds constants; after, the analysis of a soybean FAMES B20 sample, on an SLB-IL100 conventional column (30 m × 0.25 mm i.d. × 0.20 μm  $d_f$ ), was carried out. The results were then compared to those attained by using a polyethylene glycol phase (Supelcowax-10) column of the same dimensions, operated under ideal conditions. In a second phase, an optimized method for the analysis of biodiesel blends was subjected to validation both on the commercially available conventional SLB-IL100 column, and on a custom-made fast SLB-IL100 12 m × 0.10 mm i.d. × 0.08 μm  $d_f$  column.

## 2. Experimental

### 2.1. Sample and sample preparation

The diesel sample was purchased in a local gas station in Messina (Italy).

Benzene, *n*-butanol, 2-pentanone, nitropropane, pyridine, heptadecanoic acid methyl ester (used as internal standard), C<sub>7</sub>–C<sub>30</sub> alkanes, C<sub>16:0</sub>, C<sub>18:0</sub>, C<sub>18:1</sub>, C<sub>18:2</sub>, C<sub>18:3</sub>, C<sub>20:0</sub> methyl esters and C<sub>4</sub>–C<sub>24</sub> even carbon saturated FAMES were kindly supplied from Sigma–Aldrich/Supelco (Bellefonte, PA).

The FAMES were prepared from soybean oil, purchased from a local store in Messina: 500 μL of oil were transesterified in a Pyrex tube adding 5 mL of a solution of sodium methoxide (0.5%, w/v) in methanol and through heating at 100 °C for 15 min. After cooling, 5 mL of boron trifluoride-methanol (20% BF<sub>3</sub>) reagent (Merck, Milan, Italy) were added and the solution was heated at 100 °C for 30 min. After cooling, 5 mL of *n*-hexane and 2 mL of distilled water were added to the mixture, which was then agitated manually for 1 min. The upper *n*-hexane layer was then transferred to a test

tube, was added with anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then centrifugated for 2 min at 6000 rpm; after, the FAMES solution was transferred to a 7 mL vial, dried under nitrogen flow and stored at 4 °C. B20 samples were prepared by combining 200 μL of the FAMES obtained, with 800 μL of diesel, in a 2 mL vial; the B20 samples were diluted 1:20 with *n*-hexane prior to GC analysis.

For the construction of calibration curves, five different biodiesel blends were prepared (B1, B5, B10, B20 and B40), diluted 1:20 in *n*-hexane, with 1 mg of C<sub>17:0</sub> methyl ester added as internal standard.

### 2.2. GC-FID analyses

All analyses were carried out on a GC 2010 gas chromatograph (Shimadzu, Milan, Italy) equipped with a split–splitless injector, an AOC-20i autoinjector and a flame ionization detector (FID). All data were collected by GC Solution software (Shimadzu, Milan, Italy).

An SLB-IL100 30 m × 0.25 mm i.d. × 0.20 μm film thickness column (Supelco) was operated under programmed temperature conditions: 50–230 °C at 3 °C/min (FID temperature: 230 °C). Injection volume and mode: 1.0 μL; split (100:1). Helium was used as carrier gas (40 cm/s).

A custom-made SLB-IL100 12 m × 0.10 mm i.d. × 0.08 μm film thickness column (Supelco) was operated under programmed temperature conditions: 50–230 °C at 70 °C/min (FID temperature: 230 °C). Injection volume and mode: 0.2 μL; split (500:1). Hydrogen was used as carrier gas (60 cm/s).

A Supelcowax-10 30 m × 0.25 mm i.d. × 0.25 μm film thickness column (Supelco) was operated under programmed temperature conditions: 50–280 °C at 3 °C/min (FID temperature: 280 °C). Injection volume and mode: 1.0 μL; split (100:1). Helium was used as carrier gas (40 cm/s).

All analyses for the determination of the McReynolds constants, were carried out under isothermal conditions (120 °C) and at helium constant linear velocity (40 cm/s). Injection was performed by means of a 7 μm polydimethylsiloxane SPME fiber (Supelco, Bellefonte, PA) in order to avoid coelution with the solvent.

FID parameters in all applications: make-up gas was N<sub>2</sub> at a flow rate of 50 mL/min; H<sub>2</sub> flow rate was 50 mL/min; the air flow rate was 400 mL/min. FID sampling rate: 80 ms (12 ms in the fast application).

## 3. Results and discussion

### 3.1. Analysis of the standard FAME solution

As well known, the use of polyethylene glycol stationary phases for the qualitative and quantitative determination of fatty acids methyl esters in lipid matrices from different origin (*e.g.* vegetable and animal oils) is very well established [35]. A preliminary comparison, between the Supelcowax-10 [100% polyethylene glycol] and the IL100 [1,9-di(3-vinylimidazolium)nonane bis(trifluoromethyl)sulfonylimidate] stationary phases, was achieved by using a solution of standard FAMES. A solution containing C<sub>4</sub>–C<sub>24</sub> saturated FAMES was analyzed on both columns, under the same experimental conditions. The main advantage gained by using the IL stationary phase, with respect to the Supelcowax-10 one, was a reduced analysis time: the C<sub>24</sub> methyl ester eluted within 50 min on the IL phase, and in about 65 min on the polyethylene glycol one. The data obtained were then introduced in a graph (Fig. 1a and b), plotting FAMES carbon numbers (C<sub>n</sub>) against their elution temperatures. A so-called prediction line was then drawn in order to determine the highest C<sub>n</sub> FAME that could potentially elute, at the maximum operating temperature, on both columns. The results indicated that a C<sub>32</sub> FAME could potentially elute from the IL column at its maximum operat-

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