Fuel xxx (2013) xxx–xxx

Contents lists available at ScienceDirect

Fuel

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

Endogenous fluorescence of biodiesel and products thereof: Investigation of the molecules responsible for this effect

K.F. Magalhães [a], A.R.L. Caires [b], M.S. Silva [c], G.B. Alcantara [d], S.L. Oliveira [a,*]

[a] Grupo de Óptica e Fotônica, Instituto de Física, Universidade Federal de Mato Grosso do Sul, CP 549, 79070-900 Campo Grande, MS, Brazil
[b] Grupo de Óptica Aplicada, Faculdade de Ciências Exatas e Tecnologia, Universidade Federal da Grande Dourados, CP 533, 79804-970 Dourados, MS, Brazil
[c] Grupo de Estudo e Desenvolvimento de Materiais, Universidade Estadual de Mato Grosso do Sul, Dourados, MS, Brazil
[d] Grupo de RMN e Quimiometria, Instituto de Química, Universidade Federal de Mato Grosso do Sul, CP 549, 79070-900 Campo Grande, MS, Brazil

HIGHLIGHTS

- An investigation of the origin of the visible fluorescence in biodiesel was performed.
- Visible fluorescence in biodiesel should be related to tetra-conjugated molecules.
- This study may assist the development of methods to assess the quality of biodiesel.

ARTICLE INFO

Article history:
Received 22 February 2013
Received in revised form 30 October 2013
Accepted 10 November 2013
Available online xxxx

Keywords:
Biodiesel
Fluorophores
Conjugated molecules
UV–Vis absorption
Fluorescence

ABSTRACT

Regardless of the emergent use of fluorescence as an analytical method to investigate biodiesel no detailed discussion about the origin of the visible fluorescence in different biodiesel samples has been reported. Here, UV–Vis absorption and fluorescence analysis of biodiesels (soybean, corn, canola, and sunflower), standard methyl esters (stearate, palmitate, oleate, linoleate and linolenate), phenolic antioxidants, β-carotene, α-tocopherol, and chlorophyll were performed in order to investigate the molecules responsible for the fluorescence in biodiesel. Additionally, mid-infrared absorption, gas chromatography as well as ^{13}C and ^{1}H nuclear magnetic resonance measurements were also carried out. The findings reveal the presence of fluorescent conjugated molecules such as tetraenes in both the standard methyl esters and biodiesel, and so these minority compounds could explain the visible fluorescence of the biodiesel samples in the 350–500 nm range under UV excitation, excluding the contribution of free fatty acids, tocopherols, carotenoids, phenolic antioxidants and chlorophyll. The results also indicate that as higher the methyl linolenate content in the biodiesel as higher the concentration of conjugated tetraenes in the biodiesel sample, explaining the intense visible fluorescence observed mainly in the soybean and canola biodiesel.

1. Introduction

New sources of renewable energy have been the subject of numerous studies, and biodiesel has emerged as an alternative environmentally friendly biofuel [1]. Biodiesel is chemically defined as alkyl esters derived from vegetable oil or animal fat, usually obtained by transesterification reaction of triglycerides using alcohol (methanol or ethanol) in the presence of a strong base (NaOH or KOH) [2]. In general, three molecules of methyl esters and one glycerol molecule are formed after transesterification.

The physicochemical properties of biodiesel reflect the chemical composition of the vegetable oils and animal fats. The amount and type of fatty-acid esters present in biodiesel depend on the feedstock fatty-acid composition [3,4]. As vegetable oils and animal fats are mainly composed of triglycerides (about 95–98%), different concentrations of these molecules may affect both the production and quality of biodiesel [5,6]. Chemical compounds such as tocopherols, chlorophyll, carotenoids, fatty alcohols, waxes, pigments, phospholipids, triterpene acids, glycerides and phenolic compounds can also be found in vegetable oils [7]. Therefore, these compounds may also be present in the chemical composition of biodiesel produced from these oils.

Gas and liquid chromatography have been applied to analysis of biodiesel composition [8–10]. However, these techniques are costly and require pre-separation steps to perform the analysis, making it desirable to find alternative analytical methods. Optical methods such as Fourier Transform Infrared absorption (FT-IR), UV–Vis molecular absorption and fluorescence, and Raman

* Corresponding author. Tel.: +55 67 3345 7483.
E-mail address: samuel.oliveira@ufms.br (S.L. Oliveira).

0016-2361/$ - see front matter © 2013 Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.fuel.2013.11.024

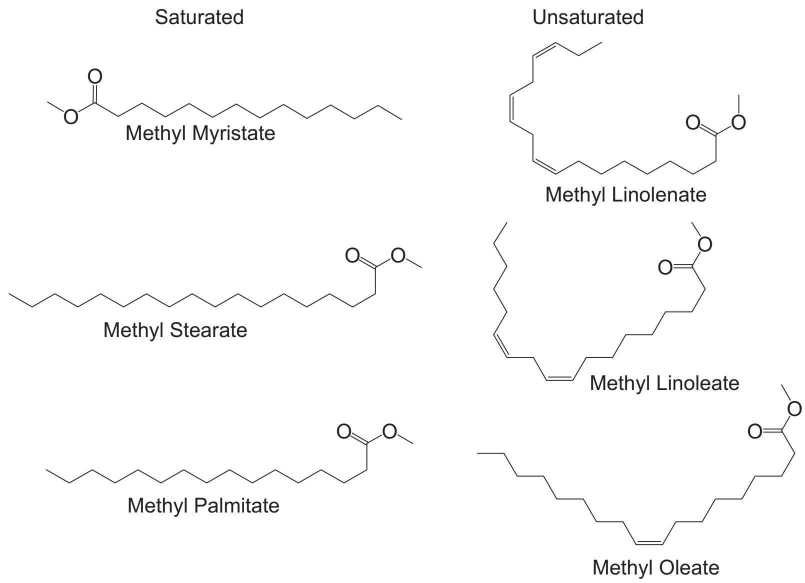

Fig. 1. Methyl esters molecules.

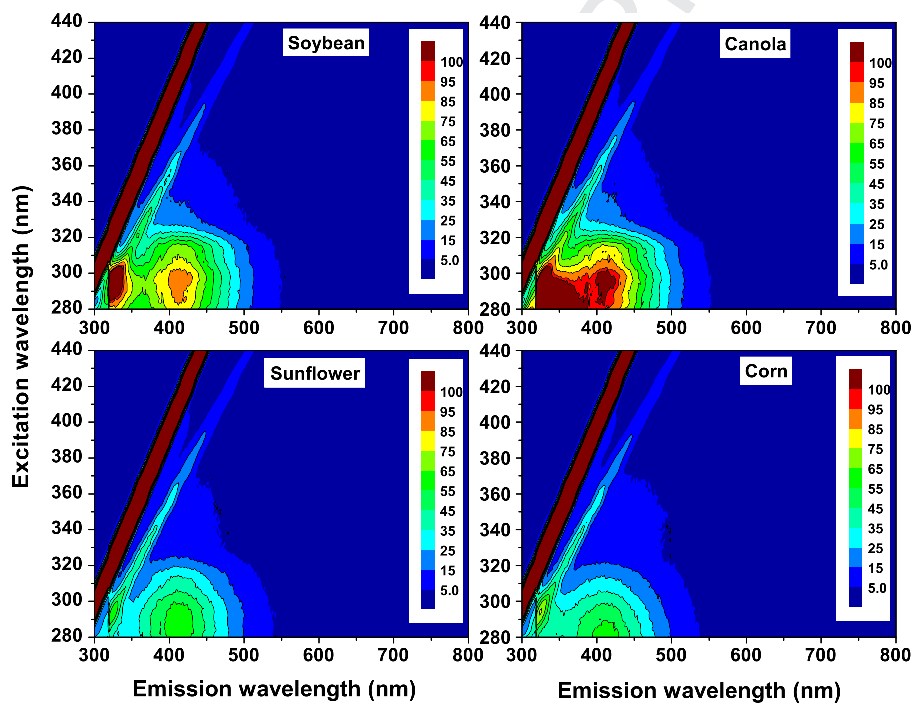

Fig. 2. Excitation/emission contour maps of biodiesel samples diluted in n-hexane. The Raman and Rayleigh scattering are also shown in the spectra.

spectroscopy have been reported for the analysis of oil and biodiesel [11–26].

Chimenez et al. showed that molecular fluorescence can be used to monitor the conversion of vegetable oil to biodiesel. They showed that the fluorescence intensity decreases about 40% after transesterification of refined vegetable oil, regardless of the feedstock oil used [24]. Meira and co-workers reported that fluorescence spectroscopy combined with multivariate analysis can be applied as an analytical tool to evaluate the oxidation stability of biodiesel and soybean oil, presenting good agreement with conventional analysis based on the Rancimat method [25]. The use of fluorescence spectroscopy as a tool to identify vegetable oil as an adulterant in biodiesel has also been reported [26].

Studies have reported that the main fluorophores of biodiesel are the same as those of vegetable oil, such as unsaturated fatty acids, tocopherols, chlorophylls, phaeophytins, phenolic compounds, and vitamins A, D, and K [27–35]. Despite the growing use of fluorescence spectroscopy as an analytical tool to characterize biodiesel samples, we are unaware of detailed study to investigate the molecules responsible for the visible fluorescence of biodiesel samples, including the contribution of methyl esters (the main constituents of biodiesel) and their byproducts.

The present study aimed to evaluate the molecules responsible for the visible fluorescence of biodiesel samples produced from four different oil sources. UV–Vis absorption, fluorescence, mid-infrared absorption, gas chromatograph (CG-FID), as well as ^{1}H

Please cite this article in press as: Magalhães KF et al. Endogenous fluorescence of biodiesel and products thereof: Investigation of the molecules responsible for this effect. Fuel (2013), http://dx.doi.org/10.1016/j.fuel.2013.11.024