



Short communication

Analysis of the oxidative degradation of biodiesel blends using FTIR, UV–Vis, TGA and TD-DES methods



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ABSTRACT

In this paper, the analysis of the oxidative degradation of biodiesel blends were explored using the following instrumental methods: Fourier transform infrared spectroscopy (FTIR), Ultraviolet–visible spectroscopy (UV–Vis), thermogravimetric analysis (TGA) and two-channel and differential dielectric spectroscopy (TD-DES). During the degradation process, a good consistency could be observed between the change of the dielectric property and that of the Rancimat conductivity, infrared peak area, ultraviolet absorbance and the residual mass. The increase of these parameters was not significant before the end of the induction period, after which they rose sharply, indicating that all these analytical methods were suitable for monitoring the degradation process of the biodiesel blends. The TD-DES technique exhibited excellent prediction performance for FTIR, UV–Vis and TGA in assessing the extent of oxidative deterioration.

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1. Introduction

Due to the presence of unsaturated fatty acid esters containing the most reactive allylic (oleate) and bisallylic (linoleate and linolenate) sites, the biodiesel and biodiesel blends are highly susceptible to thermal and/or oxidative degradation during storage [1]. The degradation of biodiesel could lead to the formation of various undesirable compounds, which not only affect the biodiesel properties, but also cause engine performance problems including filter plugging, injector coking, piston ring sticking, elastomer seal swelling, and engine lubricant degradation and dilution [2,3]. It is therefore of great importance to monitor the quality of biodiesel and biodiesel blends in storage.

To access the oxidation state of the biodiesel and biodiesel blends, many quality parameters like acid value and kinematic viscosity have been investigated in previous studies. These parameters, however, remain almost unchanged at the early stages of oxidation [4,5]. The main parameter that changes during the induction period is the peroxide value, which measures the primary oxidation products, hydroperoxides. As the hydroperoxides formed are rather unstable, which can easily decompose to numerous secondary oxidation products such as aldehydes, ketones, acids, dimers and oligomers, the peroxide value may increase with time until it reaches a plateau and then decreases [6]. Therefore,

the use of peroxide value as a measure of oxidation status is still questionable and not included in biodiesel standards.

To provide additional insight and detailed information about the oxidation state of the sample, the use of more instrumental methods of analysis is required. Fourier transform infrared spectroscopy (FTIR) is a widely used technique for monitoring biodiesel oxidative degradation, which has a characteristic absorption at around 1745 cm^{-1} due to the ester carbonyl group [7–11]. The presence of conjugated dienes in the oxidized biodiesel can be monitored by the Ultraviolet–visible spectroscopy (UV–Vis), and a strong positive linear correlation was found between the peroxide value and the UV absorbance at specific wavelength in previous studies [12–16]. The formation of high molecular weight compounds may change the thermogravimetric analysis (TGA) profile of the biodiesel, which could present different steps of mass loss attributed to decomposition and/or volatilization of methyl esters and oxidation products [11,16,17]. Easy ambient sonic-spray ionization mass spectrometry (EASI-MS) has been successfully applied to analyze biodiesel oxidation products using specific marker ions such as hydroperoxides, aldehydes and dimers [18–20]. In addition, changes in fatty acid profile in oxidized biodiesel could be determined easily by nuclear magnetic resonance spectroscopy (NMR) [16,21] and gas chromatography mass spectrometry (GC/MS) [11,22].

The pioneering work by Eskiner et al. [23,24] has proved that the dielectric spectroscopy (DES) could be a valuable method for monitoring the degradation process of biodiesel and biodiesel

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blends with domestic heating oil. To improve the dielectric/impedance detection sensitivity and eliminate the influence of substrate signal from conventional single channel DES, Gong et al. [25] proposed a new two-channel and differential dielectric spectroscopy (TD-DES) method based on AD5933 impedance converter chip. In previous studies, the TD-DES method has been successfully applied to monitor the degradation process of lubricating oil qualitatively and quantitatively with FTIR [26–28]. Being fast, non-destructive and suitable for on-line monitoring, this technique can provide insights into the polarization mechanism and relaxation characteristic of dielectric materials. However, the TD-DES technique has rarely been reported in previous studies to access the oxidation state of biodiesel or biodiesel blends. To fully exploit its potential for determination of fuel quality, the TD-DES technique combined with FTIR, UV–Vis and TGA methods were applied in this work to monitor the degradation process of biodiesel blends associated with structural and compositional changes. So far as we know, similar work has not been reported yet.

2. Materials and methods

2.1. Samples

The fresh biodiesel and petrodiesel used in this paper were provided by local refineries and fulfilled specified quality requirements. The physical and chemical properties were presented in detail in previous paper [29]. The biodiesel blends, having an induction period (IP) of 17.60 h at 120 °C, were prepared volumetrically with 80% petrodiesel and 20% biodiesel, and aged with the 873 Biodiesel Rancimat instrument according to EN 15751 method (120 °C and 10 L/h purified air). The aged biodiesel blends samples were taken after an aging duration of 4, 8, 12, 16, 20, 24, 28, 32 h.

2.2. FTIR, UV–Vis and TGA

The infrared spectra were obtained using a Perkin Elmer Spectrum 400 FTIR spectrometer in the wavenumber range of 4000–400 cm^{-1} with 2 cm^{-1} resolution and 6 scans at room temperature. The absorption spectra were obtained using a Perkin Elmer Lambda 25 UV/Vis spectrometer in the wavelength range of 400–190 nm with a 10 mm quartz cuvette at room temperature. The thermogravimetric analysis was carried out using a TGA Q500 instrument in the temperature range of 25–500 °C with 10 °C/min heating rate and 50 mL/min air flow rate.

2.3. TD-DES and data processing methods

The dielectric spectra were obtained using a TD-DES analyzer at room temperature, in the frequency range of 1–95.5 kHz with 0.5 Hz interval and 18 V_{pp} excitation voltage. The collected TD-DES raw real and imaginary data were the real and imaginary part of the response signal after discrete Fourier transform without calibration. The partial least squares (PLS) method was introduced for quantitative analysis of the dielectric spectroscopy on predicting the degradation degree of the biodiesel blends. The leave-one-out cross-validation was used to access the prediction accuracy of the PLS model due to limited number of samples. The root mean square error of cross-validation (RMSECV), coefficient of determination (R^2) and predicted errors between predicted and measured values were calculated to evaluate the prediction performance of the predictor vectors on response variables. More detailed information about the TD-DES analyzer and data processing methods is given in previous papers [26–28].

3. Results and discussion

As can be seen from Fig. 1a, the intensity of the ester carbonyl peak at 1746 cm^{-1} changed little before the induction period (17.60 h), after which this C=O stretching band noticeably broadened and shifted to lower wavenumbers (1743 cm^{-1}), revealing an increasing degradation of the biodiesel blends. The integrated peak areas at 1650 cm^{-1} and 1850 cm^{-1} were given as follows: 22.769 (8 h), 23.15 (12 h), 23.30 (16 h), 27.10 (20 h), 34.68 (24 h), and an inflection point could be observed near the end of induction period (as shown in Fig. 2). This indicated that the degradation degree of the biodiesel blends could be clearly distinguished by monitoring the intensity of the characteristic carbonyl band, in agreement with earlier reports by Araújo et al. [9]. It is known that the antioxidants could extend the induction period and delay the onset of oxidation. When they are consumed to critical levels, the induction period will end and the oxidation will proceed. The end of the induction period is accompanied by the formation of primary oxidation products, hydroperoxides, which are unstable and can further decompose to secondary oxidation products, such as aldehydes, ketones, alcohols, carboxylic acids, epoxides and oligomers [11]. The presence of aldehydes and ketones can change the shape and intensity of the ester carbonyl band as seen from Fig. 1a.

During the degradation process of the biodiesel blends, the double bonds in the unsaturated fatty acid methyl esters could isomerize to a more stable conjugated structure (C=C–C=C or C=C–C=O) [16]. The oxidation products having conjugated double bond systems could absorb energy in the ultraviolet and visible regions as shown in Fig. 1b. Low absorption coefficients can be observed in the region 245–275 nm before the induction period (17.60 h), after which there was an abrupt increase in the absorption spectrum, possibly due to the formation of α , β -unsaturated aldehydes or ketones with conjugated double bond in the molecule [19]. In this region, the maximum absorption at 8, 12, 16, 20 and 24 h were recorded as 0.39, 0.40, 0.41, 0.52 and 0.85, respectively, with a clear inflection point can be observed near the end of induction period (as illustrated in Fig. 2). Another aspect to be noted was a shift of maximum absorption towards lower wavenumbers with the increase of degradation, with the absorption maximum moving from 269 (16 h) to 256 (20 h), 254 (24 h), 253 (28 h), 253 nm (32 h). Therefore, by monitoring the ultraviolet absorption at specific wavelength, the degradation degree of the biodiesel blends could be clearly differentiated.

Apart from aldehydes, ketones and carboxylic acids, different types of oligomers may be produced through aldol-condensation or Diels Alder reactions at the advanced stage of oxidation [30]. Because of their high molecular weight and low reactivity, higher temperatures are required for thermal decomposition of severely degraded biodiesel blends with oligomers [11,16,17]. As can be seen from Fig. 1c, the residual mass of the TGA profile at 200–300 °C could clearly distinguish the biodiesel blends with different degrees of degradation, which was found to be more distinguishable than initial and final decomposition temperatures in the present work. At 275 °C, the oxidized blends at 8, 12, 16, 20 and 24 h had a residual mass of 0.36, 0.46, 0.53, 1.57 and 2.31%, respectively, which exhibited a sharp inflection point near the end of induction period (17.60 h) (as shown in Fig. 2). The residual mass increase was consistent with the increase in the degradation: the more severe the oxidative degradation, the more difficult the oligomers were to decompose, and the higher the residual mass. The presence of insoluble oligomers in biodiesel could cause serious engine problems such as fuel line plugging, fuel injector fouling, and combustion chamber deposits [30,31].

During the aging process, the formation of polar compounds, especially those high molecular weight dimers or oligomers, could

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