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Influence of synthetic antioxidants on the oxidation stability of biodiesel produced from acid raw *Jatropha curcas* oil

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ABSTRACT

In the present work, *Jatropha curcas* biodiesel was produced from a high free fatty acid raw oil (AV = 35.36 mg KOH g^{-1}) containing 76.5% *w/w* of unsaturated fatty acids. The production route consisted of a two-step method, using acid esterification, followed by conventional alkali methanolysis. Biodiesel was characterized in agreement with EN 14214:2014 and a study on the use of 4 synthetic antioxidants was conducted. The high free fatty acid content of the oil could be reduced to 0.8% *w/w* by acid esterification. A good product quality was generally observed but the very low oxidation stability, corresponding to an induction period (IP) of 1.37 h, was the highest concern. Statistically significant predictive models, which related each antioxidant concentration with the IP, were obtained. Pyrogallol (PY) showed the best results, being estimated that the use of 204 ppm in biodiesel could increase its IP to the limit imposed by the quality standard (8 h). The following rank, in terms of effectiveness, was obtained: PY > propyl gallate (PG) > butylated hydroxytoluene (BHT) > tert-butyl hydroquinone (TBHQ). In agreement, the stabilization factors (F), considering the use of 204 ppm of antioxidant, were: 5.84 for PY, 4.06 for PG, 1.85 for BHT and 0.85 for TBHQ.

1. Introduction

Biodiesel production has increased significantly in the last years; in fact, in 2011, biodiesel production in the world reached around 404 000 barrels per day, almost 12 times higher than in 2003, showing that the market accepts biodiesel as a viable substitute of fossil diesel [1].

About 95% of the biodiesel production plants use food vegetable oils as raw material [2]. When considering alternative non-food crops (second generation crops), jatropha (*Jatropha curcas* L.) is one of the most promising, because it grows very easily in adverse soil conditions where food plants have difficulties to grow and presents one of the highest oil yields compared to other non-edible oil plants (1590 kg oil/ha, 35–40 wt.% of the seed) [2,3]. Most of jatropha is cultivated in Asia, Africa and Central and South America [4–8].

The most used process for biodiesel production, due to the higher simplicity and lower cost, is the transesterification reaction between the oil and an alcohol (usually methanol), in the presence of an alkali catalyst, to produce biodiesel and the by-product glycerol [9]. For an effective alkali transesterification reaction, a low amount of free fatty acids (FFA) on the feedstock is required (usually less than 1 wt.%) [10]; this means that if a high FFA feedstock is available, it needs to be pretreated before proceeding to the transesterification process. In order to reduce the FFA content of the oil, the acid esterification of the FFA with methanol is the most used pretreatment process because it allows the production of methyl esters from the acids present [11–13], taking advantage of all the feedstock towards biodiesel production (Eq. (1)).

$$R_1COOH + CH_3OH \overset{acid}{\rightleftarrows} R_1COOCH_3 + H_2O \quad (1)$$

Oxidation of biodiesel is a major concern, occurring mostly due to air exposure and being highly promoted by the presence of unsaturated fatty acids, since the double bonds offer a high level of reactivity with oxygen. For instance, methyl or ethyl linoleate (C18:2) reacts close to 40 times faster than oleate (C18:1) [14]. The work performed on the chemistry of oxidation reports mostly the primary and secondary oxidation [15]. The primary oxidation is a free-radical chain reaction that might be represented as shown in Fig. 1 [14,15]. The initiator (I) is mostly likely a free radical that results from the decomposition of hydroperoxides present [14]. On the secondary oxidation, hydroperoxides (which are reactive molecules), which result from primary oxidation, decompose readily to form a number of stable products such as aldehydes, ketones and hydroxyl fatty acids, the last being responsible for the increased acidity of the product [14]. An increase of the viscosity generally indicates the presence of higher molecular weight materials formed by oxidative polymerization [15].

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Initiation: $RH + I \rightarrow R^{\bullet} + IH$

Propagation: $R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$ (Fast reaction)

$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$

Termination: $R^{\bullet}, ROO^{\bullet} \rightarrow$ Stable products

Fig. 1. Primary oxidation reaction mechanism.

In fact, when oxygen is present, oxidation cannot be completely prevented or reversed; in agreement, the methods used to overcome this problem work on the inhibition of the reactions, therefore delaying or significantly slowing down the accumulation of oxidized products [14]. Such inhibitors are known as antioxidants, being generally chain breakers (free radical terminators) or hydroperoxide decomposers [15]. Chain breakers are the most used and they work by removing the reactive radicals produced during the initiation and propagation steps of the primary oxidation. The two most common are phenolic and amine-type of antioxidants; however, in what concerns biodiesel applications, mostly phenolic antioxidants are used [15]. Antioxidants used to control lipid oxidation can be natural or synthetic and there are several natural and synthetic phenols that might compete, even under low concentrations, with the triacylglycerol molecule as hydrogen donor. Consequently, stabilized radicals are produced which are not able to initiate or propagate the oxidation reactions, therefore increasing the oxidation stability of the product [14,15].

Different parameters might be used to access the oxidation stability of biodiesel, namely: Iodine Value, Anisidine Value, Peroxide Value, Oxidation Stability Index and Induction Period (IP). The European Standard on biodiesel quality, EN 14214:2014, adopted the accelerated oxidation test (EN 14112:2003) for the determination of the oxidation stability in terms of the IP ("time which passes between the moment when the measurement is started and the moment when the formation of oxidation products rapidly begins to increase"). A minimum IP of 8 h is required according to this standard to ensure biodiesel quality. Most biodiesel, being produced from oils with significant amounts of unsaturated fatty acids (e.g. soybean, rapeseed and sunflower oil) cannot fulfill the requirements; palm oil is an exception since it is not as rich in unsaturated fatty acids [15]. The use of different raw materials (with variable fatty acid composition), the application of an ethylic or methylic route for the transesterification (that can lead to products with different properties, namely the acid value, viscosity and water content) and the adoption of different purification processes (e.g. water washing (more common), membranes, resins, distillation) will influence the oxidation stability of the biodiesel product [14,16]. The oxidation stability might also be improved by the use of raw material blends (for instances blending jatropha oil with palm oil) [17] and blends with fossil fuel (biodiesel + petrodiesel) [18,19].

Among the most used synthetic antioxidants to improve biodiesel oxidation stability are: pyrogallol (PY), propyl gallate (PG), tert-butyl hydroquinone (TBHQ), butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) [15]; the most studied natural antioxidants are the natural phenolic compounds—tocopherols (α, δ and γ tocopherol), that can be obtained from the refining of vegetable oils; carnosic acid, obtained for instances from rosemary; and, sesamol, present in sesame oil [14,15].

In a review by Jain and Sharma [15], the effectiveness of different antioxidants towards the improvement of oxidation stability of various types of biodiesel (e.g. from rapeseed, sunflower, soybean, palm, tallow, and frying oils) is reported, using concentrations ranging from 200 to 7000 ppm. In general, the synthetic PY and TBHQ presented the best results and synthetic antioxidants always performed better than the natural ones (α, δ and γ tocopherol). The mentioned studies included the use of: (i) edible and non-edible oils and fats to produce biodiesel with different properties through conventional alkali transesterification [20]; (ii) commercial biodiesel originated from refined oils and waste oils also produced by alkali transesterification [21–23]; and, (iii) synthetic methyl esters produced by blending pure methyl esters in the same proportions as presented in natural esters [22]. The variability of the results reveals the need to conduct dedicated studies when considering the use of antioxidants for biodiesel obtained from different raw materials, also considering different antioxidant concentrations.

From the literature review, there is clearly a lack of studies on the oxidation stability of biodiesel derived from non-edible oils such as jatropha. In the study by Sarin et al. [24], the oxidation stability of biodiesel obtained from low free fatty acid *J. curcas* oil was found to be 3.95 and a minimum of 200 ppm of BHT was required to achieve an IP of 6 h (previous limit imposed by EN 14214) [24]. Jain and Sharma [19] evaluated the oxidation stability of jatropha biodiesel by mixing it with diesel and/or by using synthetic antioxidants and found that around 100 ppm of PY was the optimum amount of antioxidant for the pure biodiesel (initial IP = 3.27 h, considering a final IP of 6 h) whereas 50 ppm would be required for a B30 blend with diesel (30 wt.% biodiesel). No studies were found on the evaluation of biodiesel production from acid raw *J. curcas* oil as well as on the oxidation of the derived biodiesel.

In agreement with what was previously stated, the objective of the present work was to evaluate the influence of the most effective and used synthetic antioxidants, namely PY, PG, TBHQ and BHT, on the oxidation of biodiesel obtained from acid raw *J. curcas* L. oil. For that purpose, biodiesel was synthetized directly from raw oil using a two-step process (acid esterification followed by alkali transesterification), purified, characterized according to EN14214 and after the oxidation stability studies were conducted considering the use of four synthetic antioxidants at different concentrations (from 100 to 2500 ppm).

2. Materials and methods

2.1. Materials

Raw *J. curcas* oil was purchased from PT Pura Green Energy, Indonesia. Methanol was supplied by VWR (brand AnalaR NORMAPUR), sulfuric acid 97% was supplied by VWR (Merck, EMSURE® ISO) and sodium hydroxide powder 97% was supplied by Sigma Aldrich (reagent grade). Sodium sulfate anhydrous pro analysis was supplied by Merck KGaA. Regarding the synthetic antioxidants, the commercial Baynox Plus®, which has as active ingredient butylated hydroxytoluene (BHT), was from LANXESS, propyl gallate was from SAFC (Sigma-Aldrich), tert-butylhydroquinone (TBHQ) was from Aldrich (Sigma-Aldrich), and pyrogallol was from Fluxa (Sigma-Aldrich). All the antioxidants used were solid powder reagents. All chemicals used for the oil and biodiesel characterization (2.2.3) were of pro analysis grade.

2.2. Methods

2.2.1. Esterification of raw J. curcas oil

The reaction was performed in a three neck round-bottom glass flask (1 L), equipped with a water controlled condenser and a magnetic stirrer, that was immersed in a thermostatic bath. A series of batch experiments using 500 mL of oil were conducted to obtain 2 L, for use in the characterization and oxidation stability studies. In the study by Kumar Tiwari et al. [13], the optimum reaction conditions to reduce the FFA content of *J. curcas* oil from 14% to less than 1% were: ~ 3% *w/w* of H_2SO_4 (relative to the oil), 0.28 *V/V* of methanol (relative to the oil), ~ 90 min of reaction time and temperature of 60 °C. Dias et al. [10] selected as optimum esterification conditions to reduce the acid value of waste lard from around 7% to acceptable values for transesterification the following: 2.0 wt.% H_2SO_4, 6:1 methanol:fat molar ratio, 5 h reaction time and temperature of 65 °C. Taking into account the mentioned studies, the following procedure was conducted: sulfuric acid (3 wt.%) was dissolved in methanol (20% *V/V* relative to oil) and then poured into the reactor [illegible] already had the raw oil, at 65 °C. The reaction

temperature was maintained at 65 °C and a vigorous magnetic stirring was performed.

To determine the optimum reaction time, the reaction was conducted for 4 h and the acid value was monitored at different time intervals, by removing 2 mL of sample from the reactor each time and further analyzing the acid value (2.2.3). After the end of the reaction, the products were poured into a separation funnel to separate the oil phase from the water/acid/alcohol phase; settling lasted 12 h. The oily phase, named mixture (mixture of *J. curcas* oil and biodiesel) was then submitted to vacuum distillation (using a rotary evaporator) at 65 °C, using a maximum vacuum of 200 mbar, to recover the excess of methanol used. The acid value was determined to confirm the effectiveness of the reaction and the absence of residual sulphuric acid.

2.2.2. Transesterification of the mixture

The reaction flask and setup was similar to the one used for the acid esterification (2.2.1). Sodium hydroxide (1% *w*/*w*) was dissolved in methanol (6:1 molar ratio relative to oil) and then poured into the reactor that already had the mixture that resulted from 2.2.1. Reaction was performed at 60 °C, during 90 min, using vigorous stirring, taking into account the results from Encinar et al. [25] and Dias et al. [10]. After the end of the reaction, the products were poured into the separation funnel to separate the biodiesel phase and the glycerol phase; settling lasted 2 h. The removal of methanol in excess both from the biodiesel and the glycerol phase was also performed by vacuum distillation at 65 °C, at a maximum vacuum of 200 mbar (using a rotary evaporator).

Biodiesel was further purified by acid and water washing and dried using an anhydrous salt as follows. Biodiesel was washed one time using 50% *V*/*V* (relative to oil) of an hydrochloric acid solution (0.5% *V*/*V*), to neutralize the catalyst, and then repeatedly with 100% *V*/*V* (relative to oil) of distilled water until the pH of the washing water was close to the pH of the distilled water (clear water). Small amounts of sodium chloride were slowly added to break the emulsion, when appeared during washing, being removed in the subsequent water washing step. After water washing, the residual biodiesel water was absorbed by using 25% *w*/*w* of anhydrous sodium sulfate, that was added to the product, vigorous stirred during 10 min and left settling overnight. The biodiesel was finally filtered by vacuum to obtain the final product. To prevent oxidation, the product was left in the freezer at −20 °C.

2.2.3. Oil and biodiesel characterization

J. curcas oil was characterized considering: the acid value, by volumetric titration as reported in NP EN ISO 660:2002; the water content, by coulometric Karl Fischer titration, according to ISO 8534:996; the iodine value, by volumetric titration using Wijs reagent, according to the standard ISO 3961:1996; and, oxidation stability at 110 °C (using 837 Biodiesel Rancimat® from Metrohm). Oil composition was obtained from the methyl ester profile evaluated by GC analysis (DANI 1000 Gas Chromatography) according to NP EN 5508:1996 and EN 14103:2003.

The following quality parameters were determined in the biodiesel product: density, by a hydrometer method, according to ISO 3675:1998; kinematic viscosity, using capillary viscometers, according to ISO 3104:1994; flash point, using a rapid equilibrium closed cup tester, according to ISO 2160:1998; methyl ester content, using GC analysis according to EN 14103:2003; acid value, according to EN 14104:2003 and oxidation stability at 110 °C, according to EN 14112:2003 (using 837 Biodiesel Rancimat® from Metrohm).

All the results are presented as mean values with relative percentage differences always less than 2% of the mean.

2.2.4. Influence of synthetic antioxidants on the oxidation stability of biodiesel

The following antioxidants were used: pyrogallol (PY), tert-butyl hydroquinone (TBHQ), propyl gallate (PG), and butylated hydroxytoluene (BHT).

The antioxidant was accurately weighted, added to 100 mL of the biodiesel obtained from 2.2.2 and dissolved by mixing to obtain the concentrated solutions (up to 2500 ppm, depending upon the antioxidant). The solutions were further diluted with biodiesel to obtain the range of antioxidant concentrations studied (100–2500 ppm).

In agreement with the standard EN 14104:2003, 3 g of sample were used in all cases to measure the oxidation stability. The measurement was conducted in duplicate for each antioxidant, at each concentration. Following the study, linear correlations were found between the concentration of antioxidant and the induction period. For each correlation, the linear regression statistical parameters were determined, including the determination coefficient (r^2) and the probability value (p), using an F test.

To validate the results obtained from the models, experiments were also performed in duplicate.

3. Results and discussion

3.1. Oil characterization

The initial acid value of *J. curcas* oil was 35.36 mg KOH/g sample (around 18% *w*/*w* of free fatty acids), iodine value was 99.3 g I_2/100 g and the water content was 0.252% *w*/*w*. Taking into account the very high acid value, a pre-treatment was required in order to enable biodiesel production through alkali methanolysis. The iodine value relates to oil composition and indicates the fulfillment of the biodiesel standard that imposes a value < 120 g I_2/100 g. Since acid esterification was performed as pre-treatment, no dehydration of the oil was performed.

Raw *J. curcas* oil immediately started to oxidize when subjected to the rancimat test; accordingly, the induction period was 0.06 h. No previous studies were found on the oxidation stability of raw *J. curcas* oil. The extremely low oxidation stability is expected due to the high free fatty acid content of the oil, since free fatty acids will more easily react with the oxygen [26]. The fatty acid composition of *J. curcas* oil might be expressed by the fatty acid methyl ester (FAME) profile obtained by gas chromatography. Table 1 shows the results obtained and a comparison with other studies on the use of this type of oil.

It can be observed that *J. curcas* oil composition is dominated by unsaturated fatty acids, mostly oleic and linoleic fatty acids, which represent 76.5% of the oil. The high unsaturated degree contributes for the low oxidation stability, together with the high FFA content, since it is known that FFA can significantly affect the oxidation stability of the oil [15]. Comparing to others studies (Table 1), the fatty acid content of the Indonesian *J. curcas* oil was found to be similar to the one from Malaysia [27], Nigeria [4] and Brazil [28].

Table 1
Composition and other properties of raw *Jatropha curcas* oil and comparison with other studies.

Fatty acid profile	*Jatropha curcas* oil, % *w*/*w*[a)] [Reference]				
	Result		[22][b)]	[4]	[21]
Myristic acid	(C14:0)	–	0.38	–	0.1
Palmitic acid	(C16:0)	14.8	16.0 max	19.5 ± 0.8	14.2
Palmitoleic acid	(C16:1)	0.8	1 – 3.5	–	0.7
Margaric Acid	(C17:0)	–	–	–	0.1
Stearic acid	(C18:0)	7.0	6 – 7	6.8 ± 0.6	7
Oleic acid	(C18:1)	42.9	42 – 43.5	41.3 ± 1.5	44.7
Linoleic acid	(C18:2)	33.6	33 – 34.4	31.4 ± 1.2	32.8
Linolenic acid	(C18:3)	1.0	>0.80	–	0.2
Arachidic acid	(C20:0)	–	0.2	–	0.2
Gadoleic acid	(C20:1)	–	0.12	–	–
Free fatty acids (wt.%)		18	NA[c)]	1.76	2.23
Iodine value (cg I_2 g^{-1})		99.3	NA	105.2	103.62

[a)] Percentages might not total 100% due to rounding.
[b)] Refined, bleached, and deodorized Jatropha curcas oil was used.
[c)] NA: not av

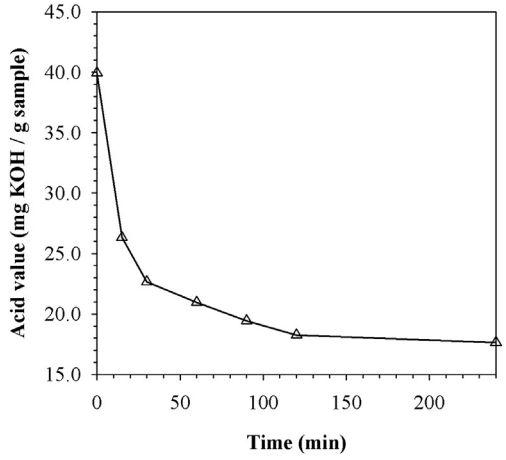

Fig. 2. Progress of the esterification reaction, monitored in terms of acid value.

3.2. Acid oil esterification

In order to determine the optimum time for the esterification reaction, the reaction was monitored at different time intervals in terms of acid value and the results are shown in Fig. 2.

The high acid value throughout the reaction relates to the presence of sulfuric acid in the reaction media [10]. We can observe that after 120 min of reaction the acid value reaches its minimum; therefore, this was considered to be the optimum reaction time, which was used for the following experiments.

After conducting the esterification reaction, removing the acid by settling and the excess alcohol by vacuum distillation, the product presented an acid value of 1.6 mg KOH/g sample which is equivalent to 0.8% *w/w* FFA, being within the requirements to conduct alkali transesterification. The results are in agreement with the ones of Kumar Tiwari et al. [13]. The analysis of the esterified oil by gas chromatography showed that, after the esterification, the oil contained 32.5% *w/w* of fatty acid methyl esters, meaning that both acid esterification and transesterification occurred.

3.3. Biodiesel quality

Following the esterification, the product was submitted to alkali transesterification to obtain the final biodiesel product. After purification, the product was characterized to evaluate its quality, considering 8 key quality parameters; the results are presented in Table 2.

From the results we can observe that three properties, namely, the methyl ester content, the acid value and the oxidation stability, do not agree with the European biodiesel quality standard. The other 5 properties evaluated show a good quality product and agree with the results presented by Sarin et al. [24].

Table 2
Quality parameters of the biodiesel product and requirements according to the European biodiesel standard EN 14214.

Property	Result	EN 14214	Units
Methyl ester content	94.0	>96.5	% *w/w*
Kinematic viscosity @ 40 °C	4.87	3.50–5.00	mm^2/s
Acid value	1.91	0.50	mg KOH/g sample
Iodine value[a]	96.0	<120	g I_2/100 g
Water content	251	<500	mg/kg
Flash point	175	>101	°C
Density @15 °C	879	860–900	kg/m^3
Oxidation stability @ 110 °C	1.37	>8	h

[a] Determined from the methyl ester composition, according to EN 14214.

In what concerns the product purity, inferred by the methyl ester content, we can see that it is less than 3% lower than required for a high quality product. Since this is raw oil, and no additional pretreatment steps were performed rather than acid esterification, it is likely that residual impurities might have led to the results obtained. Note that for raw oil this is a very good result, if we compare with the maximum purity of 83.4% *w/w* obtained after optimization studies on transesterification using raw castor oil, in a study by Dias et al. [3].

Regarding the acid value, in fact, higher values than the limit were also observed; such trends were also verified by Dias et al. [3], where the range of results for this parameter was from 0.92 to 1.87 mg KOH/g using raw oil, being explained by the presence of impurities that difficult the washing stage, causing an increase in the product acid value. The parameter that caused the greatest concern regarding the product quality was in fact the oxidation stability (IP = 1.37) since the product was very far from achieving the required quality (IP > 8 h). The results agree with the ones obtained in several other studies on biodiesel production from oils with high unsaturated fatty acid content [29]. Tang et al. [30] showed values of oxidation stability of biodiesel from different oil sources such as soybean oil (IP = 3.52), cottonseed oil (IP = 6.57), poultry fat (IP = 0.67) and yellow grease (IP = 2.25). In what relates *J. curcas* oil biodiesel, Sarin et al. [24] found an induction period of 3.95 h for this product, which although higher than the one found in the present study, is still much lower than desirable. The difference found is expected since in the mentioned study the oil presented a much higher quality, with a low free fatty acid content, that allowed direct alkali transesterification. The study by Jain and Sharma [19] showed an oxidation stability of jatropha biodiesel of 3.27; in this study, the oil presented a high free fatty acid content (15.4 wt.). The higher FFA content of the oil studied in the present work and the different oil composition and biodiesel properties might explain the variation between the results obtained.

3.4. Influence of synthetic antioxidants on the oxidation stability of biodiesel

In order to determine which would be the best antioxidant and at which concentration, to improve the quality of the biodiesel obtained using raw *J. curcas* oil, a set of experiments was conducted using the 4 most used and effective synthetic antioxidants according to the literature review [15,31]. Due to the lower effectiveness of the natural antioxidants previously reported, compared to the synthetic ones [15], they were not considered in the present study. The study started by evaluating the effectiveness of the antioxidants at a concentration up to 1000 ppm, in agreement to the literature review [15], but due to the fact that some of the antioxidants required higher concentrations, the range of concentrations studied was adjusted, taking into account their effectiveness and behavior towards the increase of the oxidation stability of the product. Therefore, PY concentrations studied varied from 100 to 1000 ppm, TBHQ concentrations studied varied from 500 to 2500 ppm, PG concentrations studied varied from 100 to 1000 ppm and BHT concentrations varied from 500 to 2000 ppm. All the experiments were performed in duplicate.

The results presented in Fig. 3 show that pyrogallol (PY) was the most effective antioxidant, allowing the fulfillment of the biodiesel quality (IP = 8 h) at the lowest concentration, close to 200 ppm. The order of effectiveness was PY > PG > BHT > TBHQ. For all the antioxidants studied, a linear correlation was found between the antioxidant concentration and the induction period. In agreement, predictive models with high coefficients of determination (r^2), varying from 0.9105 to 0.9862 were obtained (Fig. 2); all the regressions were statistically significant, with p value < 0.02, using an F test. To achieve an IP of 8 h, the models estimate that the following concentrations are required for each antioxidant: 204 ppm for PY, 354 ppm for PG, 1722 ppm for BHT and 2047 ppm for TBHQ. The effectiveness of the antioxidant concentration can also be expressed by the "stabilization factor"—F, where $F = IP_x / IP_0$ (induction period with the antioxidant is present

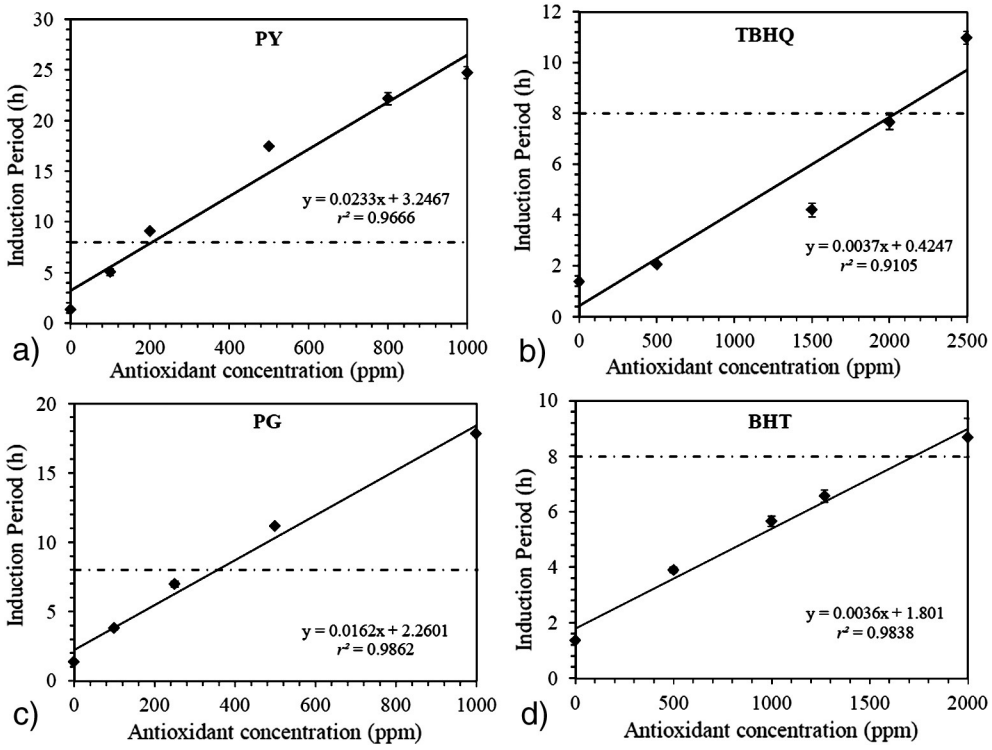

Fig. 3. Influence of antioxidant concentration on biodiesel oxidation stability and linear correlations. Dashed line indicates minimum IP according to EN 14214. a) PY—pyrogallol; b) TBHQ—tert-butyl hydroquinone; c) PG—propyl gallate; and, d) BHT—butylated hydroxytoluene.

and IP_0, IP when antioxidant is absent), as referred by the review of Fattah et al. [31] and expressed in the study by Loh et al. [32]. If we take into consideration the use of 204 ppm (the minimum optimum concentration for PY) and calculating the respective IP for each antioxidant using the linear correlations obtained (IP_x), we can also show the effectiveness of the antioxidants by showing the respective F values at such concentrations, which would be: 5.84 for PY, 4.06 for PG, 1.85 for BHT and 0.85 for TBHQ.

In the review by Jain and Sharma [15], where no studies are reported on *J. curcas* biodiesel oxidation stability, different results for several other sources of oil are presented and most use 1000 ppm of antioxidant aiming the previously imposed limit of 6 h IP; at that concentration, a significant amount of studies also report PY as the best antioxidant.

The results presented by Sarin et al. [17] showed that BHT (although not exactly the same reagent as the one used in the present study) was the most effective antioxidant, at 200 ppm, to increase the oxidation stability to an IP of 6 h (previous requirement of EN14214) of different types of biodiesel, including the one from Jatropha (initial IP = 3.95 h) and also that the use of blends with palm oil biodiesel could considerably reduce the antioxidant concentration required. The present study showed that it is possible to use effectively PY as antioxidant at much lower concentrations (<41%, considering the predicted value for the IP of 6 h), without any other blend. A further study by Jain and Sharma [19] showed the need to use 100 ppm to reach an IP of 6 h using jatropha biodiesel with an IP of 3.27; in this case the model predicts that a close concentration, of 118 ppm, would be required to achieve the previous 6 h specification. This is a very good result if we take into consideration the significantly lower initial IP of the studied biodiesel (1.37).

The good results obtained with PY agree with what is reported by Rizwanul Fattah et al. [31], being attributed to its higher number of labile hydrogen compared to other less effective phenolic antioxidants (such as BHA, BHT and TBHQ). Since phenolic antioxidants are free radical terminators, the existence of highly labile hydrogen, more easily abstracted by a peroxyl radical than an ester hydrogen, forms a stable free radical antioxidant or a radical that further reacts to form a stable molecule (resistant to the chain oxidation process) [31,33], which has a great relevance in the effectiveness of the antioxidant. As both PY and PG present high number of labile hydrogen, the differences between the results using both antioxidants might be related to the poor solubility that PG has in vegetable oil derivatives [31,33].

In order to validate the predictive linear models obtained, experiments were conducted with each antioxidant at concentrations to achieve an IP between 6 and 10 (close to the 8 h limit imposed by EN 14214:2014) and the experimental results were compared to the ones obtained by the models, being presented in Table 3.

The validation of the results reflects the high accuracy of the models in predicting the IP, meaning that the obtained models might be further used to estimate the concentrations required for each antioxidant.

4. Conclusions

Biodiesel was produced from high free fatty acid raw *J. curcas* oil (around 18% *w/w*) using acid esterification followed by conventional alkali transesterification. The product showed generally a good quality and the very low oxidation stability (Induction Period of 1.37 h) was the highest concern, being very far from the standard limit of 8 h, imposed by EN 14214:2014.

Table 3
Validation of the model: experimental and predicted IP values for each antioxidant studied.

Antioxidant	Concentration (mg L^{-1})	Predicted IP	Experimental IP	RPD (%)[a]
Pyrogallol	300	10.24	10.40	1.56
Tert-butyl hydroquinone	1750	7.01	6.90	1.57
Propyl gallate	220	5.82	6.04	3.78
Butylated hydroxytoluene	1500	7.18	7.23	0.65

[a] RPD—relative percentage difference to the predicted value.

The study on the use of 4 synthetic antioxidants allowed obtaining statistically significant predictive models, which considered a linear correlation between each antioxidant concentration and the induction period (IP).

Pyrogallol (PY) showed the best results and according to the validated models, it was estimated that the use of 204 ppm of PY in biodiesel obtained from raw *J. curcas* oil could increase the IP to the value required according to EN14214:2014. The results showed the following rank, in terms of effectiveness: PY > propyl gallate (pg) > butylated hydroxytoluene (BHT) > tert-butyl hydroquinone (TBHQ).

The study demonstrated that biodiesel could be effectively produced from raw *J. curcas* oil and that the quality problems associated with the lower oxidation stability could be overcome by the use of synthetic antioxidants, from which PG has shown to be, technically, the most promising.

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