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# Ultrafast gas chromatographic method for quantitative determination of total FAMEs in biodiesel: An analysis of 90 s

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ABSTRACT

Several physicochemical parameters must be determined in order to verify the quality of commercial biodiesel, and the analysis of total fatty acid methyl esters (FAMEs) is the main parameter. Therefore, an efficient and alternative analytical method using gas chromatography coupled with ultrafast module is important. This method was developed to quantify FAMEs in biodiesel commercial samples that originated from different feedstock (babaçu, coconut, rapeseed, corn, soybean, animal/palm oil and sunflower). The chromatographic run time is 90 s. When compared with the official methods, we had a much faster one, which provided an analytical frequency of up to 205 samples a day. This analytical method has been validated according to in-house validation parameters, such as linearity, repeatability, reproducibility (intermediate precision) and accuracy. Two analytical curves were prepared, one for determinate long carbon chain FAMEs (C16–C24) and another for short carbon chain FAMEs (C6–C14). The coefficient of determination (which represents the percentage of the data that is closest to the line of best fit) was 0.9992 for the C18 curve (long chain) and the C12 curve (short chain). Repeatability and reproducibility presented a relative standard deviation of 0.75% and 1.68% for the C18 curve and 0.44% and 1.05% for the C12 curve, respectively. The accuracy had a standard error of 0.2 for soybean biodiesel, 0.4 for animal/palm commercial biodiesel and 0.2 for babaçu biodiesel.

## 1. Introduction

The growing demands for automotive fuels coupled with the economics and environmental problems motivate the search for alternative routes for energy production. In this context, biofuels arise as viable options, being defined as: alternative fuels obtained from renewable sources, technically plausible, economically competitive, immediately available and environmentally acceptable. Biodiesel, especially, has its participation in the energetic world matrix growing frequently [1,2].

Biodiesel is constituted by fatty acid alkyl esters (FAAEs) obtained from transesterification and/or esterification of triglycerides present in vegetable oils and/or animal fats with methanol and/or ethanol. On January 13, 2005, biodiesel was introduced into the Brazilian energy matrix by Law 11097, thus the necessity to control its quality, logistic and marketing as well. Biodiesel quality is provided by the determination of several physicochemical characteristics, established by several specifications. In Brazil, these specifications are set by the Agência Nacional do Petróleo, Gás Natural e Biocombustíveis (ANP), through Resolution ANP n. 45. In the United States and Europe, such specifications are set by the American Society for Testing and Materials (ASTM) and European Committee for Standardisation (EN), through standards ASTM D6751 and EN 14214 [3].

FAMEs analysis is the main physicochemical characteristic that should ensure the marketed biodiesel quality. In quality control, the determination of the FAMEs profile content is a key parameter and its content is expressed as a mass fraction in percentage. The total FAME content should be greater than 96.5%. FAMEs determination is done according to standards EN 14103 [4] or ABNT NBR 15764 [5]. EN 14103 is the European standard for determining the total content of FAMEs, while ABNT NBR 15764 is the Brazilian standard. In Brazil, both standards are recognized by ANP as reliable methods for total FAMEs. Both standards use conventional gas chromatography (GC) as an analytical technique and take approximately 30 min in their analyses [4,5].

The ABNT NBR 15764 method specifies the total FAMEs content with carbon chains between C8:0 and C24:0 in biodiesel using an

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external analytical curve. However, this method has a limitation because it uses chloroform as a solvent in sample preparation [4]. Conversely, EN 14103 determination and calculation of FAMEs content is achieved with the response of a single internal standard. In version EN 14103:2003, the range of FAMEs is set from C14:0 (methyl myristate) to C24:1 (methyl nervonate) using methyl heptadecanoate (C17:0) as an internal standard. Version EN 14103:2011 extends the carbon chains range from C6:0 to C24:1 and employs methyl nonadecanoate (C19:0) as an internal standard in order to analyze FAMEs of animal origin since animal fat can contain higher C17:0 levels [5].

The demand for biodiesel quality analyses accompanies its growth in the international market. It is therefore important to develop analytical methods that are increasingly faster and more reliable. The present work envisions ultrafast gas chromatography coupled with flame ionization detector (UFGC-FID) as an alternative, a more efficient and appropriate technique to be used in routine analyses of quality control laboratories.

The UFGC system contains a greater number of innovations compared to conventional gas chromatography (GC), i.e.: smaller internal diameter and column length, and higher heating rate in the temperature column. The high-speed analysis was provided by directly resistive heated column in a modular system. All these factors cause the organic compounds to volatilize more rapidly in order to get a faster analysis; i.e., in a few minutes or less [6,7]. Literature has shown that the use of this technique reduces the chromatographic run time in matrix such as gasoline fuel, essential oils, fresh and frozen pork, tea and others [8–12].

Biodiesel is a consolidated product in the Brazilian market, and the amount of research involving biodiesel and its analysis shows the global importance of this product. Taking chromatography as the main FAMEs determination analysis technique for biodiesel samples has led to some authors worrying about the betterment of conditions and the shortening of the analysis time [13,14].

The objective of the present study is the development of an ultrafast gas chromatography method for quantification of FAMEs in pure biodiesel and in biodiesel blends, originated from different feedstocks (babaçu, coconut, rapeseed, corn, soybean, animal/palm and sunflower). To demonstrate the suitability of the proposed method, results obtained after analyzing the certified reference materials SRM 2772 (soy-based) and commercial blend biodiesel samples are presented. These results provide the application of UFGC into routine analyses of biodiesel in quality control.

## 2. Materials and methods

### 2.1. Chemicals and reagents

A 10% (w/w) heptane mix solution of each of the 19 standards (C6:0–C24:1) was produced using FAME standards of saturated and unsaturated carbon chains provided by Nu-Check (Elysian, MN, USA) and Sigma-Aldrich (St. Louis, MO, USA). Standard FAMEs were methyl hexanoate (C6:0), methyl octanoate (C8:0), methyl decanoate (C10:0), methyl undecanoate (C11:0), methyl dodecanoate (C12:0), methyl tetradecanoate (C14:0), methyl hexadecanoate (C16:0), methyl palmitoleate (C16:1), methyl octadecanoate (C18:0), methyl oleate (C18:1), methyl linoleate (C18:2), methyl linolenate (C18:3), methyl nonadecanoate (C19:0), methyl eicosanoate (C20:0), methyl docosanoate (C22:0), methyl erucate (C22:1), methyl tetracosanoate (C24:0) and methyl nervonate (C24:1), all within 99.0% of purity.

The FAMEs standard solutions (used to build the analytical curve) were diluted in heptane for UFGC analyses and chloroform for ABNT NBR 15764. Biodiesel samples were diluted in ethanol for ABNT NBR 15764. Heptane and chloroform were purchased from Vetec Química Fina (Duque de Caxias, RJ, Brazil) and ethanol from SigmaAldrich (St. Louis, MO, USA), all within 99.5% p.a. The certified reference material (CRM) NIST (SRM 2772) B100 biodiesel soy-based (Gaithersburg, MD, USA) was used for validation purposes. The FAMEs contents in the CRM are given as certified concentration for eight compounds (C14:0, C16:0, C16:1, C18:0, C18:1, C18:1, C18:2 and C20:0) and as reference values for other four (C15:0, C17:0, C18:3 and C22:0).

**Table 1**
Transesterification reaction conditions of different feedstocks.

| Raw material | Temperature (°C) | Catalyst concentration (% w/w) | Molar rate (Oil:MeOH) | Reaction time (min) |
|---|---|---|---|---|
| Coconut | 40 | 1 | 1:6 | 60 |
| Babaçu | 40 | 1 | 1:6 | 60 |
| Canola | 40 | 1 | 1:6 | 60 |
| Sunflower | 40 | 1.5 | 1:6 | 60 |
| Corn | 40 | 1 | 1:6 | 120 |

Hydrogen gas, nitrogen gas and synthetic air gas were provided by White Martins Gases Industriais (Sertãozinho, SP, Brazil), all within a minimal purity of 99.999%.

### 2.2. Biodiesel samples

Five biodiesel samples of different vegetable-based feedstock were investigated. These samples were obtained by transesterification reaction of refined oils of coconut, babaçu, canola, sunflower and corn, bought at supermarket, with methanol using KOH as catalyst. Table 1 shows transesterification conditions used for each raw-material.

The soybean biodiesel was a NIST CRM 2772 certified reference material. Additionally, a blend commercial biodiesel sample (constituted by 70% bovine tallow and 30% palm oil) provided by a JBS S/A biodiesel producer was also analyzed.

### 2.3. Standard solutions and biodiesel sample preparations

All working standard solutions were prepared in a gravimetric dilution in ethanol for GC-FID ABNT NBR 15764 and n-heptane for UFGC analyses. Biodiesel samples were prepared in a gravimetric dilution in chloroform for GC-FID ABNT NBR 15764 and n-heptane for UFGC analyses. Biodiesel samples dilution was ca. 1:70 in UFGC and 1:100 in ABNT NBR 15764. Preparation step was performed as 0.1 g of biodiesel sample using 20 mL vials and analytical balance (Ohaus, Adventure series, max. 210 g). Total FAMEs concentration was expressed in weight percentage (% w/w). Standard solutions concentration is based on the total FAMEs expected in commercial biodiesel samples.

In the ABNT NBR 15764 analyses, two analytical curves were constructed with three standard solutions from 60 to 90 (% w/w) and using ethanol as solvent. One analytical curve (C18 curve) was used for determination and quantification of long carbon chain FAMEs (C16–C24) and another (C12 curve) for short carbon chain FAMEs (C6–C14).

In the UFGC analyses, two analytical curves were constructed with six standard solutions with concentrations ranging from 20 to 100 (% w/w). One analytical curve (C18 curve) was used for determination and quantification of long carbon chain FAMEs (C16–C24) and another (C12 curve) for short carbon chain FAMEs (C6–C14). Standard solutions dilution is shown in Table 2.

### 2.4. GC-FID analyses

Parallel FAMEs analysis was performed by using a GC-2010 Plus gas chromatograph (Shimadzu Corporation, Kyoto, Japan) equipped with a flame ionization detector (FID) and on-column injector. Separations were performed in a ZB-5HT column (5% phenyl and 95% dimethylpolysiloxane, 30 m × 0.32 mm ID × 0.1 µm) provided by Phenomenex. Data was processed with a GCSolution Version 2.0 data system.

Experimental conditions and oven program are those indicated in