Short communication

Behaviour of the antioxidant *tert*-butylhydroquinone on the storage stability and corrosive character of biodiesel

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ABSTRACT

The behaviour of the antioxidant *tert*-butylhydroquinone (TBHQ) on the storage stability of biodiesel was investigated. Storage conditions were simulated through static immersion corrosion tests in biodiesel (with and without TBHQ) using copper coupons. Measurements of oxidation stability (Rancimat induction period) and metal release at different stages of corrosion were performed. After 24 h of the static immersion test, the neat and TBHQ-doped biodiesels presented induction times below the EN 14214 limit (6 h). Copper release was more intense in the neat biodiesel which evidenced that TBHQ retarded the corrosion process as a corrosion inhibitor. Ion trap–time-of-flight mass spectrometry (IT–TOF-MS) revealed the presence of considerable amounts of *tert*-butylquinone (TBQ) in the TBHQ-doped biodiesel exposed to the corrosion process. As TBHQ molecules adsorb at the copper surface to inhibit corrosion, these molecules are catalytically oxidised to TBQ. IT–TOF-MS also indicated the formation of new molecules of high molecular weight only presented in the TBHQ-doped biodiesel deteriorated by the corrosion process. MS² spectra gave clear evidence of the formation of new complexes between free radicals of long-chain molecules (fatty acid derivatives) and TBQ radicals during biodiesel deterioration.

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1. Introduction

The investigation into alternative energy sources has become essential worldwide due to diminishing petroleum reserves and increasing environmental pollution. Biodiesel is a very promising substitute for petroleum-based fuels, particularly for diesel oil. The physical properties of biodiesel and diesel oil are similar, and for this reason, the modification of diesel engines and storage infrastructure is not required [1].

Vegetable oils, residual frying oils or animal fats have been considered for biodiesel production through the transesterification reaction with short chain alcohols (methanol or ethanol) in the presence of a catalyst (a base such as NaOH or KOH). Glycerol is obtained as the main co-product but other molecules can be found in biodiesel such as residual alcohol, catalysts and free fatty acids. Additionally, water (absorbed from the air) and trace metals (corrosion of containers and automotive materials) can be introduced to biodiesel during storage and handling. These two events are related with fuel deterioration which results in operational and environmental problems [2,3].

One of the major restrictions related to the use and commercialisation of biodiesel is its poor oxidation stability [4]. Compared

to diesel fuel, biodiesel is more susceptible to oxidation or auto-oxidation during long-term storage and its instability is proportional to the amount of unsaturated fatty acids derived from the raw materials typically used for obtaining the biofuel [4]. Oxidation processes are accelerated in the presence of air (exposure to water and oxygen), heat, light and pro-oxidants (hydroperoxides and trace metals). As a consequence, changes in the physical and chemical characteristics of biodiesel occur, such as an increase in viscosity, density and polymer content, which result in the formation of gums and sediments. Inside the engine, the latter may lead to filter blocking, injector fouling, deposit formation in the engine combustion chamber and corrosion of engine components [5–10].

The quality control of biodiesel through the establishment of policies is required to increase market acceptance of this biofuel. Specifications related to oxidative stability have been included in the European Norm EN 14214 (automotive fuels – fatty acid methyl esters for diesel engines – requirements and test methods), which has established the measurement of oxidation stability at 110 °C by the Rancimat method with a minimum induction time of 6 h (EN 14112) [4]. In the case of non-conformity with the standard EN 14112, antioxidants can be introduced into the biofuel in order to retard the oxidation process. Synthetic antioxidants such as (butyl-hydroxytoluene) BHT, (butyl-hydroxyanisol) BHA and (*tert*-butyl-hydroquinone) TBHQ and natural antioxidants have been evaluated as potential antioxidants in soybean oil biodiesel

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[6,7]. TBHQ has a proven superior antioxidant activity [6,7]. Jain and Sharma compared the efficiency of eight synthetic antioxidants in different biodiesels and they concluded that only three antioxidants significantly increased the stability of biodiesel in the order of TBHQ > PY (pyrogallol) > PG (propyl gallate) [5].

Biodiesel oxidative studies in the presence of metal contaminants and antioxidants have also been reported [9–12]. Knothe and Dunn verified that trace metals reduce the oxidation stability of biodiesel, and that this effect is dependent on the particle size [8]. Copper was pointed out as the strongest catalyst for biodiesel deterioration based on the oxidation stability parameter [8–12]. The addition of antioxidants at a certain concentration into metal-contaminated biodiesels can increase their oxidation stability values in order to obtain the required 6-h induction time by the Rancimat method [9–12].

In this study, we investigated the influence of the antioxidant *tert*-butylhydroquinone (TBHQ) on the storage stability of biodiesel. Storage conditions were simulated through static immersion tests in biodiesel in order to evaluate the effect of the antioxidant during the corrosion process using copper coupons. Measurements of oxidation stability of the biodiesel by the Rancimat method (induction time) and metal release were performed. Additionally, mass spectrometry analysis was performed during the different stages of corrosion.

2. Experimental

2.1. Reagents and samples

High-purity deionised water (resistivity $\geqslant$ 18 MΩ 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 phosphoric acids (85% 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 a copper reference solution (1000 mg L^{-1} Titrisol) were purchased from Merck (Darmstadt, Germany).

2.2. Synthesis of biodiesel and its physical-chemistry properties

The recycled cooking oil was obtained from a local restaurant. Biodiesel from recycled cooking oil was prepared by a transesterification process involving the reaction of the oil with methanol under reflux conditions. The recycled oil was previously filtered to remove particulate matter. Methanol (7.5:1 M ratio, alcohol/oil) was added to the reactor followed by the slow addition of a catalyst (2% w/w of KOH) under stirring until the complete dissolution of the catalyst (for 60 min at 25 °C). After the end of reaction, the glycerine phase was removed and the biodiesel was washed with hot water (~85 °C) four or five times (until obtaining a final pH around 6). After a water-removal step by evaporation, the biodiesel was kept inside amber glass flasks until analysis. Table 1 lists the physical–chemical properties of the obtained biodiesel.

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 injection volume (injector at 250 °C), oven at 170 °C, flame ionization detector (FID) at 390 °C with a hydrogen pressure of 200 kPa and flow rate of 2 mL min^{-1}. Table 2 presents the fatty acid methyl ester composi-

Table 1
Physical–chemical properties of the recycled cooking oil biodiesel.

Property (units)	Mean	EN 14214 limits	EN 14214 method
Flash point (°C)	176	Min. 120	EN ISO 3679
Viscosity (mm^2/s, at 40 °C)	4.21	3.5–5.0	EN ISO 3104
Density (g/cm^3, at 15 °C)	0.880	0.860–0.900	EN ISO 3675
Acid value (mg of OH/g)	0.21	Max. 0.5	EN 14104
Free glycerol (% w/w)	0.0006	Max. 0.01	EN 14105, EN 14106
Oxidation stability (h, at 110 °C)	6.79	Min. 6	EN 14112
Carbon residue (% w/w)	0.0038	Max. 0.3	EN OSO 10370
Peroxide value (meq/kg)	5.05	–	–[a]

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

tion of the recycled cooking oil biodiesel. The analysis was carried out in triplicate.

2.4. Mass-spectrometry analysis

Biodiesel samples were analysed using an ion trap–time-of-flight mass spectrometer (IT–TOF, Shimadzu, Japan) with an atmospheric pressure chemical ionisation (APCI) source. Samples (aliquots of 1 µL) were directly introduced in the mass spectrometer. APCI–IT–TOF-MS data were acquired in positive and negative ion modes simultaneously.

2.5. 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 method for Laboratory Immersion Corrosion Testing of Metals [13]. A piece of copper foil 25 µm thick and 150 mm^2 in area was immersed into 30 mL biodiesel. This procedure was individually performed in the absence and in the presence of the antioxidant TBHQ for five different exposure times (t = 24, 36, 48, 96 and 168 h). Each experiment was carried out inside amber glass flasks in order to reduce light interference. The initial TBHQ concentration was kept at 5000 ppm.

2.6. Oxidation stability

Oxidation stability measurements were carried out using Rancimat equipment model 743 (Metrohm, Herisau, Switzerland) in accordance with EN 14112. In this method, the oxidation of biodie-

Table 2
Fatty acid methyl ester composition of the recycled oil biodiesel.

Fatty acid methyl ester	CN/DB abbreviation[a]	wt.%
Lauric	C12:0	0.0
Myristic	C14:0	0.2
Palmitoleic	C16:1	1.1
Palmitic	C16:0	12.8
Linolenic	C18:3	4.8
Linoleic	C18:2	46.5
Oleic	C18:1	28.9
Stearic	C18:0	4.3
Eicosenic	C20:1	0.4
Arachidic	C20:0	0.3
Arachidonic	C22:1	0.1
Behenic	C22:0	0.4
Nervonic	C24:1	0.1
Lignoceric	C24:0	0.0
Saturated	–	18.0
Unsaturated	–	81.9

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

sel was induced by passing air at a flow rate of 10 L/h through the sample (3 g) and then through a water trap (deionised water). At the same time, the sample flask was kept at 110 °C. Volatile oxidation products (mainly formaldehyde and short-chain acids) were absorbed by the water, causing an increase in conductivity. Water conductivity was monitored to determine the onset of oxidation and to determine an induction time. The induction time is the breaking point of the curve conductivity versus time registered by the Rancimat equipment. For the automatic determination of the induction time, the second derivative of the measured curve was used. All samples were tested in triplicate.

2.7. Copper determination in biodiesel

Our research group developed an electro-analytical method for the determination of copper based on the highly sensitive stripping analysis [14]. This method was fully validated and presents similar performance to atomic absorption spectrometric methods applied to metal determination in oils [15,16]. The biodiesel sample was diluted in an ethanol–water solution (containing 0.1 mol L^{-1} HCl) inside the electrochemical cell (cylindrical glass container of 12 mL). The three-electrode system was immersed into the solution and stripping electrochemical analysis was performed [14].

Electrochemical recordings were carried out using a μ-Autolab Type III potentiostat (EcoChemie, Utrecht, the Netherlands). The working, reference and auxiliary electrodes were a gold (2 mm diameter) disc-electrode, a miniaturised Ag/AgCl (saturated KCl) electrode and a platinum wire, respectively. All samples were analysed in triplicate and by the standard addition method.

3. Results and discussion

3.1. Analysis of the recycled cooking oil biodiesel

All the physical–chemical properties evaluated for the obtained biodiesel met the minimum or maximum limits of the EN 14214 (Table 1). Although this biodiesel was produced from recycled cooking oil (waste frying oil), its oxidation stability met the minimum limit of 6 h of induction time. The biodiesel (Table 2) mainly consisted of unsaturated fatty acid methyl esters (81.9 wt.%), which mainly included linoleic (C18:2), oleic (C18:1), and linolenic (C18:3).

3.2. Effect of TBHQ on oxidation stability of biodiesel under immersion corrosion tests

The addition of antioxidants in the biodiesel should significantly increase the induction time. On the other hand, as long as the biodiesel is exposed to pro-oxidative conditions such as contact with a metallic container, deterioration of the biofuel will occur. With the intention of simulating real storage conditions, metallic coupons were immersed into the biodiesel following the ASTM method for the Laboratory Immersion Corrosion Testing of Metals [13]. Copper coupons were selected due to the strongest catalytic effect of this metal as stated in previous works [9–12]. Different authors have reported that TBHQ was the most effective antioxidant for increasing the oxidation stability of different types of biodiesel [5–7,10].

Fig. 1A shows the variation in oxidation stability (EN 14112 induction time) of the recycled oil biodiesel with time of contact with a copper coupon under the static immersion test (1) in the absence and (2) in the presence of TBHQ. The concentration of copper released is presented in Fig. 1B.

The oxidation stability of neat biodiesel was considerably decreased during the static immersion test (mainly over 24 h of the experiment, curve 1 in Fig. 1A, from 6.79 to 1.32 h induction time). The concentration of copper in the biodiesel increased with the exposure time, indicating a continuous corrosion process (curve 1 in Fig. 1B). For control experiments, the oxidation stability of the neat biodiesel (at which the coupon was not immersed) was measured after 168 h of similar storage conditions and the induction time was 6.50 h (practically constant). For this reason, we can assume that the exposure to copper caused significant biodiesel degradation and strong corrosion process due to the corrosive characteristic of the biodiesel (probably due to increase of the total acid number [17]).

As expected, the oxidation stability of the TBHQ-doped biodiesel was significantly increased (from 6.8 to 24.0 h induction time). However, the oxidation stability of this biodiesel tremendously decreased after 24 h of the static immersion test (curve 2 in Fig. 1A, from 24.0 to 2.42 h induction time). Similar control experiments were performed for the TBHQ-doped biodiesel and induction time remained constant (without copper).

Copper release during the corrosion process was considerably lower in the presence of TBHQ (curve 2 in Fig. 1B). The copper concentration in the TBHQ-doped biodiesel was only quantifiable after 96 h of the corrosion experiment (1.16 μg g^{-1}), whilst the copper content in the neat biodiesel for the same corrosion time was 3.62 μg g^{-1} (more than three times higher). There is clear evidence that the antioxidant retarded the corrosion process. Phenolic molecules can act as a corrosion inhibitor by the formation of a protective film layer on the metallic coupon [18–21]. Based on this, TBHQ molecules may participate on the partial blocking of the coupon (protective film layer) and consequently the corrosion of copper was delayed or reduced in the TBHQ-doped biodiesel. Another consequence of the participation of TBHQ as a corrosion inhibitor is its consumption during the corrosion experiment (this evidence is later supported by the MS results).
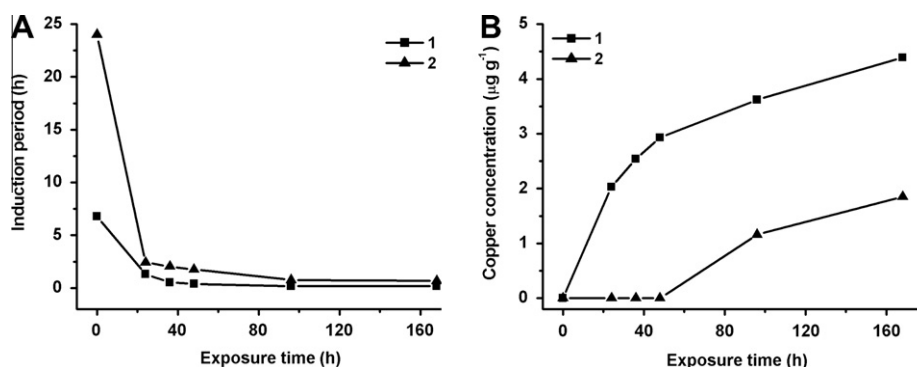

Fig. 1. (A) Variation in the oxidation stability (induction time) of recycled oil biodiesel with time of contact with a copper coupon during a static immersion test (1) in the absence and (2) in the presence of TBHQ; (B) concentration of copper released during the static immersion test (1) in the absence and (2) in the presence of TBHQ.

The induction time measurements after 24, 36 and 48 h immersion revealed slightly higher values for the TBHQ-doped biodiesel (2.42, 2.04 and 1.76 h, respectively) in comparison with the neat biodiesel (1.32, 0.53 and 0.40 h, respectively). However, the difference of induction times between inhibited and uninhibited cases can be considered not significant (Fig. 1A) if comparing with the initial induction time values (before immersion tests). A possible explanation to the comparable induction period values is that the mechanistic pathways of biodiesel oxidation are different in the presence and absence of the antioxidant. TBHQ may be involved
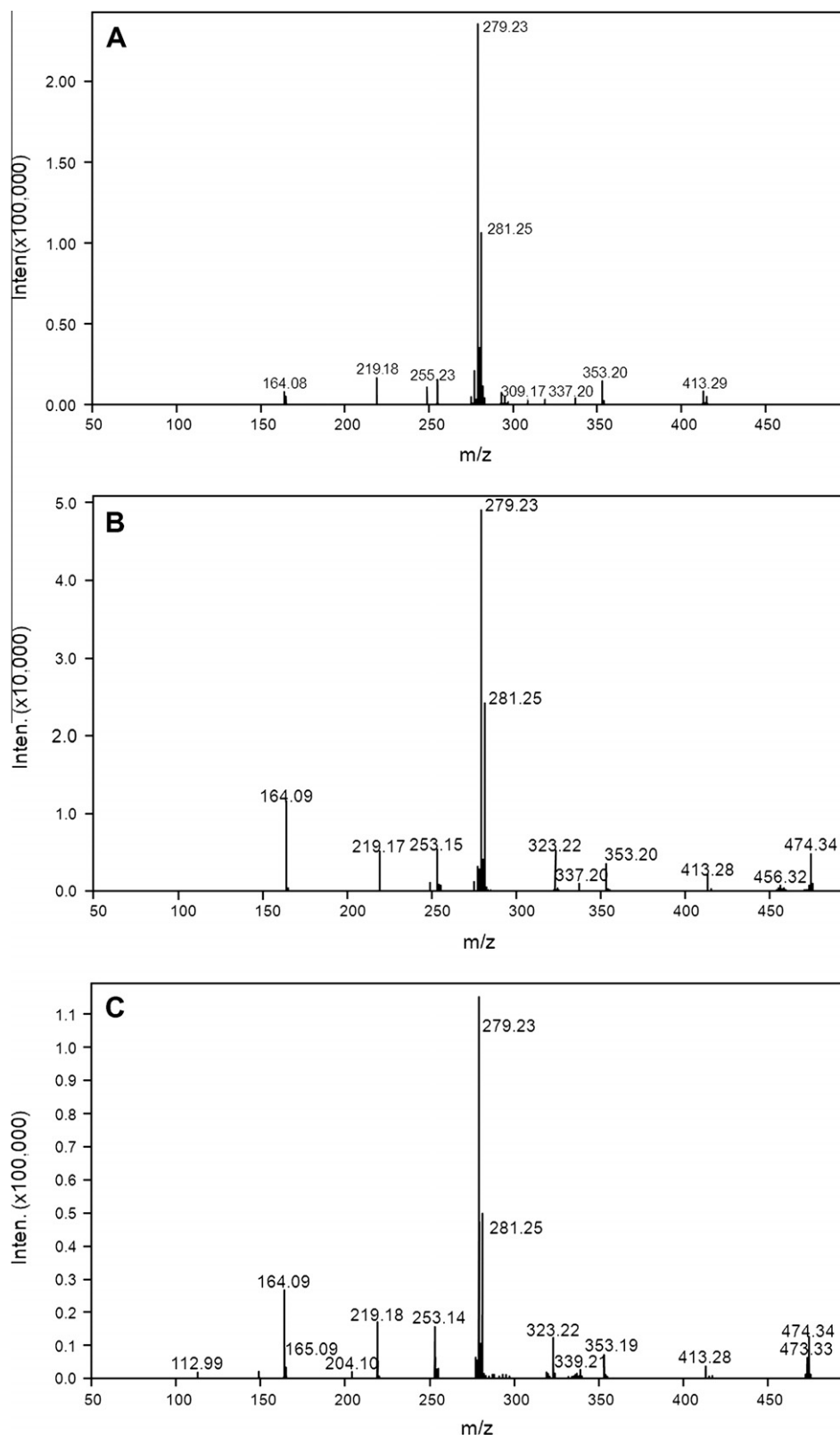

Fig. 2. IT–TOF-MS spectra of (A) TBHQ-doped biodiesel, (B) TBHQ-doped biodiesel exposed to corrosion for 24 h and (C) TBHQ-doped biodiesel exposed to corrosion for 168 h (immersion test).

not only on the interruption of biodiesel autoxidation (by donating its labile hydrogen atom) but also on beside reactions such as a corrosion inhibitor.

Fig. 2 presents the mass spectrometry spectra of (A) TBHQ-doped biodiesel, (B) TBHQ-doped biodiesel after 24 h of corrosion and (C) TBHQ-doped biodiesel after 168 h of corrosion (immersion test).

All spectra presented a common set of ions comprised of m/z 279 and 281 which correspond to linoleic and oleic fatty acids (in agreement with the GC results presented in Table 2). Samples exposed to corrosion (B and C) contained ions of m/z 164, 323 and 474 which were not present in the TBHQ-doped biodiesel (A).

In accordance with the literature, TBHQ was only detected by mass spectrometry in the negative ion mode and with the presence of the ion of m/z 165 $[C_{10}H_{14}O_2–H]^-$ [22,23]. Such a de-protonated molecule was also detected in all spectra of Fig. 2 but at low relative abundance (lower than 2). However, the ion of m/z 164 $[C_{10}H_{13}O_2–H]^-$ was detected in both biodiesel samples which were exposed to the metallic coupon (relative abundance of approximately 20). This de-protonated molecule was probably due to the presence of *tert*-butylquinone (TBQ), which is the oxidation product of TBHQ. TBQ was also detected in the TBHQ-doped biodiesel (A), but at very low content (relative abundance of 1) which can be considered negligible.

This result indicated that the low oxidation stability (induction period) verified by samples exposed to copper (B and C in Fig. 1A) may be associated with the presence of TBQ.

The presence of the ions of m/z 323 and 474 revealed that new molecules of high molecular weight were formed during deterioration of the TBHQ-doped biodiesel. In order to identify the chemical structure of these new molecules, MS^2 spectral analysis was performed (not shown). The main product ions of m/z 323 were m/z 139, 225 and 125 with relative abundances of 100, 64 and 50, respectively. The main product ions of m/z 474 were m/z 164, 287 and 373 with relative abundance of 100, 23 and 15, respectively. The major product ion of m/z 474 was clearly associated with a TBQ fragment, while the product ions of m/z 323 were related to long-chain fatty acid derivatives.

We were not able to clearly identify all the de-protonated fragments based on possible elemental composition provided by the Formula Predictions software. The molecules with m/z 323 and 474 formed during the corrosion process were identified as $C_{19}H_{32}O_4$ and $C_{29}H_{47}O_5$, respectively. Based on the MS^2 spectrum of the molecule with m/z 474, there was clear evidence of the formation of new complexes between free radicals of long-chain molecules (fatty acid derivatives) and TBQ radicals during biodiesel deterioration. Hence, TBHQ was converted to TBQ radicals and/or associated with long-chain fatty acid derivatives already after 24 h immersion test (sample B in Fig. 2) and this result was correlated with the abrupt decrease of its induction time (from 24.0 to 2.42 h, Fig. 1). Since these new molecules were only detected after corrosion tests, the copper coupon may have acted as a catalyst of oxidation reactions involving TBHQ. Indeed some authors have proved that copper at micromolar level behaves as a strong catalyst of the conversion of TBHQ to TBQ in the presence of oxygen through the formation of a semiquinone anion radical [24–26]. At the same time, acting as a corrosion inhibitor, TBHQ molecules adsorb on the copper surface at which they undergo catalytic oxidation to TBQ. The delay on copper release in the presence of TBHQ is evidence of its corrosion inhibitor behaviour.

4. Conclusions

The oxidation stability of biodiesel was considerably affected after 24 h of the static immersion test using copper coupons. Sim-

ilar result was verified for the TBHQ-doped biodiesel already after 24 h of immersion which indicated that the antioxidant did not retard biodiesel degradation under the same conditions. On the other hand, copper release was less intense in the TBHQ-doped biodiesel, which provided evidence that the antioxidant retarded the corrosion process acting as a corrosion inhibitor through the formation of a protective film layer (partial coverage). IT–TOF-MS indicated the presence of a considerable amount of *tert*-butylquinone (TBQ) in the TBHQ-doped biodiesel exposed to the corrosion process which is correlated with its abrupt decrease in induction time (after 24 h immersion test). In this way TBHQ molecules absorb on the copper surface (acting as a corrosion inhibitor) and TBHQ is catalytically oxidised to TBQ at the copper surface. IT–TOF-MS also revealed the formation of new molecules of high molecular weight only present in the TBHQ-doped biodiesel deteriorated by the corrosion process. MS^2 spectra gave clear evidence of the formation of new complexes between free radicals of long-chain molecules (fatty acid derivatives) and TBQ radicals during biodiesel deterioration. Therefore, the antioxidant can also react with long-chain molecules in an additive fashion.

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