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Caffeic and ferulic acids: An investigation of the effect of antioxidants on the stability of soybean biodiesel during storage

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HIGHLIGHTS

- ▶ Improve on the oxidative stability of soybean biodiesel.
- ▶ Accelerated methods indicate same tendency against oxidation of biodiesel samples.
- ▶ Ferulic acid and TBHQ has lower antioxidant activity than caffeic acid.
- ▶ Caffeic acid maintains induction period of biodiesel during storage.

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ABSTRACT

Soybean oil is widely used in many countries and its application for the synthesis of biodiesel is usual. The drawback of this raw material is its susceptibility to oxidative rancidity leading to the need of the development of antioxidants. In this paper, different antioxidants, caffeic acid, ferulic acid, and *tert*-hydroquinone, were added into soybean biodiesel during storage period with evaluation of its stability by accelerated techniques: Rancimat, PetroOXY and P-DSC (pressurized differential scanning calorimetry). According to the values of induction period (IP) by standard Rancimat method, the three antioxidants were effective in retarding the oxidation processes at the initial time of storage. Using the parameters assessed, the efficiency of the antioxidant took the following efficiency order: caffeic acid > ferulic acid > *tert*-butylhydroquinone. The efficiency of caffeic acid in maintaining the IP values during the entire storage period (6.66 h at 90 days) was noticeable, fulfilling the limit specified by EN 14214.

1. Introduction

In biodiesel production, the fatty acid profile influences the properties of the fuel. In the conventional transesterification process to obtain biodiesel, the nature and proportion of carbon chains remain practically unchanged from source material being similar to original oils or fats [1]. The chemical reactivity of the olefin chain is determined by the configuration and unsaturation of the ester alkyl chain [2], which are associated with the oxidative processes. Besides composition, factors relevant to fatty acid degradation are exposure to air, high temperatures and the presence of metals [3–7]. The oxidation products (aldehydes, ketones, alcohols, peroxides, etc.) cause problems in motors [8]. To avoid such problems, the European Standardization Committee established the standard EN 14214 [9], which states that all biodiesels must undergo an induction period (IP) of at least 6 h, obtained using the Rancimat method. Soybean biodiesel has high amounts of unsaturated fatty acid esters, in particular, oleic (C18:1), linoleic (C18:2), and linolenic (C18:3) acids being susceptible to the development of oxidative rancidity [3,10].

According to the literature [2,3,11], different antioxidants have been tested to extend the lifetime of oils and biodiesels. Phenolic acids are widely recognized for their antioxidant activity [11–14]. Among them caffeic acid (CA) and ferulic acid (FA) stand out as representative compounds of the hydroxycinnamic fatty acids [11].

Some papers report the use of caffeic and ferulic acids as antioxidants for oils. Kowalski [15] observed the efficiency of caffeic acid in the inhibition of oxidation of linoleic acid present in oils from different sources (corn, grape seed, peanut, rapeseed, sesame and soybean) during storage and heating. The antioxidant activity varied according to the type of oil, being more evident when added into the grape seed one. Marinova et al. [16] showed the antioxidative properties of caffeic acid and chlorogenic acid during autoxi-

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dation of sunflower oil. The effectiveness of the two acids was practically the same at the concentration of 2.8×10^{-4} mol L^{-1}, while a higher concentration of caffeic acid led to a higher activity. Sun-Waterhouse et al. [11] investigated the effects of caffeic acid on the storage stability of avocado and coconut oils. The oils deterioration decreased at different extents, which were dependent on temperature and time storage. Réblová [17] observed that antioxidant activity of caffeic and ferulic acids in pork lard decreased with increasing working temperature. The caffeic acid showed higher antioxidant activity than ferulic acid at 150 °C.

In relation to the use of caffeic and ferulic acids as additive into biodiesel, some studies were found, but none of them report the efficiency of these antioxidants during storage. Santos et al. [3] investigated the antioxidant profile of CA added into soybean biodiesel contaminated with metals, comparing its efficiency with more usual commercial antioxidants, such as butylated hydroxytoluene (BHT) and *tert*-butylhydroquinone (TBHQ). Contamination with metals led to a meaningful decrease of the oxidative stability of biodiesel. This drawback was overcome when small amounts of caffeic acid (500 mg L^{-1}) were also present in the biofuel, which lead to IP values higher than 6 h. Recently Luo et al. [18] evaluated the activity of ferulic acid, caffeic acid and other antioxidant additives for enhancing the oxidation stability of soybean oil biodiesel. Caffeic acid exhibited higher performance in the concentration range from 500 to 1500 ppm.

Thus, this study aimed to evaluate the antioxidant activity of CA, FA and TBHQ, widely used in industry, added into ethyl soybean biodiesel in function of storage time.

2. Materials and methods

2.1. Biodiesel

Soybean biodiesel was obtained from the transesterification reaction of commercial soybean oil, in the proportion of 1:6 (oil:ethanol) using 1% of KOH (w/w) as catalyst. The detailed synthesis was already described in the literature [3]. According to the manufacturer specifications, the soybean oil sample was free from antioxidants.

2.2. Physicochemical analysis

The physicochemical properties of the biodiesel were evaluated according to the European (EN-14214) [10] and American (ASTM D-6751-11b) [19] standards besides the 14/2012 Resolution specification from ANP (Brazilian National Agency of Petroleum, Natural Gas and Biofuels) [20].

2.3. Identification of fatty acid esters

The identification of fatty acid esters in the biodiesel sample was performed by gas chromatography coupled to mass spectrometry (GC-MS), Shimadzu, model GCMS-QP2010. The capillary column used was a Durabond – DB-23 (30 m × 0.25 mm and 0.25 μm film thickness). Helium gas was used as the carrier gas with a flow rate of 3 mL min^{-1} and an injection volume of 1 μL, using the split mode with a splitting ratio of 1:50. The MS detector temperature was 230 °C.

2.4. Antioxidants and oxidative stability

Caffeic acid, ferulic acid and *tert*-butylhydroquinone were acquired from Sigma–Aldrich. The amount of caffeic acid added into biodiesel was optimized before storage, with variation of its concentration from 500 to 2500 mg kg^{-1}. Rancimat method was used to evaluate these results.

The oxidative stability of the ethyl soybean biodiesel with and without antioxidants was evaluated during storage for a period

Table 1
Physicochemical properties of ethylic soybean biodiesel before storage.

Properties	Results	Method	Limits		
			ANP 14/2012 resolution	ASTM D 6751-11b	EN 14214
Kinematic viscosity at 40 °C ($mm^2\ s^{-1}$)	4.5	ASTM D 445	3.0–6.0	1.9–6.0	3.5–6.0
Cold filter plugging point (°C)	9.0	ASTM D 6371	19	–	–
Acid value (mg KOH g^{-1})	0.23	Value D-664-11	Max 0.5	0.5	0.5
Water content (mg kg^{-1})	377	EN ISO 12937	Max 500	–	Max 500
Density at 20 °C (kg m^{-3})	879.3	ASTM D 4052	850-900	–	860-900
Carbon residue (g)	0.061	ASTM D 4530	0.050	Max 0.05	0.3
Flash point (°C)	109.5	ASTM D 93	Min 100.0	Min 130	Min 101
Iodine value (g I_2 100 g^{-1})	125.2	EN 14111	–	–	120
Oxidative stability at 110 °C (h)	4.34	EN 14112	Min 6	Min 3	Min 6
Clouding point (°C)	−3.0	ASTM D 7683-11	–	Note	–
Melting point (°C)	−4.0	ASTM D 6749-02	–	–	–

Table 2
Composition of ethyl soybean biodiesel fatty acid esters.

Fatty acid ester	%
C16:0 (Palmitate)	13.8
C18:0 (Stearate)	4.7
C18:1 (Oleate)	24.6
C18:2 (Linoeate)	48.2
C18:3 (Linolenate)	7.3
C20:0 (Arachidate)	0.3
Saturated	19.0
Unsaturated	80.2

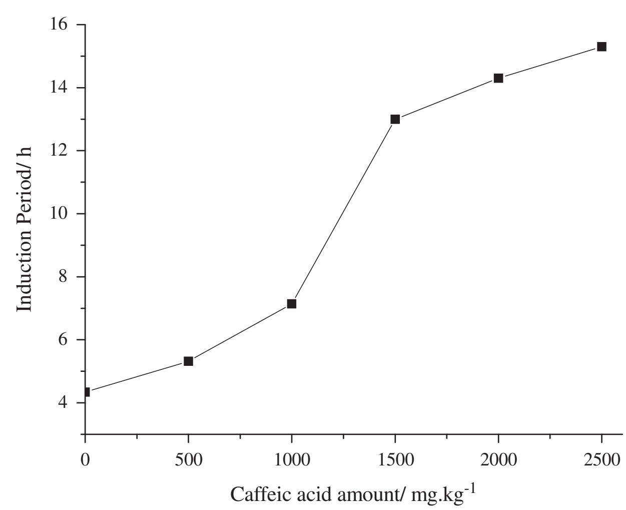

Fig. 1. Values of induction period obtained by the Rancimat method of the biodiesel with and without caffeic acid before storage.