Stability evaluation of biodiesel supplemented with synthetic and bio-based antioxidants by a pressurized accelerated oxidation method

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Abstract

This work examines pressurized accelerated oxidation by a RapidOxy tester as an alternative method for determination of biodiesel oxidation stability. Sunflower oil-based biodiesel was synthesized and treated with antioxidants: tert-butylhydroquinone (TBHQ) - a synthetic antioxidant known for its powerful protective effect, and a mixture of bio-based antioxidant compounds extracted from vinery waste, VWE_{eth}. The antioxidant potency of TBHQ was evaluated at varying temperatures (110 - 140 °C) and concentrations (250 - 2,000 mg dm^{-3}) by the RapidOxy method; assessment of selected results was performed by comparison with relevant data obtained by the standard Rancimat method. VWE_{eth} was added in two high dosages to biodiesel (87,500 and 150,000 mg dm^{-3}) and analyzed at 140 °C by the RapidOxy method. Both antioxidants at all applied dosages showed beneficial effects on improving the oxidative stability of biodiesel, but not all of the achieved improvements reached the stability minimum identified by the EN14214 standard. The lowest addition of TBHQ seemed to have a similar effect as the tested dosages of VWE_{eth} but these additions did not increase the induction period above the limit of 8 h; two-fold higher quantity of TBHQ was successful in this respect, increasing the initial oxidation stability by a factor of about 2, which was determined by both methods. The RapidOxy method proved to be a very fast method suitable for testing a large number of samples, which is particularly important for efficient testing of different types and doses of antioxidants.

Keywords: induction period; Rancimat; RapidOxy; *tert*-butylhydroquinone TBHQ; vinery waste ethanolic extract.

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1. INTRODUCTION

Currently, biodiesel represents the most widely used renewable substituent for conventional fuel for diesel engines. It is a biofuel consisting of fatty acid alkyl esters (FAAEs) that can be derived from different oleo feedstocks such as vegetable oils (edible and non-edible), waste cooking oils, animal fats, and algal or microbial oils. However, its usage is linked with some disadvantages over conventional fuel for a diesel engine as a consequence of distinct chemical composition that differs from the hydrocarbon (HC) nature of the fossil diesel. One of the most prominent lacks of biodieselis its low oxidation stability. Oxidation stability indicates the potency of a fuel to resist oxidative degradation. This property of biodiesel is linked to the presence of unsaturated fatty acid chains inherent in the oily feedstock composition. Fatty acid chains that exist in molecules of feedstock's triglycerides (or free fatty acids) are introduced into the molecules of FAAEs by the reaction of transesterification (or esterification) during the synthesis of biodiesel. By transesterification with, for instance, methanol, triglycerides are converted to fatty acid methyl esters (FAMEs) and glycerol. Double bonds in FAAEs represent the weakest points of biodiesel under the attack of aggressive oxidative species. In brief, deterioration of biodiesel composition by the oxidative degradation starts with the removal of hydrogen in (bis)allylic position relative to the double bond in (poly)unsaturated fatty acid chains in the presence of free

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radicals, further creating reactive species through a multi-step reaction process [1-3]. Peroxides and hydroperoxides are primary oxidation products, but being unstable they further react forming various secondary products, including shorter-chain compounds such as aldehydes, alcohols, and low volatile acids, as well as polymers [3-5]. The composition change induced by the oxidation of unsaturated fatty acid chains of FAAEs deteriorates standardized fuel properties, primarily the acid value, viscosity, and sediment content. For biodiesel fuel applications, oxidative degradation can occur during storage or use in the vehicle's engine, causing the formation of deposits or mechanical component failure, involving injector blockage, filter plugging, and pump wear [1,4].

The use of antioxidant additives is the most usual way to improve the biodiesel oxidation stability towards reaching or maintaining the standardized quality. Concerning the origin, antioxidants can be synthetic or natural. Despite the efficiency, synthetic antioxidants exhibit significant drawbacks including toxicity, low biodegradability, and the high price that increases the already high cost of biodiesel. Thus, natural antioxidants attract increasing attention as an alternative for controlling oxidation in biodiesel with some of the studies reporting significant efficiencies of such additives [6-10]. Considering the type of stabilizing mechanism, antioxidants can be regarded as primary and secondary: primary antioxidants interrupt the oxidation chain reaction, while the secondary ones act indirectly, *e.g*. by complexing a metal acting as a catalyst for oxidation reaction, decomposing the existing hydroperoxides to a non-radical species, or by absorbing radiation in the initiation stage of oxidative processes [11]. Chemically, there are amine-based substances with antioxidant effects (*e.g*. N,N'-di-*sec*-butyl-*p*-phenylenediamine) [12], but phenolic antioxidants such as butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), *tert*-butylhydroquinone (TBHQ), pyrogallol (PY), propyl gallate (PG), have been applied more frequently [13].

Several methods exist to determine the oxidation stability of biodiesel, with the most applicable being a method of accelerated degradation in a Rancimat instrument. A sample is placed in the heating block and intensively oxidized by air flow, resulting in the formation of volatile secondary oxidation products (mainly formic and acetic acids) that are transferred into a measuring flask with distilled water; after some time of analysis, large quantities of the oxidation products introduced into the water induce a sudden increase in the water conductivity. The time that corresponds to the inflection point in the oxidation curve (conductivity *vs.* time) is the so-called induction period [14]. The induction period determined by the Rancimat method under the standardized conditions (EN14112) is directly comparable with a limit of 8 h defined as the minimum oxidation stability by the European standard on biodiesel quality EN14214. However, this method is time-consuming particularly when testing or formulating different antioxidant additives. It also provides an incomplete analysis of the sample oxidation stability because the results are based only on detected highly volatile oxidation products [15]. An alternative method reported by Neumann *et al.* [16] is more rapid and it is based on the induction period determination as a consequence of the pressure loss in the oxygen atmosphere above the sample in a sealed reaction chamber due to oxygen consumption by all sample compounds (volatile and non-volatile) susceptible to oxidation [15]. This so-called PetroOXY method is standardized in the USA (ASTM D7545-14). In the EU it is included in a draft standard prEN16091:2021, which specifies the determination of the oxidation stability of middle distillate fuels, FAMEs, and their blends. The PetroOXY method provides the induction period as a time of accelerated oxidative degradation of the sample by heat (140 °C) in the atmosphere of oxygen (initial pressure of 700 kPa) till the moment when a pressure drop of 10% is detected in relation to the maximum pressure recorded. It has been determined that the time needed to achieve a fixed pressure drop is directly related to the fuel oxidation stability [16]. In both methods, Rancimat and PetroOXY, longer induction periods indicate better oxidation stability. However, none of the standards on biodiesel fuel quality define the oxidation stability limit towards the induction period determined by a pressurized accelerated method such as the PetroOXY. This is why several studies compared Rancimat and PetroOXY methods with the aim to establish a correlation between the results for biodiesel [15-17]: a linear dependence between the results of these two methods was confirmed, and it has been concluded that the regression models largely depends on the origin of biodiesel and the presence of antioxidant additives.

The aim of the present study was to evaluate the effect of antioxidant additions to biodiesel by the RapidOxy stability tester, which determines the induction period on the same principle as the pressurized PetroOXY method. The antioxidant potency of TBHQ as a synthetic antioxidant was evaluated at different temperatures and concentrations. Additionally, a

vinery waste ethanolic extract (VWE_{eth}) was prepared and preliminarily tested as an alternative bio-additive for the enhancement of biodiesel oxidation stability. The RapidOxy data were compared with selected values obtained by the Rancimat method at 110 °C. The study contributes to previous efforts to collect new data on the pressurized accelerated method for determination of biodiesel oxidation stability, and it also explores local biowaste as a source of valuable antioxidant additives.

2. MATERIALS AND METHODS

2. 1. Biodiesel synthesis

Biodiesel was synthesized from commercial refined sunflower oil (Serbia). The fatty acid composition is determined by the gas chromatographic (GC) method and presented in Table S-1 in the Supplementary Material. Oil was transesterified with methanol (p.a., Lachner, Czech Republic) in the presence of KOH (p.a., Alkaloid Skopje, North Macedonia) as a catalyst in a 2 dm^3 stainless steel reactor (methanol to oil mole ratio 5:1; 1 mas.% KOH catalyst in oil) at a temperature ~64 °C for 1 h. After the reaction, the product mixture was allowed to settle: the upper layer of biodiesel was collected, while the lower glycerol layer was discarded. Methanol was removed from biodiesel by rotary vacuum evaporation. Biodiesel was purified with warm distilled water and finally dried with silica gel. Characterization of biodiesel was performed in accordance with selected requirements of the EN 14214 standard.

2. 2. Preparation of vinery waste extract as an antioxidant bio-additive

Waste after the production of red wine in a local vinery (Vojvodina Province, Serbia) was collected in early autumn 2019 and dried at about 50 °C till constant mass. VWE_{eth} was prepared as follows: a sample of dried vinery waste (10.0 g) was grounded by a laboratory mixer and added to 50 cm^3 of absolute ethyl alcohol (*p.a.*, Zorka Pharma, Serbia). This mixture was shaken by a laboratory shaker (Promax 2020, Heidolph, Germany) at 140 rpm for 48 h and then filtered into a 50-cm^3 volumetric flask followed by addition of ethanol to bring the volume to the mark. Multiple extracts were prepared in order to test repeatedly the addition of two extract's dosages to the synthesized biodiesel: 25 and 50 cm^3. After evaporation of the selected VWE_{eth} dosage till dryness by a rotary vacuum evaporator (Laborota 4000, Heidolph, Germany), a known volume of biodiesel was added into the same evaporator rotating flask that kept rotating for about 20 min before analyzing the oxidation stability. Before the addition of biodiesel, the extract's dry matter was weighed in order to calculate the VWE_{eth} dosages relative to the biodiesel volume. In this way, the tested dosages of VWE_{eth} were 87,500 mg dm^{-3} (VWE_{eth1}) and 150,000 mg dm^{-3} (VWE_{eth2}). Finally, the oxidation stability of biodiesel samples blended with the extract's dry matter was analyzed using the RapidOxy instrument.

2. 3. Determination of biodiesel oxidative stability

A sample of synthesized biodiesel (before the treatment with antioxidant, *i.e*. untreated) was analyzed for oxidation stability by both Rancimat and RapidOxy methods.

Equipment for determination of oxidation stability in accordance with the Rancimat method was tailored as described in the EN 14112 standard (Figure D1, Supplementary Material). A portion of biodiesel (3 cm^3) was simultaneously subjected to heating at 110 °C and airflow of 10 dm^3 h^{-1} following the requirements of the EN 14112 standard. Electrical conductivity was measured by a conductometer (HQ440d multi, Hach, USA) with a probe inserted into a measuring flask containing 50 cm^{-3} of distilled water [14]. Pairs of conductivity values and time were recorded to obtain the oxidation curve (conductivity *vs* time). The inflection points of the curve represented the Rancimat induction period (in h). The Rancimat induction period is directly comparable with the limit on oxidation stability defined by the EN 14214 standard. The Rancimat method was used for testing the oxidation stability of untreated biodiesel and also of biodiesel treated with different dosages of the synthetic additive TBHQ, known for its potent antioxidant activity in fuels.

Induction period determined by the oxidation stability tester RapidOxy 100 (Anton Paar, Germany, Figure D2) represents the time (in min) that elapsed between the start of the test (*i.e*. when the oxygen pressure is stabilized at 700 kPa in the sealed instrument test chamber with the sample portion of 4 cm^{-3} before heating to the specified temperature)

to the pressure drop of 10 % with respect to the maximum pressure recorded at the specified temperature. The analytical run consists of the following steps: purging of the instrument test chamber containing the sample portion with oxygen, pressurizing the chamber with oxygen to 700 kPa, heating to the selected temperature, measuring of the pressure drop (till the specified value of the drop), cooling (to 20°C), discharging, and final purging with air. The RapidOxy measurement of untreated biodiesel and the TBHQ-treated biodiesel were performed at different temperatures, *i.e*. at 110, 120, 130, and 140 °C. The effect of different concentrations of TBHQ (250, 500, 1,000, and 2,000 mg dm^{-3}) was also tested by the RapidOxy method but only at 140 °C. The induction period of biodiesel with VWE_{eth} was determined at 140 °C by the RapidOxy method, too. In this way, TBHQ was used as a proved, well known potent antioxidant for comparison of the RapidOxy *vs*. standard Rancimat method, as well as to evaluate preliminary VWE_{eth} as an alternative natural additive. Efficiency of the added antioxidant, *i.e.* its antioxidative potency was expressed as a stabilization factor, calculated by dividing the induction period obtained for biodiesel after the antioxidant addition (treated biodiesel) with the induction period of the untreated biodiesel at the same test temperature. All experiments were performed in duplicates.

3. RESULTS AND DISCUSSION

3.1. Oxidation stability of untreated and TBHQ treated biodiesel

The results of biodiesel characterization are presented in Table 1 with the test methods used. Based on the average induction period of 3.76 h determined at 110 °C by the Rancimat method (Table 1), biodiesel failed to satisfy the limit set by the standard EN 14214. This was not surprising, knowing that the iodine value (*i.e*. the total unsaturation level) of sunflower oil is usually higher than the value for rapeseed oil (usual feedstock for biodiesel in the EU) because of higher contents of linoleic acid: the inherited fatty acid composition of the sunflower oil-based biodiesel results often in non-compliance with the EN standard requirements for iodine value and oxidation stability [18].

Induction periods of freshly synthesized biodiesel determined at different temperatures by the RapidOxy tester are given in Table 2 and Figure D3 (Supplementary Material). It can be easily seen how this method is fast if compared to the Rancimat: 12 times shorter induction period at 110 °C was obtained for untreated biodiesel. Results in Table 2 also proved repeatability of measurements by the RapidOxy instrument: the range of the relative standard deviations was 2.24-5.13 %, with higher RSDs obtained at two higher test temperatures (130 and 140 °C) at which the induction periods were 1.6- and 1.8-fold shorter than the period at 110 °C (Table 2). This high precision coincided with the results of Neumann *et al.*, who reported repeatability and reproducibility for biodiesel induction periods determination by the PetroOXY method to be <5 % and <8 %, respectively [16]. The EN14112 standard (Annex A of EN14214) defines the precision (in h) of the oxidation stability measurement by the equation:

$$\text{Precision} = 0.26X + 0.23 \quad (1)$$

where X is the mean value of two results on induction period that are compared.

According to the eq. (1) acceptable deviation for the Rancimat induction period of biodiesel synthesized in this study is 1.21 h, accounting for ~32 % of the measured value (3.76 h). The EN14214 standard defines reproducibility of 2.3 h at the oxidation stability limit, accounting for 28.7 % of the 8 h-minimum specified by this standard. Neumann *et al.* [16] concluded that the significantly enhanced reproducibility by the pressurized method over the Rancimat method improves the consistency of test results, and that testing of antioxidant dosages can be more precise, *i.e.* much closer to the actual required level.

Table 1. Selected properties of biodiesel synthesized in this study and compared with the limits set by the EN 14214 standard

Property	EN 14214 limit	Average value (SD*)	Method
Ester content, wt.%	> 96.5	98.9 (0.6)	EN 14103
Density at 20°C, kg m^{-3}	860-900	861 (1.4)	EN ISO 3675
Kinematic viscosity at 40 °C, $mm^2 s^{-1}$	3.5-5.0	4.6 (0.1)	EN ISO 3104
Water content, mg kg^{-1}	< 500	250 (7.1)	EN ISO 12937
Acid value, mg KOH g^{-1}	< 0.5	0.47 (0.01)	EN 14104
Methyl ester of linolenic acid, mas.%	< 12	0.97 (0.04)	EN 14103
Oxidation stability at 110 °C, h	> 8	3.76 (0,37)	EN 14112

*SD-standard deviation

Table 2. Induction periods of synthesized biodiesel determined at different temperatures by the RapidOxy tester

t / °C	Number of analyzed sample aliquots	Average induction period, min	RSD[a], %
110	5	19.25	2.25
120	5	14.60	3.63
130	6	11.95	5.13
140	6	10.51	4.80

[a]Relative standard deviation (RSD) is determined as the standard deviation of measured values for the given temperature relative to the corresponding average value multiplied by 100 to obtain the percentage

Stabilization factors reflecting the antioxidant potency of TBHQ in biodiesel at different temperatures are given in Table 3. Comparison of the induction periods obtained at 140 °C for varying additions of TBHQ is presented in Table 4.

Stabilization factors proved the beneficial effects of TBHQ on retarding oxidative degradation of biodiesel under the testing conditions. Within the range of applied temperatures, the initial induction period was increased for about 3 to 7 times, with the highest increase observed at the highest TBHQ dosage and the lowest testing temperature (Table 3).

As expected, the induction period was reduced with the increase in the test temperature; an exponential trend described the dependence of the average induction period, *IP* / min, of untreated biodiesel (neat) on temperature, *t* / °C, which can be presented with the equation (2):

$$\ln IP_{neat} = 3.1078 - 0.193t \quad (2)$$

The coefficient of determination was $R^2 = 0.9599$. Induction periods of the biodiesel samples treated with two dosages of TBHQ similarly depended on the testing temperature described with equations (3) and (4):

$$\ln IP_{TBHQ1} = 5.1704 - 0.466t \quad (3)$$

$$\ln IP_{TBHQ2} = 5.2720 - 0.446t \quad (4)$$

where eq. (3) describes experimental results obtained for TBHQ dosage of 1,000 mg dm^{-3} (TBHQ1) with the coefficient of determination of $R^2 = 0.9845$, while eq. (4) describes experimental results obtained for TBHQ dosage of 2,000 mg dm^{-3} (TBHQ2) with the coefficient of determination of $R^2 = 0.9912$.

Table 3. Stabilization factors as indicators of antioxidant potency of TBHQ added to biodiesel at two levels (TBHQ1: 1,000 mg cm^{-3} and TBHQ2: 2,000 mg cm^{-3}) determined at different temperatures by the RapidOxy tester

Temperature, °C	Stabilization factor[a]	
	TBHQ1	TBHQ2
110	6.14	6.68
120	4.40	5.41
130	3.44	3.98
140	2.68	3.18

[a]Stabilization factor is calculated as a ratio of the induction period obtained for biodiesel after the addition and the induction period of biodiesel prior the addition at the same test temperature.

Table 4. Induction periods of biodiesel treated with varying concentrations of TBHQ determined at 140 °C by the RapidOxy oxidation stability tester and the corresponding stabilization factors

TBHQ dosage, mg dm^{-3}	IP, min	Stabilization factor	Stabilization factor per dosage, dm^3 mg^{-1}
250	13.30	1.23	0.0048
500	22.20	2.05	0.0042
1000	28.98	2.68	0.0027
2000	34.38	3.18	0.0016

Hence, a negative effect of temperature on the oxidation stability was observed regardless of the treatment, while the reduction in stability (*i.e*. induction periods) followed different trends depending on the TBHQ absence/presence. The similarity of respective coefficients in equations (3) and (4) suggested similar degradation mechanisms in the TBHQ-treated biodiesel under applied conditions of accelerated oxidation regardless of the TBHQ dosage. On the other hand, coefficients in eq. (2) differed from the corresponding ones in eqs. (3) and (4), implying different mechanisms of the induction period disturbance with increasing temperature in the untreated biodiesel. It was indicated in a study of changes of selected biodiesel fuel parameters during accelerated oxidation at different temperatures that at

temperatures above 75 °C thermal degradation of original biodiesel composition occurs along with the oxidative decomposition [19]. Accordingly, it might be expected that thermal degradation is more pronounced at higher temperatures. This could be the explanation for the obtained exponential dependence of induction periods on temperature. Differences between the equations for untreated (eq. 2) and treated (eqs. 3 and 4) biodiesel might be ascribed to the presence of TBHQ and its active antioxidant action superimposed over the oxidation and thermal degradation of unsaturated fatty acid methyl esters. Besides the consumption of TBHQ during its protective antioxidative action, its thermal degradation might be also presumed to occur; the formed degradation products may affect the induction periods [22], as is explained hereafter.

High antioxidant potency of TBHQ is well known and explained by its unique molecular structure. It consists of two -OH groups linked to aromatic ring in *para*(1,4-) position and one *tert*-butyl group in *ortho*(2-) position. Such dihydroxyl aromatic structure interrupts more easily the propagation step of the free radical chain reaction than phenolic antioxidants with only one -OH group in molecules [14,20,21]. The presence of alkyl groups is also important for efficient protection from oxidation. In this way, the electron density on the -OH groups is increased, which facilitates the release of a hydrogen radical, enabling more efficient stabilization of ester radicals formed during the oxidation stress [21]. Apart from the favorable structure, high efficiency of TBHQ is additionally related to the products known to be formed during its antioxidative activity that may also exhibit antioxidant properties, synergistically retarding the oxidation [14,22].

Dependence of RapidOxy induction periods, IP_i / min, on different dosages of TBHQ, i / mg dm^{-3}, also did not follow a linear trend (Table 4):

$$IP_i^{RapidOxy} = 10.102 \ln i - 41.564 \text{ with } R^2 = 0.9876 \quad (5)$$

The shape of the curve (Figure D4) suggested changes in rates of stability enhancement in the range of tested dosages: faster increase at lower and slower at higher dosages of TBHQ. This might be also illustrated by stabilization factors at different TBHQ dosages (Table 4).

Induction periods for the biodiesel supplemented with different TBHQ dosages determined at 110 °C by the Rancimat method and the corresponding stabilization factors are presented in Table 5. The difference between the RapidOxy and Rancimat results should be ascribed to different phenomena behind these two methods and their repeatability as explained previously. Still, both methods showed a 2-fold increase in the induction period with the TBHQ dosage of 500 mg dm^{-3}, and according to the Rancimat results it was sufficient for achieving the oxidation stability above the EN14214 standard limit. A preliminary exponential model correlating the respective results obtained by the Rancimat (at 110 °C) and PetroOxy (at 140 °C) methods is presented in Figure D5 (Supplementary Material); however, further study is needed to confirm the applicability of the model.

Table 5. Induction periods of biodiesel treated with varying concentrations of TBHQ determined at 110 °C by the Rancimat method and the corresponding stabilization factors

TBHQ dosage, mg dm^{-3}	IP, h	Stabilization factor
250	4.9	1.3
500	9.2	2.4
1000	15.7	4.2

3.2. Oxidation stability of biodiesel treated with VWE_{eth}

As mentioned previously, the high price, nonrenewable origin, and toxicity of conventional synthetic fuel additives have triggered the search and development of alternative, cheaper, non-toxic, and renewable additives for biodiesel, which efficiently address known disadvantages in the fuel properties. Substantial achievements have been recorded in recent years and they are reviewed in the work of Lawan *et al.* [6]. The majority of studies dealing with bio-based additives explored extracts of varying plants such as rosemary [22], ginger [23], oregano [22], basil [22], *Moringa oleifera* [8], etc. However, it is worth mentioning that the use of plants known for their therapeutic and/or nutritional values in the fuel industry additionally contributes to the already raised controversy of biodiesel regarding food *vs.* fuel dilemma. Thus, a more sustainable option is to obtain alternative bio-based antioxidants from non-edible feedstock, especially from food and agro-industry waste. Utilizing biowaste as feedstock for bio-based additives could reduce the biofuel cost providing

also a good waste management strategy [10]. Some of biowaste examined as sources of antioxidants for biodiesel were barley waste [8], potato peel [9], and spent coffee grounds waste [10]; regardless of the applied extraction procedures, addition of the obtained extracts to biodiesel of various origins proved to be beneficial for the fuel oxidation stability. For instance, extract of 10 g of dried potato peels by 100 cm^{-3} of absolute ethanol for 3 h was added as dry matter at different dosages (100 - 250 ppm) to biodiesel synthesized from Nahor oil (*Mesua ferrea*) [9]. Rancimat induction periods of the treated biodiesel were in the range of 5.95 h for 100 ppm extract to 7.02 h for 250 ppm extract, whereas the initial induction period of the untreated biodiesel was 5.63 h [9]. Thus, stabilization factors were in the range 1.06 to 1.25.

Natural antioxidants obtained in the present study from vinery waste also proved protective capacity as induction periods of the VWE_{eth}-treated biodiesel samples were improved for a factor of about 1.3 (Table 6). The slightly higher stabilization factors achieved here in comparison to those obtained for the previously mentioned potato peel extract might be the consequence of the higher quantity of dried feedstock extracted (0.2 g vinery waste per cm^{-3} of solvent *vs*. 0.1 g potato peel per cm^{-3} of solvent), longer extraction periods, and/or different antioxidant compounds present in the extracts. The exponential equation describing the relationship between the Rancimat and RapidOxy induction periods (Figure D5, Supplementary Material) was applied to the VWE_{eth}-related values measured by the RapidOXY method resulting in the corresponding Rancimat periods of 4.8 and 5.0 h. This result implies that the tested additions of VWE_{eth} were not sufficient to enhance the biodiesel oxidation stability above the EN14214 standard limit. Comparison of the RapidOxy induction periods obtained for additions of natural VWE_{eth} and synthetic TBHQ implies that the tested dosages of the former additive had protective power similar as the TBHQ dosage of 250 mg dm^{-3}. If eq. (5) is applied for the VWE_{eth}-induction periods presented in Table 6, the equivalent TBHQ concentrations of 231 and 248 mg dm^{-3} are obtained. Knowing that the TBHQ addition of 250 mg dm^{-3} led to the Rancimat induction period of 4.9 h (Table 5), this equivalency also showed that the applied VWEs dosages were not sufficient to improve the biodiesel oxidation stability above the EN14214 standard limit.

It is interesting to note that the linear regression model of Botella *et al.* [15], correlating the Rancimat and PetroOXY induction periods (in min) for biodiesel with additives, applied on the RapidOxy periods for VWE_{eth} additives, predicted similar values for the Rancimat periods: *i.e*. 4.3 h and 4.4 h. The comparison proved that the obtained model may be used as a quick means for converting the RapidOxy measurements into the Rancimat values for the tested biodiesel with VWEs additives, and that such value may indicate if the oxidation stability reached the standard limit. Nevertheless, more data are needed to obtain a more accurate and general correlation.

Rather similar factors of stability enhancement obtained for two dosages of VWE_{eth} could be explained by possible aliquot (in)homogeneity during the transfer to a flask for blending with biodiesel. Markedly lower stabilization factor per dosage calculated for VWE_{eth} (Table 6) in comparison to TBHQ (Table 4) suggested that only a certain part of the VWE_{eth} could be related to antioxidants with protective power for biodiesel and/or the presence of less potent antioxidant compounds. Higher quantities of vinery waste (>0.2 g cm^{-3}) are necessary to be tested as potential means for increasing the antioxidant potency.

Table 6. Induction periods determined at 140°C by the RapidOxy method and the corresponding stabilization factors after addition of vinery waste ethanolic extracts (VWE_{eth}) as bio-based antioxidants

VWE_{eth} dosage, mg dm^{-3}	IP, min	Stabilization factor	Stabilization factor per dosage, dm^3 mg^{-1}
87,500	13.41	1.28	0.0000153
150,000	14.12	1.34	0.0000085

4. CONCLUSION

The results suggested the RapidOxy method as a high-throughput analytical technique with high repeatability. Dependence of RapidOxy induction periods on test temperatures was described by an exponential equation, capturing the effects of oxidative stress and thermal degradation in the applied range of temperatures; different equations obtained for untreated and TBHQ-treated biodiesel, reflected the additional antioxidation action of TBHQ. The addition of TBHQ to sunflower oil-based biodiesel in a dosage of 500 mg dm^{-3} enabled compliance with the EN14214 standard.

The VWE_{eth} extract showed protective potency as an antioxidant additive for biodiesel, but the tested dosages were not sufficient to achieve the EN14214 standard limit.

Further studies are needed to characterize VWEs since by knowing the VWEs composition, particularly compounds exhibiting antioxidant properties, the mechanism of its interaction with biodiesel may be proposed. Continuation of the present study should aim at determination of VWEs dosages, applied either individually or in combination with a powerful synthetic antioxidant such as TBHQ, sufficient to reach the relevant limit without impairment of the other fuel properties. Investigation of different extraction methods/conditions would reveal if a more powerful antioxidant action of VWE_{eth} might be achieved. Techno-economic analysis and life cycle assessment would confirm the sustainability of the final results.

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Procena stabilnosti biodizela sa sintetičkim i bio-antioksidansima primenom ubrzane metode pod pritiskom

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Izvod

U radu je ispitana metoda ubrzane oksidacije pod pritiskom pomoću RapidOxy uređaja kao alternative za određivanje oksidacione stabilnosti biodizela. Pripremljen je biodizel od suncokretovog ulja i tretiran je antioksidansima: sintetičkim antioksidansom terc-butil hidrohinonom (engl. *tert*-butylhydroquinone, TBHQ), koji je poznat po svom snažnom zaštitnom dejstvu, i smeša jedinjenja sa antioksidativnim dejstvom ekstrahovana etanolom iz otpada vinarije, (engl. vinary waste ethanolic extract, VWE_{eth}). Antioksidaciona moć aditiva TBHQ je ispitana pri različitim temperaturama (110 do 140 °C) i koncentracijama (250 do 2000 mg dm^{-3}) primenom RapidOxy metode; procena odabranih rezultata je izvršena njihovim poređenjem sa relevantnim podacima dobijenim pomoću standardne Rancimat metode. Oba antioksidansa u svim testiranim dozama su pozitivno uticali na poboljšanje oksidacione stabilnosti biodizela, ali nisu sve doze dovele do postizanja minimalne stabilnosti definisane standardom EN14214. Najmanja doza aditiva TBHQ je pokazala dejstvo slično testiranim dozama ekstrakta VWE_{eth}, ali ove doze nisu povećale indukcioni period iznad granične vrednosti od 8 h; dvostruko veća doza aditiva TBHQ je bila uspešna, povećavajući početnu oksidacionu stabilnost za faktor 2, što je utvrđeno pomoću obe korišćene metode. RapidOxy metoda se pokazala kao veoma brza metoda pogodna za ispitivanje velikog broja uzoraka, što je naročito važno za efikasno ispitivanje dejstva različitih vrsta i doza antioksidanasa.

Ključne reči: etanolni ekstrakt otpada vinarije; indukcioni period; Rancimat; RapidOxy; *terc*-butil hidrohinonTBHQ