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Commercial antioxidants and thermal stability evaluations

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ABSTRACT

Synthetic and natural antioxidants are used in the biodiesel and food industries to increase product shelf lives. Rancimat, which is regulated by EN 14112, is the official analytical method used to determine the oxidation stability of biodiesel, oils and fats. It involves subjecting samples to a temperature of 110 °C for prolonged periods. Some antioxidants decompose or volatilize below 110 °C, leading to false results. A TG/DTA technique with both dynamic and isothermal (110 °C) analysis methods was used to evaluate the thermal stability of commercial antioxidants. Synthetic antioxidants exhibited thermal resistances in the following order: PG > TBHQ > BHA > BHT. Initial thermal decomposition temperatures were lower than 110 °C, and BHT, BHA and TBHQ volatilized during the first few hours of the analysis. Natural antioxidants are resistant to heat and displayed stabilities in the following order: α-tocopherol > caffeic acid > ferulic acid > gallic acid. Subjecting chelating agents to a temperature of 110 °C for prolonged periods resulted in the following order of thermal stabilities: ascorbic acid > citric acid > EDTA. The initial thermal decomposition temperatures for both gallic acid and EDTA were lower than 110 °C.

1. Introduction

Oils and fats with high contents of unsaturated fatty acids are highly susceptible to oxidation. Exposure to air, heat, light or metal contaminants accelerates oxidative reactions [1,2]. The reaction products are primarily aldehydes, ketones, acids, peroxides, and polymers that affect the physical and chemical properties of the oils [2]. Biodiesels derived from such oils and fats are also prone to oxidation [3]. The oxidation of biodiesels during storage affects the physical and chemical properties of the fuels and may cause engine malfunctions [4].

Antioxidants are used to increase the oxidation induction period or decrease the rate of oxidation [1]. The actions of antioxidants have been extensively studied [5–8], and they can be functionally classified as primary, biological, or mixed antioxidants, synergists, oxygen removers, or chelators [4,8]. Primary antioxidants promote the removal or inactivation of free radicals in the initiation and propagation stages of the oxidation by donating hydrogen atoms to interrupt the chain reaction [3,4,8]. Synergists are substances with little or no antioxidant activity, but they may increase the activity of primary antioxidants when used in an appropriate combination [8].

BHA, BHT, TBHQ and PG are the synthetic antioxidants that are most commonly used in industry [8,9]. Among the most widely used natural antioxidants are the tocopherols and phenolic acids [10,11]. Citric acid and ethylenediaminetetraacetic acid (EDTA) salts are the main chelating agents used [8,12]. The same industrial antioxidants used in oils and fats have also been studied and used for biodiesel fuels [13–17].

Maia et al. [4] evaluated the stability of soybean biodiesel when fortified with either pure or mixed BHA, BHT and TBHQ by using a centric simplex plan. The results showed that BHA and TBHQ generally offered a higher degree of protection, both separately and in mixtures, with induction periods of up to 6 h at 110 °C.

Other researchers [18,19] have examined phenolic acids as potential replacements for synthetic antioxidants, which are widely used in lipidic food storage. Phenolic compounds are powerful antioxidants that can prevent the oxidative deterioration of polyunsaturated fatty acids. Among these compounds, caffeic and ferulic acids are widely recognized as natural antioxidants [18,20].

The official analytical method used to determine the oxidative stability of biodiesels, oils, and fats is the Rancimat EN 14112 standard, which measures the induction period (IP) [21]. The American (ASTM D 6751-11b) [22] and European (EN 14214) [23] standards specify 3 h and 6 h, respectively, as the minimum IP limits for which biodiesel must resist oxidation.

Researchers have used the Rancimat method to optimize the amounts of antioxidants necessary to achieve the limits specified

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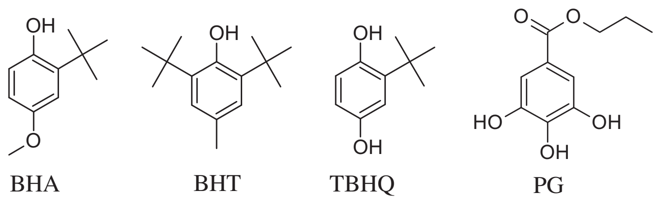

Fig. 1. Structure of synthetic antioxidants.

by the international standards for commercialized products [4,14]. The oxidation process is accelerated by temperature and oxygen in the air. In this method, the sample is heated to 110 °C, and air flow of 10 L h^{-1} is injected. Any oxidation products formed are sent to a conductivity cell containing deionized water. The induction time is determined by the inflection point of the conductivity curve [24]. Some antioxidants volatilize or decompose at this temperature, leading to a false IP [17,20]. The aims of this study were to analyze the thermal profiles of commercial antioxidants, determine the initial temperatures of decomposition and measure the time it takes to decompose or vaporize these compounds at 110 °C.

2. Materials and methods

2.1. Antioxidants

TBHQ, BHT, BHA, PG, α-tocopherol, caffeic acid and ferulic acid were obtained from Sigma–Aldrich. L-(+)-Ascorbic acid and gallic acid were obtained from VETEC. EDTA was obtained from F. Maia. Citric acid was obtained from Cargill.

2.2. Thermal analysis

Non-isothermic thermogravimetric curves (TG) were obtained on a Shimadzu Thermal Analyzer, Simultaneous DTA-TG, DTG model H-60, in a synthetic air atmosphere at a heating rate of 20 °C min^{-1}. Approximately 10 mg of sample was heated over a temperature range of 25–1000 °C. Differential thermal analysis (DTA) curves were obtained simultaneously.

Samples that showed mass variation before 110 °C using the non-isothermal method were analyzed by the isothermal method. The TG curves in the isothermal mode were obtained on a Shimadzu Thermal Analyzer, Simultaneous DTA-TG, DTG model H-60, in a synthetic air atmosphere, using approximately 10 mg of sample. The following heating schedule was used: an initial heating rate of 10 °C min^{-1} was maintained until the temperature reached 100 °C, followed by a rate of 2 °C min^{-1} until reaching 110 °C, at which point the isotherm measurement was performed.

3. Results and discussion

3.1. Synthetic antioxidants

BHA, BHT, TBHQ and PG are the most commonly used synthetic antioxidants in the biodiesel and food industries (Fig. 1). The structures of these phenolic compounds allow for the donation of hydrogen atoms protons to free radicals, thus inhibiting the oxidative process [25].

In the dynamic method, the thermogravimetric curves for BHA, BHT and TBHQ (Fig. 2a–c) indicated that mass loss is initiated at temperatures lower than 100 °C (Table 1), and each compound

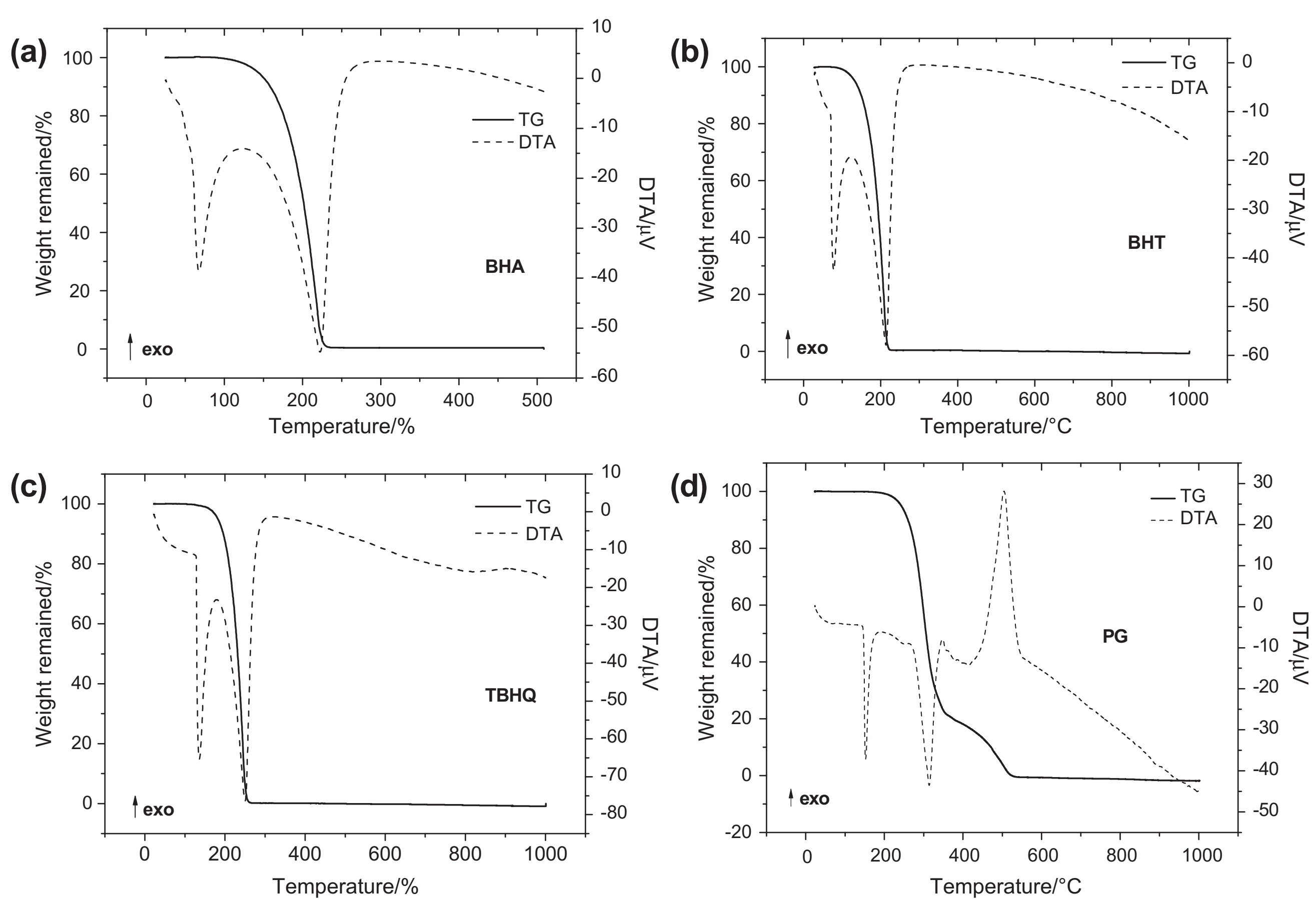

Fig. 2. TGA/DTA dynamic (a) BHA, (b) BHT, (c) TBHQ and (d) PG.