

Influence of drying processes on oxidative stability of ethyl corn biodiesel by differential scanning calorimetry

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ICTAC2008 Conference
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Abstract The influence of drying processes in the biodiesel oxidation was investigated by means of the oxidative induction time obtained from differential scanning calorimetry data. For this purpose, corn biodiesel was dried by different methods including: chemical (anhydrous sodium sulfate) and thermal (induction heating, heating under vacuum and with microwave irradiation). The drying efficiency was evaluated by monitoring IR absorption in the 3,500–3,200 cm^{-1} range and by the AOCS Bc 2-49 method. In general, the oxidative induction times increased inversely to the heating degree, except that of microwave irradiation, which was selective to water evaporation and caused low impact over the unsaturation of biodiesel. The DSC

technique was shown to be a powerful tool to evaluate with high level of differentiation the influence of the drying process on the oxidative stability of biodiesel.

Keywords Biodiesel · Humidity · Oxidative stability · DSC

Introduction

Thermal analytical methods have been used for characterization of triacylglycerides and determination of auto-oxidation of oils and fats [1]. Furthermore, as a consequence of the growing demand of biodiesel in the world energy matrix, these techniques have also been employed to these biofuels for several purposes.

Biodiesel is a renewable source of energy, efficiently obtained by the conversion of oils and fats to fatty acid esters by base-catalyzed transesterification. Residual water during the synthesis causes reduction in the yield of the reaction, due to hydrolysis and saponification processes, beyond emulsion formation [2, 3]. After the synthesis, biodiesel is washed with water and a residual humidity remains in the product [4]. Unlike the fossil diesel that is hydrophobic and absorbs 50 ppm of water, biodiesel is highly hydrophilic, holding more than 1,500 ppm, depending on its composition. Castor bean biodiesel, for instance, retains eight times more water than soybean biofuel [5]. Residual humidity in biodiesel is associated to the biofuel quality parameters and its content is limited by the ASTM D standard to a maximum of 0.05%. The humidity contributes to the ester hydrolysis, increasing the biodiesel acidity and hampering its useful life.

The removal of humidity is generally carried out, submitting the biodiesel to heating at 105 °C in an oven

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until the complete dehumidification. Under these conditions, the biodiesel stability may be affected by oxidative processes initiated with singlet oxygen formation and propagated the combination of this oxygen to unsaturated esters, which are highly susceptible to oxidation and are the main constituent of corn biodiesel. The process is continued with the peroxide formation, followed by the polymerization or decomposition of these peroxides. Figure 1 displays the stages of the biodiesel oxidation process.

From these implications, the thermo-oxidative stability assumes relevant meaning within the established parameters for biodiesel quality control, because it is straightly related to the fuel integrity, from its synthesis and purification up to the storage, distribution and use. The European standard EN 14214, through the EN 14112 method (Rancimat test), limits the induction period of biodiesel to at least 6 h [8–10]. However, due to the elevated analysis time of Rancimat method, new methodologies are being developed for evaluating the thermal stability of fuels, lubricants and biodiesel by calorimetric methods [11]. These studies focus on the utilization of Differential Thermal Analysis (DTA), for describing decomposition profiles (enthalpy behavior), and Differential Scanning Calorimetry (DSC), which evaluates the heat evolution during oxidative processes (exothermic phenomena). Another significant application of DSC technique is the oxidative induction time determination (OIT) [12].

The calorimetric analyses become more elucidating when associated to other analytical methodologies, such as the infrared spectroscopy (IR) and multivariate data analyses. Such combinations allow the simultaneous study of chemical and thermal profiles for several complex matrixes as biofuels or lubricants [13]. The IR spectroscopy analysis gives information on the overall humidity and on the oxidative indexes by evaluating the O–H and C=C and ROO absorption groups intensities.

In that context, this work aimed at applying the DSC technique to verify the influence of different drying processes on the oxidative stability of corn biodiesel. For this purpose, the OIT's were related to the heating period and the humidity degree of the samples.

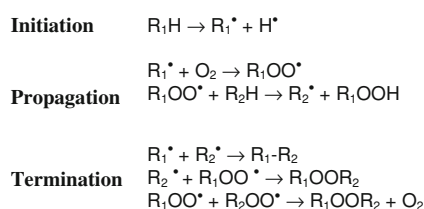


Fig. 1 Auto-oxidation of unsaturated biodiesel fatty acids [6, 7]

Experimental

The corn biodiesel was synthesized by the alkaline catalysis transesterification, using the ethanol route. The biodiesel was purified, as elsewhere detailed [14]. The product identified as Bio_{HU} (humid biodiesel) was partitioned in four samples of 5 g each, each one of them dried by a different process. For the thermal process, Bio_{HU} was heated at 105 °C in an oven for 1 h being denominated as Bio_H. Another portion of Bio_{HU} was heated at 60 °C under 0.8 bar for 1 h (Bio_{HV}). The microwave irradiation was employed to heat the Bio_{HU} at 105 °C for 1 h in a microwave oven LG model MS-74MLA (frequency of 2.450 GHz and 1,050 W of power), adapted with magnetron coupled to an external type K thermocouple and also to an external INCON model CNT-120 temperature controller [15]. The resulting sample was identified as Bio_{HM}. In the chemical process of drying, anhydrous sodium sulfate was added to Bio_{HU} and the mixture was stirred for 30 min and then it was allowed to rest for the same period. Then, the sample was vacuum-filtered and the solids were discarded. This last sample was called to Bio_C. The final masses were determined in a Mettler Toledo scale model AG 285 with an accuracy of 0.1 mg, allowing a precision in the humidity measurements better than 0.01%.

The humidity contents, after the drying, were determined by the sample mass losses in a FANEM oven model SE 315 at 105 °C in agreement with the AOCS Bc 2-49 method, in which about 5 g of the sample is heated at such temperature. Sub-samples are removed from the oven at constant 1 h intervals for the determination of the humidity variation with time. The final constant mass obtained allows the determination of the humidity value [16–18].

The spectroscopy data were also used to monitor the oxidative degradation by means of investigating the unsaturations and hydroperoxides. The IR spectra were acquired in a BOMEM IR spectrometer, model MB-102, from 4,000 to 400 cm⁻¹. The samples were prepared in KBr disk. More details on the IR experiments are elsewhere reported [19, 20].

The thermoanalytical studies were conducted by means of DSC—Differential Scanning Calorimetry—by using a TA Instruments model DSC Modulated 2920 calorimeter. The heating rate was 1 °C min⁻¹, under a flowing nitrogen (99.5% purity) purging in the temperature range from ambient temperature up to 110 °C. At such temperature, the gas was changed to oxygen and the temperature is kept at 110 °C for a proper time, in order to detect variations in the heat flux. The data from such heat flux variations, as a function of time, were plotted and analyzed with the aid of the TA Universal Analysis software, yielding the onset values corresponding to the different OIT's, as previously reported by Dunn, utilizing the PDSC technique [21].

Results and discussion

The drying processes showed different efficiency degrees. The untreated sample (HU) presented 1.2% of moisture. Except for the vacuum method, the humidity of the dried samples were inside the limits established by the European Standard [22] (lower than 0.05%; Table 1). The remaining humidity values increased in the following sequence: Bio_{HM}, Bio_C, Bio_H, and Bio_{HV}, evidencing the efficiency of each drying process. The process conducted at 60 °C under vacuum presented the worst efficiency, which was not suitable for biodiesel under these conditions. The microwave irradiation drying is affected by the power and frequency of the equipment, beyond the composition, mass, density, initial temperature, volume and humidity content of the sample, parameters that influence the thermal conductivity and specific heat [23]. These parameters were such that the drying occurred under the conjugated actions of the heating of esters and the residual water. The heating of biodiesel is lower than that of water because the former has a lower polarity and specific heat than the latter, due to its lipid chain. More sophisticated methods, such mass spectroscopy and thermogravimetry would supply very relevant information on moisture levels, but they require a more expensive infrastructure, than, for instance, the AOCs method.

In the calorimetric study, the DSC curves (Fig. 2) revealed that OITs were considerably different for each drying process, as it can be seen in Fig. 3.

The OIT's increased inversely to the heating degree and showed that Bio_H and Bio_{HM} underwent the higher oxidative pre-inductions when compared to Bio_{HV} that presents OIT three times higher than that of conventional method (Bio_H), while Bio_C promoted the smallest impact. A surprising result was the 27% superiority of Bio_{HM} OIT in relation to Bio_H, since both were submitted to the same temperature (105 °C) and time (1 h). This shows that microwave irradiation causes less impact over the esters unsaturations and it is more active to the water molecules due to its lower magnetic coupling effect. Therefore, microwave irradiation is more efficient when compared to conventional thermal treatment, in which the energy is evenly distributed in the water and ester molecules.

As it was expected, the OIT value of the sample Bio_C was much higher than the ones of the other samples, once

Table 1 Humidity of the biodiesel samples before (HU) and after different drying processes

| Sample | BioHU | BioHV | BioH | BioC | BioHM |
|-------------|-------|-------|-------|-------|-------|
| *Humidity/% | 1.200 | 0.061 | 0.033 | 0.020 | 0.004 |

* European standard maximum limit = 0.05%

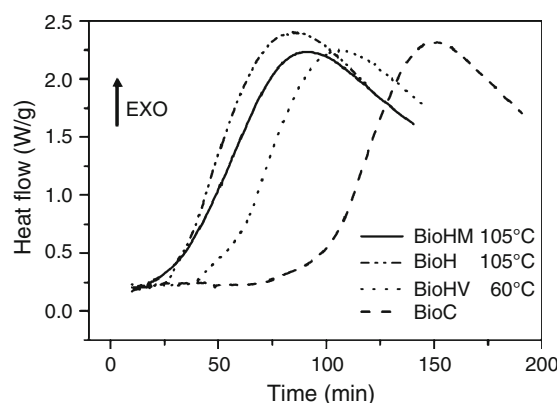


Fig. 2 DSC curves of Bio_{HM}, Bio_H, Bio_C, and Bio_{HV}

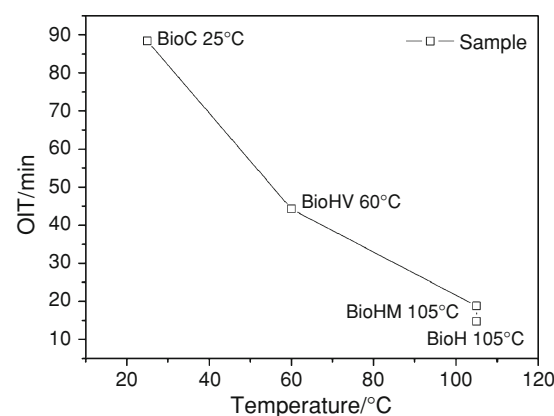


Fig. 3 OIT values of the biodiesel samples determined by DSC

the previous heating diminishes the oxidative stability of the samples. Accordingly, the Bio_H sample, which underwent the most rigid heating cycle exhibited the lowest OIT value. The Bio_{HV} sample, which presented an intermediate OIT value, received a milder heating than the Bio_H sample.

Figure 4 shows the infrared spectra of the Bio_U, Bio_{HM}, Bio_H, Bio_C and Bio_{HV} samples. The most significant bands for the present study are (a) at around 3,500 cm⁻¹ related to the OH groups, (b) at about 3,050 cm⁻¹ related to the C–H groups of alkenes, (c) two peaks near to 2,900 cm⁻¹ are ascribed to the stretching of the C–H bonds of saturated carbons, (d) at 1,740 cm⁻¹ related to the C=O carbonyl bonds of esters, (e) at 1,450 cm⁻¹ related to the H–C–H angular deformation of saturated carbons, (f) at a round 1,200 cm⁻¹ attributed to the O–CO ester stretching, (g) at 725 cm⁻¹ related to the asymmetric H–C–H angular deformation of the (CH₂)_n long chains.

The intensities of the peaks at about 3,500 cm⁻¹ did not show a meaningful difference among the samples of the different drying processes. Similarly the peaks ascribed to the unsaturation compounds (≈1,640 cm⁻¹) did not show meaningful differences among the different drying

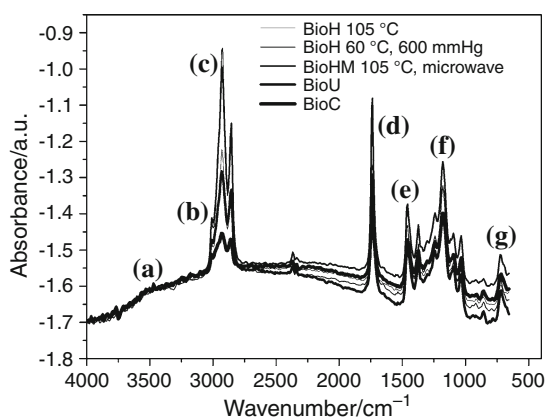


Fig. 4 Infrared spectra of Bio_U, Bio_{HM}, Bio_H, Bio_C, and Bio_{HV} samples

processes. The reason for such facts is that infrared spectroscopy is not a quantitative technique.

Conclusions

The drying processes evaluated by the AOCS method show different efficiency levels. The DSC technique was shown to be an efficient tool to evaluate the influence of the drying process over the biodiesel's oxidative stability represented by the OIT values. Microwave irradiation was more effective than the conventional method for biodiesel drying, besides it causes less impact on its oxidative stability. For the other methods, there was a direct decrease in the oxidative stability with increasing process temperatures.

Acknowledgements The authors acknowledge CNPq and UEMA for the financial support of this work.

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