Abstract
A new method for determination of the oxidative stability of biodiesel using near infrared emission spectroscopy

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Introduction

The oxidative stability is an important chemical property in lipid science, being frequently evaluated in analyses of oils, fats and, more recently, biodiesel samples. It is represented by the resistance time to oxidation, called induction time (IT), which is determined by heating the sample at a constant temperature, and continuously measuring a physical or chemical parameter, until it starts varying significantly. Although there are several methods for determination of IT, a method intensively employed since 1993, called Rancimat, based on the content of low molar mass acids, has been defined as the standard method for determination of the oxidative stability. In addition, European and Brazilian standards specify a minimum IT value of six hours, determined by the Rancimat method, for biodiesel commercialisation. However, the Rancimat method, commonly employed at 110°C, takes a long time, can fail when used at temperatures higher than 140°C, and does not sense the effects of antioxidant agents added to the sample. Therefore, this work proposes a new method for determination of the oxidative stability of biodiesel, already employed for edible oils, based on near infrared emission spectroscopy.

Materials and methods

Four samples of biodiesel were analysed for oxidative stability using the new method. The method employs a near infrared emission spectrometer, which is composed, briefly, of an electrical heater, an acousto-optical tuneable filter and a PbS detector. For each analysis, 10 µL of the sample were heated at a constant temperature (commonly 170°C) and emission spectra were continuously acquired in the region between 2650 nm and 3000 nm, using a nominal resolution of 10 nm. The area of the emissivity signal between 2710 and 3000 nm divided by the area of the emissivity signal between 2650 nm and 2700 nm ($E_{2710-3000}/E_{2650-2700}$) was used as the parameter related to the oxidation of the sample. IT was determined by means of a $E_{2710-3000}/E_{2650-2700}$ versus heating time graph (stability curve).

Results and discussion

Figure 1 shows a set of consecutive emissivity spectra obtained for a sample of biodiesel being heated at 170°C.

As can be observed, the spectra remain practically unaltered (except for some baseline variation) at the beginning of the oxidation process but, after a determined time interval, the intensity and the width of the band at 2900 nm both start to increase continuously. Figure 2 shows three stability curves for different samples of biodiesel, obtained from emissivity spectra similar to those shown in Figure 1.

The sudden increase of the $E_{2710-3000}/E_{2650-2700}$ ratio after a determined time interval, which defines IT, is clearly visible. Therefore, IT can be calculated from the intersection between two linear regression curves, as shown for one of the stability curves at Figure 2. The effects of nitrogen insertion and heating temperature (160°C to 180°C) on IT were evaluated. The new method, compared to Rancimat, presents the advantages of higher analytical throughput, lower sample consumption and can be applied at higher temperatures, constituting an interesting alternative method for determination of the oxidative stability of biodiesel.

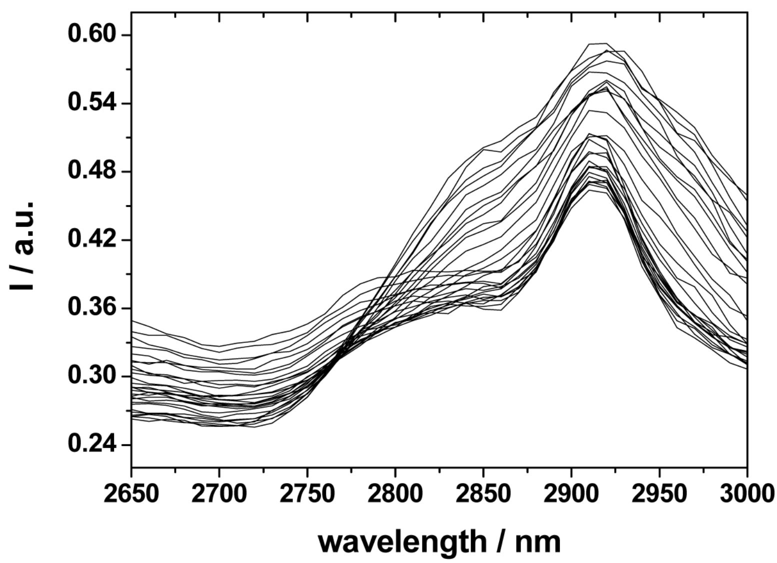

Figure 1. Emissivity spectra obtained during the heating time of a sample of biodiesel.

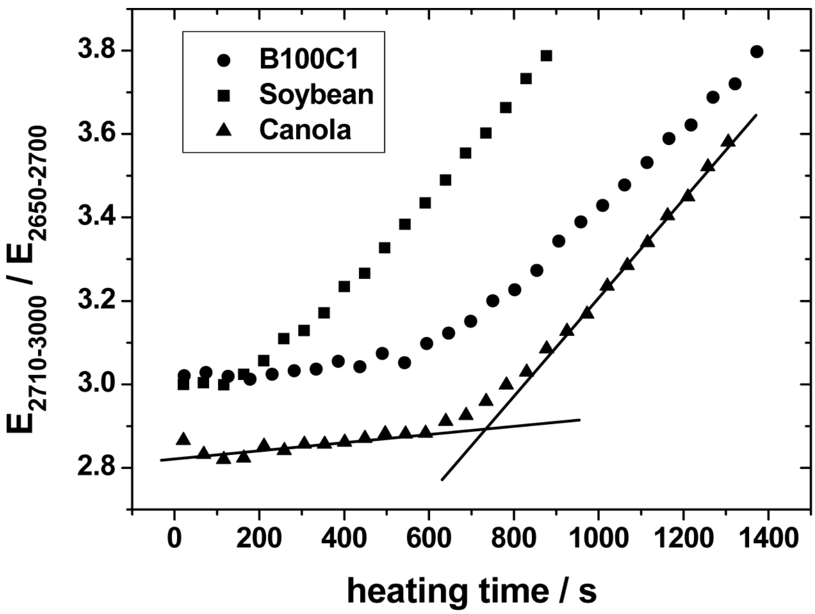

Figure 2. Stability curves for different samples of biodiesel.