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Thermal degradation of ethanolic biodiesel: Physicochemical and thermal properties evaluation

Wellington Costa Silva [a], Maria Priscila Pessanha Castro [a, *], Victor Haber Perez [b], Francisco A. Machado [a], Leonardo Mota [a], Marcelo Silva Sthel [a]

[a] Physics Science Department, Center of Sciences and Technology, State University of Northern of Rio de Janeiro, Rio de Janeiro, Brazil
[b] Processes Engineering Sector, Center of Sciences and Agropecuary Technologies, State University of Northern of Rio de Janeiro, Rio de Janeiro, Brazil

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ABSTRACT

The aim of this paper was to study the thermal degradation of soybean biodiesel attained by ethanolic route. The soybean biodiesel samples were subjected to heating treatment at 150 °C for 24 h in a closed oven under controlled atmosphere. During the experiments, samples were withdrawn at intervals of 3, 6, 9, 12, 15 and 24 h for physicochemical and thermophysical properties analysis. The biodiesel degradation was validated by Thermogravimetric analysis since their profiles for control and treated biodiesel were different. Also, ^{1}H NMR confirmed this result due to a significant reduction at the signals related to the ^{1}H located near to the double bonds in the unsaturated ethyl esters in agreement with an iodine index reduction and viscosity increase observed during degradation. Nevertheless, degraded biodiesel, under study conditions, preserved its thermophysical properties. These results may be relevant to qualify the produced biodiesel quality and collect physicochemical and thermophysical data important for applications in combustion studies including project of fuel injection systems.

1. Introduction

One of the most global challenges is the reduction of the greenhouse gases emissions, that result in environmental problems associated with global warming [1–6]. In this sense, renewable energy sources for instance, biodiesel appear as alternative to attenuate these drawbacks.

Recent studies suggest that biofuels may reduce the emissions of exhaust gases [7–9] such as carbon dioxide (CO_2), carbon monoxide (CO), hydrocarbons (HC), sulfur and soot due to their chemical and oxygen content and unsaturated bonds. Thus, the knowledge of their production and supply chain as well as characterization methodologies for biodiesel quality evaluation are needed [10–12].

Biodiesel can be defined as a mixture of fatty acid alkyl esters, derived of vegetable oils or animal fat compounds, that can be produced by transesterification with a short-chain alcohol such as methanol or ethanol under catalyst presence, for use in a diesel engine, either in pure form or as an additive to diesel fuel [13–15].

Nowadays, Brazil is one of global leaders in biofuels production, including both, bioethanol and biodiesel. In addition, Brazil have excellent climate conditions, but due its large agricultural area the feedstock used for biodiesel production may also depend from several geographic factors. However, soybean oil is the principal feedstock used in Brazil for biodiesel production (91.47%), followed for beef tallow (5.58%) and other sources in minor quantities such as: cottonseed oil (2.88%), waste frying oil (0.01%), pork fat (0.03%) and other fat sources (0.02%) [16]. Nevertheless, other oleaginous crops are in highlight such as palm oil, sunflower, babassu, peanut, jatropha, among others, by their high oil contents and in some cases, due their inedible properties [17–21]. Thus, the demands for the Brazilian and global energy markets to implement programs seeking employment generation and income from the production of biodiesel, in order to achieve environmental, economic and social benefits are clear [22,23].

Vegetable oil and biodiesel are biofuels that consist of high carbon and hydrogen concentrations. Such fuels when used in diesel engines have large amounts of calorific value that are comparable to those obtained from fossil fuel such as diesel [24]. On the other hand, the potential of vegetable oils as fuels has extensively been discussed being one of their major restrictions the high

* Corresponding author. UENF/CCT/LCFIS, Av. Alberto Lamego. 2000, Pq. Califórnia Campos dos Goytacazes, Rio de Janeiro, 28013-602. Brazil.
E-mail address: pila@uenf.br (M.P.P. Castro).

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viscosity values, i.e., about 10 times greater than the petro diesel. However, as known, its transformation into biodiesel by chemical transesterification or another physical method enables their satisfactory use in a diesel engine, resulting in a biofuel with lower viscosity and in fact, with similar characteristics to the petro diesel [25–27].

Biodiesel can be sensitive to thermal and/or oxidative degradation during storage and handling resulting in technical problems on the diesel engines when used as pure biodiesel (B_{100}) or as a component in the petro diesel/biodiesel blends. For this reason, biodiesel must be in accordance to standard specifications to ensure their quality as biofuel and under adequate storage conditions especially when stored for long periods.

In this respect, several authors have focused their studies on the understanding of the phenomena and processes that contribute to the reduction of biodiesel stability due to degradation problems including thermal stability [28–31] and/or storage stability as consequence of the oxidation [32–34] or thermo-oxidative effects in a combined way [35,36].

Biodiesel degradation that results in the breakdown of molecules with double bonds present for instance, in the fatty acids usually leads to the formation of undesirable compounds and subproducts, like free radicals, peroxides, hydroperoxides, and short chain compounds including acids with low molecular weight, aldehydes, ketones and alcohols which decrease the flash point and may favor corrosion and the acidity [37] and can also affect other properties such as viscosity, cetane number and acid value of this biofuel [35]. On the other hand, the thermal stability is more relative to vaporization and biodiesel polymerization problems and consequently this study can be useful to provide information for determinate several thermal properties such as effusivity, diffusivity, conductivity, heat capacity, boiling point, among others, which may be relevant to qualify the biodiesel quality and for applications during combustion studies including project of fuel injection systems.

Several analytical methods such as thermogravimetric analysis – TGA [31], infrared spectroscopy - FTIR [38], nuclear magnetic resonance - ^{1}H NMR [39], ultraviolet spectroscopy [40] and Rancimat (EN 14214) have been used in combine way or not to evaluate thermal stability and oxidation problems. Moreover, unconventional procedures based in photothermal techniques have been attractive to determination of different thermal properties such as effusivity, thermal diffusivity and thermal conductivity, among others, of biodiesel from several feedstocks [41,42]. In this context, the aim of work was to study the thermal stability of soybean biodiesel attained by ethanolic route in order to evaluate simultaneously some physicochemical and thermophysical properties of biodiesel under heating treatment in controlled atmosphere.

2. Materials and methods

2.1. Biodiesel production

The biodiesel production was carried out by chemical transesterification through ethanolic route using sodium ethoxide ($CH_3CH_2O{-}Na^+$) as catalyst. The reactions were conducted in a spherical glass reactor with a total volume of 500 mL containing soybean oil: ethanol molar ratio of 1:6 and 1 wt%/v of catalyst. The soybean oil, commercial quality, was purchased from Campos dos Goytacazes local market, Rio de Janeiro-Brazil and anhydrous ethanol (99.99%) was attained from Sigma-Aldrich.

The reactor was coupled to a reflux condenser in order to avoid the loss of ethanol by evaporation. Reactions were performed for 2 h at 65 °C and under 200 rpm and the formed biodiesel was purified to remove residual glycerol and others undesirable components according steps reported Silva et al. [42] for further characterization.

2.2. Procedure for thermal degradation of biodiesel

The biodiesel thermal degradation study was performed under thermal heating of the samples in Fisher Scientific™ Isotemp™ Model 282A Vacuum Oven (Iowa, USA). Briefly, samples were placed in ceramic crucibles and exposed at 150 °C during 24 h. The samples were withdrawn at regular intervals of 3 h for further analysis.

2.3. Analytical procedures for biodiesel characterization

2.3.1. Biodiesel characterization by GC/MS

The produced biodiesel was characterized by gas chromatography according to their fatty acid ethyl esters profile (FAEEs) using a Shimadzu gas chromatograph coupled with mass spectrometer detector (GC-MS), model GC/MS-QP-2010 plus (Shimadzu, Kyoto, Japan).

The injector temperature was held at 250 °C. Helium was used as carrier gas at 0.91 mL/min and 100:1 split ratio. The samples were injected into BPX-5 column with 30 m length, 0.25 mm I.D. and 0.25 μm film thickness. Initially the oven temperature was 100 °C for 2 min; increased by 10 °C/min up to 230 °C, kept for 2 min and finally increased by 10 °C/min up to 280 °C kept for 2 min. Shimadzu integrated software was used for chromatogram analysis, while the mass spectra data were collected in a range of 50–500 *m/z* with MS operating in positive electron impact mode with ionization energy of 70 eV. The products identification in the mass spectra was carried out using NIST 11 Mass Spectral Library.

2.3.2. Physicochemical analyses using standard methods

Physicochemical analyses were carried out to evaluate the biodiesel quality according to several standard methods (US Standard - ASTM D6751 and European Standard - EN 14213) [43]. Thus, specific gravity (ASTM D1298), kinematic viscosity (ASTM D445), acid number (ASTM D664) [43] and iodine index [44].

2.3.3. Optical density of biodiesel by the UV–Vis spectrometer

The UV spectra were obtained in a Shimadzu UV-1800 spectrophotometer, using 1:4000 (v/v) dilution ratio in dichloromethane (Vetec, Brazil). All data were collected in the 200–500 nm range.

2.3.4. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was carried out to verify the influence of the heating rate on the biodiesel thermogravimetric profile using a thermogravimetric analyzer model STA PT 1750 from LINSEIS (Germany) adopting the following conditions: nitrogen flow rate of 50 mL/min, heating rate of 10 °C/min in the range of 25–600 °C.

2.3.5. Biodiesel characterization by ^{1}H NMR

The qualitative analysis of untreated (control) and treated biodiesel after thermal condition at 150 °C was carried out by ^{1}H NMR using Bruker DPX-300 (300 MHz) equipment. The spectra were attained dissolving samples in deuterated chloroform ($CDCl_3$) at a ratio of 1:1 by volume and analyzed using a 5 mm ^{1}H NMR tube.

2.3.6. Thermal properties of biodiesel using photothermal techniques

The photothermal techniques such as photo-pyroelectric and thermal lens were used to determine the following thermophysical variables of interest to the soybean biodiesel: a) thermal effusivity