



Thermal stability enhancement of biodiesel induced by a synergistic effect between conventional antioxidants and an alternative additive



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ABSTRACT

The thermodegradation of soybean biodiesel stabilised with conventional antioxidants BHT (butylated hydroxytoluene) and PG (propyl gallate) in combination with an alternative additive based on the anthraquinone compound DHQ (1,4-dihydroxyanthraquinone) was investigated by simulating an accelerated storage process at temperatures from 85 to 110 °C. The effectiveness of different combinations of PG and BHT with DHQ were also evaluated by using the Rancimat[®] method. The results revealed that combinations of the conventional antioxidants and anthraquinone were more effective at imparting biodiesel stability than the individual compounds. By considering the optimum combination containing PG and BHT with DHQ, it was also determined that the final cost of biodiesel may be markedly reduced since the amount of additives used to stabilise the biodiesel can be decreased by 70–88%, requiring a lower content of conventional antioxidant in the mixture to meet the EN-14112 specification.

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1. Introduction

Biodiesel is a renewable, biodegradable, and non-toxic fuel, which has gained attention as the most important substitute for fossil diesel fuel and can be directly used in the diesel engines when blended with petrodiesel [1,2]. Currently, aiming to reduce the environmental impact caused by fossil fuel emissions, a mandatory addition of biodiesel in fossil diesel is regulated in several countries around the world [3,4]. For instance, a compulsory addition of 20% of biodiesel in the DBB (diesel/biodiesel blend) is required in the United States and Canada, and 30% in the Czech Republic and Slovak, 5% in Europe Union and Argentina, while in Brazil the biodiesel content must be 7% [3,4].

Despite the environmental advantages associated with the use of biodiesel in the DBB, the biodiesel has some limitations such as low calorific value, hydrolysis sensitivity and especially poor oxidative stability [1,2,5]. The major factor affecting the biodiesel degradation by oxidation processes is associated with the chemical

composition of some fatty acid methyl (or ethyl) esters, which has a high degree of unsaturations [1]. In fact, biodiesel may easily degrade during manufacturing, storage, and transportation when exposed to the presence of oxygen, metals, high temperatures and UV-light exposition [6,7]. Therefore, aiming to improve the oxidative stability of biodiesel, the use of effective additives for retarding the oxidation is necessary for preserving the biodiesel quality. In this context, synthetic antioxidants have been widely used to preserve biodiesel by retarding rancidity or deterioration due to autoxidation during long-term storage [2,5,8]. Due to the diversity of raw materials used for obtaining biodiesel, the development and application of innovative technologies are needed to find more effective and cheaper additives, which can be applied for maintaining the physicochemical features of the biodiesel and preserving its quality [2,6,8–10].

Synthetic antioxidants, such as TBHQ (tert-butylhydroquinone), BHA (butylated hydroxyanisole), BHT (butylated hydroxytoluene) and PG (propyl gallate), have been widely used as additives to prevent biodiesel degradation. It is well established that synthetic antioxidants, either individually or in combination, can block the oxidation process by reacting with free radicals to form stable compounds [11–14]. However, synthetic antioxidants have been

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reported to be less effective in the prevention of biodiesel degradation by exposure to electromagnetic radiation and/or interactions with metals during handling or production [11,15–18]. Commercial antioxidants also have a cost implication, as they are expensive chemicals, and are commonly added in high concentration to produce the desired effect. In addition, the presence of trace metals can lead to a less stable biodiesel by catalysing oxidation processes [11,15–18], which form gums and solids, and consequently cause pump deposits, filter and fuel injector obstructions, and corrosion of engine metal parts [15,16].

Aiming to improve the stability of biodiesel (or its blends), several studies have been performed analysing the oxidative stability of biodiesel when treated with conventional antioxidants, for instance TBHQ, BHA, BHT and PG [5,19,20]. These studies include new green methodologies to prevent biodiesel deterioration after analysing acid and iodine values [21–24]. However, only a limited number of studies have been dedicated to the evaluation of the synergistic effect of conventional antioxidants and alternative compounds. In fact, a few papers have reported the synergistic effect of metal deactivators and antioxidants on the stability of biodiesel contaminated with metals [11,15–18], wherein it was shown that combinations containing antioxidant-chelating agents provide a satisfactory synergistic antioxidant effect by removing metal ions that tend to catalyse the oxidation process. Nevertheless, to the best of our knowledge, there is no information about the synergistic effects of conventional antioxidants and anthraquinone compounds. In the present study, DHQ (1,4-dihydroxyanthraquinone), an anthraquinone compound, was tested as an alternative additive for biodiesel preservation as well as its synergistic effects when used in combination with the conventional synthetic antioxidants PG and BHT.

2. Experimental

2.1. Applied materials and instrumentation

Butylated hydroxytoluene (BHT, 99%), propyl gallate (PG, 98%) and 1,4-dihydroxyanthraquinone (DHQ, 96%) were purchased from Sigma–Aldrich (São Paulo, Brazil). All chemicals – ethanol (anhydrous, 99.9%), methanol (anhydrous, 99.5%), hexane (99%), sodium hydroxide (pallets, 99.5%), chloroform (anhydrous, 99.5%), sodium sulfate (anhydrous, 99%), sodium chloride (anhydrous, 99%), potassium iodide (anhydrous, 99%), starch solution, 1.0% (w/v), potassium permanganate (anhydrous, 99%), sodium thiosulfate (anhydrous, 99%), acetic acid (anhydrous, 99%) – were of analytical grade and purchased from Vetec (São Paulo, Brazil).

pH measurements, when necessary, were made by using a combined glass electrode (Hanna[®], model HI 1131B) connected to a digital pH-meter (Hanna[®], model HI 3221). Highly purified water ($R \geq 18.2 \text{ M}\Omega \text{ cm}$) obtained in a Milli-Q Plus system (Millipore[®]) was used for preparation of the work solutions. Ultrasound (Unique[®], model USC 1400A) was used for the dissolution of the chemicals in the prepared solutions, and for homogenization of samples. The oil and biodiesel stability measurements were carried out on a Rancimat[®] Instrument (model 873, Metrohm, Switzerland).

2.2. Soybean oil preparation and biodiesel synthesis

Soybean oil was obtained via a Soxhlet extraction procedure. After extraction, the oil was stored in an amber bottle at a temperature of around $-10 \text{ }^\circ\text{C}$. For the target Soxhlet extraction, 500 mL of hexane was poured into the round bottom flask, and 200 g of the soybean was placed in the thimble and inserted into the centre of the extractor. The Soxhlet system was heated in a

heating mantle (Fisatom, Model 102) at a temperature of $60 \text{ }^\circ\text{C}$. The procedure was repeated at least four times and the weight of extracted oil was determined for each 30 min interval. At the end of the extraction, the excess solvent in the oil was recuperated in a rotary evaporator (Fisatom, Model 801) at a temperature of $70 \text{ }^\circ\text{C}$.

The biodiesel preparation was performed via transesterification, by reacting 100 mL of the extracted soybean oil, 45 mL of methanol and 1.50 g of potassium hydroxide, with heating at $45 \text{ }^\circ\text{C}$ for about 90 min. To separate the ester from glycerol and undesirable contaminants, such as methanol, potassium hydroxide and other products, the reaction products were decanted into a separation funnel, and washed three times with 50 mL portions of deionized water and once with a 20 mL portion of saturated sodium chloride. Finally, the washed biodiesel was dried with addition of anhydrous sodium sulfate, before filtration on Whatman No. 42 filters.

2.3. Preparation of the samples

Combination antioxidant-anthraquinone compound solutions were then added to soybean biodiesel samples in the amount to reach the required concentrations (mg kg^{-1}). The effectiveness of different combinations containing PG or BHT and DHQ, as well as solitary additives, was then determined by measuring their corresponding physicochemical parameters. The nomenclature used to differentiate the various doped and undoped samples, is shown in Tables 1 and 2, and the chemical structure of DHQ, PG, and BHT are represented in Fig. 1a, b, and c, respectively.

2.4. Accelerated storage study and analytical methods measurements

The soybean biodiesel samples, each containing 5.0 g and doped as shown in Tables 1 and 2, were treated with the following procedure. Following an initial analysis, the biodiesel samples were subjected to continuous heating on a laboratory oven at a temperature of 85 or $110 \text{ }^\circ\text{C}$, for up to 62 consecutive hours. This forced degradation process was designed to simulate biodiesel deterioration when analysed using Rancimat[®] equipment. During storage, samples were extracted periodically, every 2–3 h, to monitor the oxidation stability, acid value and peroxide value.

The determination of acid value was performed by weighing about $2.00 \text{ g} (\pm 0.001)$ of the soybean biodiesel samples, which were dissolved in a mixture of water and ethanol (20 mL; 2:3 v/v). A solution of at 1.0% phenolphthalein was then added, and the titration was carried out with a 0.01 mol L^{-1} KOH hydroalcoholic solution (40:60 v/v, water/ethanol) until the development of the pink colour persisted for at least 30 s. The acid value was calculated using Equation (1), in which V (mL) is the titrant solution volume obtained for the sample titration, M (mol L^{-1}) is the real titrant solution concentration standardized against potassium hydrogen phthalate, and W_{sample} (g) is the mass of the sample.

$$\text{Acid value} \left(\text{mg}_{(\text{KOH})} \text{g}^{-1} \right) = \frac{V \times M \times 56.1}{W_{\text{sample}}} \quad (1)$$

The peroxide index was determined according to the American Oil Chemists' Society (AOCS) Standard method. A mass of $2.50 \pm 0.01 \text{ g}$ of each soybean biodiesel samples was weighed directly into 250 mL stoppered glass erlenmeyer flasks. To these samples, 15 mL of a 30:20 (v/v) acetic acid/chloroform solution was added and vigorously mixed with a magnetic stirrer for about 2 min until dissolution was complete. After addition of 1.00 mL of saturated potassium iodide solution, the erlenmeyer flasks were covered and swirled for exactly 1 min. The resultant solution was titrated with 0.010 mol L^{-1} sodium thiosulfate until the blue-grey

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