



Line shape analysis of the Raman spectra from pure and mixed biofuels esters compounds



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HIGHLIGHTS

- Experimental spectra of biodiesel are fit based on theoretical calculations.
- The biodiesel ester composition can be determined using Raman spectroscopy.
- We derived a protocol to be used for determining the bio-origin of biodiesels.

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ABSTRACT

This work provides a systematic and comprehensible lineshape analysis of the Raman spectra from (i) the main esters that compose the soybean biodiesel, namely Palmitate, Stearate, Oleate, Linoleate and Linolenate, (ii) mixtures of these esters, (iii) a soybean biodiesel reference material. Using theoretical spectral simulation as a guide, the experimental spectra are fit considering all the 3N-6 vibrational modes, where N is the number of atoms in the molecule. We demonstrate that while intensity analysis may lead to uncertainty in the definition of the relative ester contents in a mixture, a complete spectral analysis involving all parameters, including peak frequencies, allows spectral determination of esters composition. Finally we define a protocol that can be used for defining the specific composition of unknown, including adulterated biodiesels, important for quality control.

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1. Introduction

The prediction of future oil scarcity and the unprecedented high rates of carbon emission in the atmosphere have forced society to seek for clean and renewable alternative energy resources, with particular emphasis given to biofuels [1–5]. The goal of this paper is to provide a systematic and comprehensible analysis of the Raman spectra of biodiesel.

Biodiesel is a clean, biodegradable, renewable, and nontoxic biofuel. It can be defined as monoalkyl esters derived from transesterification and hydro-esterification of vegetable oils, animal fats or waste oils with short-chain alcohols. It is composed of a mixture of several esters, which can be, usually, methyl or ethyl, saturated or unsaturated. This mixture of esters gives rise to important fuel properties in comparison to petrodiesel, such as relatively high lubricity, low sulfur content, high flash point and high cetane num-

ber values [6–10]. Several plants as well as its seeds, can be used as source of biodiesel, such as, soybean, canola, palm, crambe, macauba, castor, sunflower, olive and buriti [11]. The soybean oil is one of main raw material used to produce biodiesel [12]. The soybean biodiesel has its composition formed basically by five different esters: Palmitate, Stearate, Oleate, Linoleate and Linolenate [13]. For this reason, here we focus on the analysis of prepared mixtures of these esters, as the main components of the soybean based biofuels.

The molecular structures of methyl esters in biodiesel is varied, and so is their Raman spectra [8,14,15]. The main parameters are the total number of carbon atoms and of unsaturated carbons in the molecule. Esters are, therefore, named by these numbers, e.g. Methyl Linolenate is the (18:3), which means 18 carbons in the chain, with a total of 3 unsaturated carbon atoms [16].

Unlike other conventional methods of characterization, Raman spectroscopy is fast and simple, appropriated for *in situ* characterization. Beattie et al. [16] reported experimental measurements of Raman spectroscopy for the analysis of lipids: fatty acid methyl esters (FAME). An extensive discussion on the various parameters is presented, monitoring the number of carbons in a chain, number

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of unsaturated carbons, liquid and solid phases, and *cis* vs. *trans* bond configuration. Ghesti et al. [14] used FT-Raman spectroscopy to monitor and quantify differences between the Raman spectra of pure soybean oil and ethyl esters. Zerbi et al. [17] studied the structural evolution with temperature of a few fatty acids using Raman and infrared spectroscopy. Calibration models based on multivariate analysis (PCR – Principal Component Regression, PLS – Partial Least Square Regression, ANN – Artificial Neural Network) were combined with FT-Raman and FT-NIR to quantify adulteration of biodiesel with vegetable oils and accuracies in biodiesel blends (principally B2 and B5) [18–20]. Guedes et al. [21] used absorption and emission spectroscopies to characterize oil samples obtained from buriti palm tree fruits. Farhad et al. [22] measured the Raman spectra of edible oils with an emphasis in the high-frequency 2800–3200 cm^{-1} region, enabling the measure and quantification of the unsaturations in edible oils. Lewis et al. [23] showed that a relative peak-height intensity ratio, I_{2850}/I_{2880} , serves as an index of the strength of the lateral interchain packing interactions. A decrease in this empirical peak-height intensity ratio reflects stronger lateral chain–chain interactions arising from a decrease in the spacing between lipid chains [23,24]. Brown et al. [25] determined the range $I_{2890}/I_{2850} = 1.39\text{--}1.48$ for liquid hydrocarbons while for the solids hydrocarbons the range was $I_{2890}/I_{2850} = 1.61\text{--}1.72$.

Theoretical studies of lipids compounds has been performed in order to establish the general rules which govern the relative energies of the conformers in short-chain FAME [26]. Density functional calculations have been used to investigate the conformations and Raman spectra of long-chain FAME [27]. Properties such as chain length and degree of unsaturation were determined.

Our work is distinguished as the search for the complete set of parameters that reveal the bands that make up the line shape of the Raman spectra of esters, mixtures of esters and real biodiesels. This paper is organized as follows: Section 2 presents the experimental and theoretical details; Section 3 presents the experimental results: in Section 3.1 the Raman spectra of pure esters are detailed; in Section 3.2 the mixture of esters and the Raman spectra of soybean biodiesel are discussed, including a comparison of prepared mixtures with real soybean biodiesel; in Section 3.3 a protocol for analyzing the Raman spectra of a unknown soybean biodiesel is discussed, including possible routes for treating an adulterated sample; in Section 4 we present our conclusions.

2. Methodology

2.1. Sample details

Table 1 lists the methyl esters used in this study, (16:0), (18:0), (18:1), (18:2) and (18:3), chosen for being the main components of the soybean biodiesel, plus the (12:0) and (14:0), chosen as references for saturated esters that are liquid at room temperature. Methyl esters of high purity (99 + $m/m\%$) provided from Aldrich®

Table 1

Pure methyl esters and their nomenclatures, according to ($n:m$), where n is total number of carbon atoms in the chain and m is the total number of unsaturated carbon-carbon bonds [28].

Ester	($n:m$)
Methyl laureate	12:0
Methyl myristate	14:0
Methyl palmitate	16:0
Methyl stearate	18:0
Methyl oleate	18:1
Methyl linoleate	18:2
Methyl linolenate	18:3

were kept refrigerated for sample conservation. The measurements were performed with the esters at room temperature. The (16:0) and the (18:0) are solid (powder) at room temperature. For the (16:0) and (18:0), both solid and liquid phases were measured, where in the later case the temperature was raised up until reaching the melting point ($T = 30.5\text{ }^\circ\text{C}$ for the (16:0) and $T = 39\text{ }^\circ\text{C}$ for the (18:0)) [28].

Different mixtures of the pure esters (Table 1) were prepared, as displayed in the first five lines of Table 2. The mixtures were obtained by the addition of pure ester to an amber glass bottle and prepared by weighting using a analytical balance (Mettler Toledo AB265-S, $\pm 0.01\text{ mg}$). The mixtures were homogenized using a Mixer (approximately 10 s) and an ultrasonic bath (30 min). Esters were combined ranging from binary mixtures to quaternary mixtures. In the last two lines of Table 2 we present the composition of soybean biodiesels. The first is a reference material (SRM 2772) [29] provided by the National Institute of Standards and Technology (SB-NIST) in collaborative work with the Instituto Nacional de Metrologia, Qualidade e Tecnologia (Inmetro). The mixture “SB-like” was produced with ester compositions similar to the SB-NIST standard. The second, mixture “SB-UNKN” is a sample of pure soybean biodiesel with ester compositions initially unknown. The reference and the “unknown” samples will be used here to discuss the protocol for determining ester composition, as well as adulterations in biodiesel. The methyl ester content of the “SB-UNKN” sample was independently determined by chromatography, in accordance with the EN 14103:2011 standard.

Finally, five mixtures of adulterated biodiesel were prepared by adding soybean oil in the SB-UNKN sample, as displayed in Table 3. The mixtures were prepared on an amber glass bottle using an analytical balance (Mettler Toledo AB265-S, $\pm 0.01\text{ mg}$). The mixtures were homogenized using both a Mixer (approximately 10 s) and an ultrasonic bath (30 min).

2.2. Spectra acquisition

The Raman spectra of pure esters, mixtures and biodiesel were measured in two systems: (1) a Horiba T64000 Raman spectrometer, equipped with a coupled charged detector (CCD) cooled with liquid N_2 and excited with an argon laser at 514.5 nm (2.41 eV), with power of (25.7 ± 0.1) mW; (2) a “home built” system using a spectrometer Andor™ Technology-Sharmrock sr-303i equipped with a coupled charged detector (Andor™ Technology-iDus Spectroscopy CCD) excited with a He–Ne laser (17 mW) at 632.8 nm (1.96 eV). Both systems are equipped with 600 grooves/mm diffraction gratings. For each spectrum, 5 accumulations were added, 30 s each. The spectra were obtained in the 400–3800 cm^{-1} range, where we observe several first and higher-order Raman bands. An Hg lamp was used to calibrate the spectra.

Table 2

Mixtures of esters studied in this work and their compositions in percentage ($\pm 0.1\%w/w$). The last two lines bring the composition in percentage of two biodiesels, first a well defined reference material provided by NIST (SB-NIST), and second an initially unknown biodiesel (SB-UNKN), the percentages provided here being defined in this work by chromatography, in accordance with the EN 14103:2011 standard ($\pm 0.01\%w/w$).

Mixtures	(16:0)	(18:0)	(18:1)	(18:2)	(18:3)	(others)
35 × 65	35.0	–	65.0	–	–	–
2 × 50	49.8	–	–	50.2	–	–
25 × 45 × 30	24.8	–	45.1	30.1	–	–
4 × 25	24.8	–	24.7	25.0	25.4	–
SB-like	11.2	04.7	23.6	52.5	08.1	–
SB-NIST	10.70	04.30	23.30	52.30	07.82	01.58
SB-UNKN	9.57	2.71	25.74	47.84	3.69	10.45

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