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Storage stability and corrosive character of stabilised biodiesel exposed to carbon and galvanised steels

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HIGHLIGHTS

- Galvanised and carbon steels have proven to be compatible with biodiesel.
- Biodiesel properties were not affected for a storage time of 56 days.
- Zinc release in non-stabilised biodiesel did not stimulate biodiesel deterioration.
- TBHQ was rapidly consumed in the first days of the corrosion immersion test.
- TBHQ acted as a corrosion inhibitor and enhanced storage stability of biodiesel.

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ABSTRACT

The storage stability and corrosive character of soybean biodiesel stabilised with *tert*-butylhydroquinone (TBHQ) was investigated through static immersion corrosion tests. Coupons of carbon steel and galvanised steel were immersed in soybean biodiesel with and without TBHQ for 12 weeks. Measurements of total acid number, peroxide value, oxidation stability (Rancimat induction period), metal release, and TBHQ consumption at different stages of corrosion were performed. After 12 weeks of the static immersion test with both steels, the non-stabilised biodiesels presented induction times below the EN 14214 limit (6 h); these results were in agreement with increase in the peroxide values. Zinc release was only detected in the non-stabilised biodiesel exposed to galvanised steel, whilst iron was not detected in any biodiesel samples exposed to carbon steel. The absence of zinc in the TBHQ-doped biodiesel exposed to galvanised steel indicates that TBHQ may have acted as a corrosion inhibitor. Additionally, TBHQ was rapidly consumed in the first 3 days of experiments, providing evidence of its activity. For a storage period of up to 56 days, both galvanised and carbon steels were shown to be compatible with biodiesel even in the absence of an antioxidant. The presence of zinc (>2 μg g^{-1} after 28 days of immersion) due to corrosion did not promote biodiesel deterioration.

1. Introduction

Biodiesel is the main biofuel currently being produced in the world to replace diesel oil. Plant or animal lipids have been used for biodiesel production through the transesterification reaction with short chain alcohols (methanol or ethanol) in the presence of an alkaline catalyst [1]. Biodiesel has been used in diesel engines mixed with petroleum diesel in blends up to 20% v/v. Since January 2010, the commercialisation of the B5 blend (diesel containing 5% v/v biodiesel) in Brazilian gas stations has been obligatory by federal law in order to reduce imports of diesel oil. The use of B10 (diesel containing 10% v/v biodiesel) blend would allow the total replacement of diesel oil imported by Brazil [2].

Biodiesel is composed of a mixture of esters and is considered chemically stable. However, the chemical properties of biodiesel can be altered during storage and transportation by the presence of water (absorbed from the air), heat, light, trace metals originating from the corrosion of containers and automotive materials, and attack by microorganisms [3–5]. Diesel engine components that come into contact with fuel are made from a variety of metals, non-metals, and elastomers. The main parts of the diesel engine components that come into contact with fuel are the fuel tank, fuel feed pump, fuel lines, fuel filter, fuel pump, fuel injector cylinder, piston assembly, and exhaust system, which are made of several

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different metallic materials including carbon steel and galvanised steel [6,7]. When biodiesel oxidation is accelerated there is an increase in viscosity, density and polymer content, resulting in the formation of gums, sediments (inside the engine leading to filter blocking and injector fouling), and corrosion of engine components [8–14].

To solve the major drawback related to the low oxidation stability of biodiesels, antioxidants have been added to biofuels in order to reduce or retard the oxidation process. This parameter is measured by the Rancimat method with a minimum induction time (approximately 6 h) in accordance with the European Norm EN14214. Synthetic antioxidants such as butyl-hydroxytoluene (BHT), butyl-hydroxyanisol (BHA) and *tert*-butyl-hydroquinone (TBHQ) have been evaluated as potential antioxidants in biodiesels obtained from different oil sources [8–11]; TBHQ seems to be the most efficient antioxidant for B100 (100% v/v biodiesel) [8–11]. Antioxidant molecules contain a highly labile hydrogen which is more easily abstracted by a peroxy radical than a fatty oil or ester hydrogen [8].

The negative effect of the presence of metal contaminants on biodiesel oxidation stability is well-documented [12–17]. The addition of antioxidants can overcome the low oxidation stability of biodiesels contaminated with metals (organometallic standards or in powdered form) in order to re-establish the required 6 h induction time [13–17]. This fact is especially important considering the presence of metals in biodiesel due to the corrosion of containers and engine components. However, it has not been trivial to calculate the metal concentration released from the corrosion process due to several factors related to metallic material composition, the nature of the biodiesel, and environmental conditions. It is also a difficult task to identify how the metallic species came to be present in biodiesel (free or associated with organic molecules) and if different species present similar catalytic power for the oxidation of biodiesel [12]. Moreover, antioxidants present in biodiesel may also act as a corrosion inhibitor in such a way that these molecules may be consumed in a second pathway [3].

In this study, we investigated the storage stability and the corrosive character of stabilised biodiesel that had been exposed to carbon steel and galvanised steel. Storage conditions were simulated through static immersion tests in soybean biodiesel stabilised with TBHQ. Measurements of total acid number (TAN), peroxide value, oxidation stability of the biodiesel by the Rancimat method (induction time), metal release, and TBHQ consumption were performed in an experiment carried out over 12 weeks.

2. Experimental

2.1. Reagents and samples

High-purity deionised water (resistivity $\geqslant 18\ M\Omega\ cm$) obtained from a Milli Q water purification system (Millipore, Bedford, MA, USA) was used for preparing all aqueous solutions. Concentrated perchloric (70% m/v), acetic (65% m/v), and hydrochloric (37% m/v) acids, hydrogen peroxide (30% m/v) and sodium acetate (Vetec, Rio de Janeiro, Brazil) were used without further purification (analytical grade). *Tert*-butylhydroquinone (TBHQ) (97% m/m) was purchased from Acros Organics (USA). HPLC grade ethanol and methanol and reference solutions of Fe, P, S, and Zn (1000 mg L^{-1}) were purchased from Merck (Darmstadt, Germany). Methylic soybean biodiesel was donated by a local biodiesel producer.

2.2. Physical–chemical properties of soybean biodiesel

Table 1 lists the physical–chemical properties of the soybean biodiesel used in this study.

Table 1
Physical–chemical properties of the methylic soybean biodiesel.

Property (units)	Mean	EN 14214 limits	EN 14214 method
Flash point (°C)	103	Min. 120	EN ISO 3679
Viscosity (mm^2/s, at 40 °C)	4.168	3.5–5.0	EN ISO 3104
Density (g/cm^3, at 15 °C)	0.882	0.860–0.900	EN ISO 3675
Acid value (mg of OH/g)	0.27	Max. 0.5	EN 14104
Free glycerol (% w/w)	0.01	Max. 0.01	EN 14105, EN 14106
Total glycerol (% w/w)	0.23	Max. 0.38	EN 14105, EN 14106
Moisture (ppm)	258	500	EN ISO 12937
Oxidation stability (h, at 110 °C)	7.80	Min. 6	EN 14112
Peroxide value (meq/kg)	2.90	–	–[a]

[a] American Oil Chemists' Society – Official method Cd8-53.

2.3. Gas chromatography analysis

The fatty acid methyl ester composition of the biodiesel was determined by a gas chromatograph model 7890A (GC, Agilent Technologies, USA) with a CPWAX 52CB capillary column (30 m × 0.25 mm × 0.15 μm), 0.5 μL as the injection volume (injector at 250 °C), oven at 170 °C, flame ionisation detector (FID) at 390 °C with a hydrogen pressure of 200 kPa and a flow rate of 2 mL min^{-1}. Table 2 presents the fatty acid methyl ester composition of the soybean biodiesel. The analysis was carried out in triplicate.

2.4. Laboratory immersion corrosion test

The corrosion process of fuel containers was simulated through static immersion tests in biodiesel. This procedure was executed in accordance with the ASTM G31-72 method for Laboratory Immersion Corrosion Testing of Metals [18] (the corresponding Brazilian norm is ABNT NBR 7413). A piece of either carbon steel or galvanised steel foil, 1 mm thick and 10.5 cm^2 in area (considering both faces of the coupon, thickness, and subtraction of the mounting hole area) was immersed into 210 mL of biodiesel at room temperature (the minimum solution volume-to-specimen area ratio is 20 mL cm^{-2} in accordance with ASTM G31-12 and ABNT NBR 7413). This procedure was individually performed for each steel foil (carbon and galvanised) in the absence and presence of the antioxidant TBHQ (500 mg kg^{-1}) for different exposure times (t = 3, 7, 14, 21, 28, 56, and 84 days), resulting in 28 static immersion experiments. Each experiment was carried out in amber glass flasks in order to reduce light interference. Two amber glass flasks containing biodiesel, with and without TBHQ, were kept under the same conditions (closed flasks at room temperature) but not exposed to steels (immersion tests) for control purposes.

Table 2
Fatty acid methyl ester composition of the methylic soybean biodiesel (n = 3).

Fatty acid methyl ester	CN/DB abbreviation[a]	MB (wt%)
Palmitic	C16:0	11.0 ± 0.1
Stearic	C18:0	3.7 ± 0.1
Oleic	C18:1	23.7 ± 0.1
Linoleic	C18:2	54.1 ± 0.1
Linolenic	C18:3	6.4 ± 0.1
Others	–	1.1
Saturated	–	15.1
Unsaturated	–	84.9

[a] CN = carbon number; DB = number of double bonds.