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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.

Keywords: Raw oil; jatropha; oxidation stability; synthetic antioxidants.

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 a 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).

$$R_1COOH + CH_3OH \xrightleftharpoons{\text{acid}} R_1COOCH_3 + H_2O \quad (1)$$

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 instances, 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 showed 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].

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 *Jatropha 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

134 studies were found on the evaluation of biodiesel production from acid raw *Jatropha*
135 *curcas* oil as well as on the oxidation of the derived biodiesel.
136 In agreement with what was previously stated, the objective of the present work was to
137 evaluate the influence of the most effective and used synthetic antioxidants, namely PY,
138 PG, TBHQ and BHT, on the oxidation of biodiesel obtained from acid raw *Jatropha*
139 *curcas* L. oil. For that purpose, biodiesel was synthetized directly from raw oil using a
140 two-step process (acid esterification followed by alkali transesterification), purified,
141 characterized according to EN14214 and after the oxidation stability studies were
142 conducted considering the use of four synthetic antioxidants at different concentrations
143 (from 100 to 2500 ppm).
144
145
146 **2. Materials and Methods**
147
148 2.1 Materials
149 Raw *Jatropha curcas* oil was purchased from PT Pura Green Energy, Indonesia.
150 Methanol was supplied by VWR (brand AnalaR NORMAPUR), sulfuric Acid 97% was
151 supplied by VWR (Merck, EMSURE® ISO) and Sodium Hydroxide powder 97% was
152 supplied by Sigma Aldrich (reagent grade). Sodium Sulfate anhydrous pro analysis was
153 supplied by Merck KGaA. Regarding the synthetic antioxidants, the commercial
154 Baynox Plus®, which has as active ingredient Butylated hydroxytoluene (BHT), was
155 from LANXESS, Propyl gallate was from SAFC (Sigma-Aldrich), Tert-
156 Butylhydroquinone (TBHQ) was from Aldrich (Sigma-Aldrich), and Pyrogallol was
157 from Fluxa (Sigma-Aldrich). All the antioxidants used were solid powder reagents. All

158 chemicals used for the oil and biodiesel characterization (2.2.3) were of pro analysis
159 grade.
160
161 2.2 Methods
162 2.2.1. Esterification of raw *Jatropha curcas* oil
163 The reaction was performed in a three neck round-bottom glass flask (1 L), equipped
164 with a water controlled condenser and a magnetic stirrer, that was immersed in a
165 thermostatic bath. A series of batch experiments using 500 mL of oil were conducted to
166 obtain 2 L, for use in the characterization and oxidation stability studies. In the study by
167 Kumar Tiwari et al. [13], the optimum reaction conditions to reduce the FFA content of
168 *Jatropha curcas* oil from 14 % to less than 1 % were: ~ 3 % w/w of H_2SO_4 (relative to
169 the oil), 0.28 V/V of methanol (relative to the oil), ~ 90 min of reaction time and
170 temperature of 60 ˚C. Dias et al.[10] selected as optimum esterification conditions to
171 reduce the acid value of waste lard from around 7% to acceptable values for
172 transesterification the following: 2.0 wt.% H_2SO_4, 6:1 methanol:fat molar ratio, 5 h
173 reaction time and temperature of 65 ºC. Taking into account the mentioned studies, the
174 following procedure was conducted: sulfuric acid (3 wt.%) was dissolved in methanol
175 (20 % V/V relative to oil) and then poured into the reactor which already had the raw
176 oil, at 65 ºC. The reaction temperature was maintained at 65 ˚C and a vigorous magnetic
177 stirring was performed.
178 To determine the optimum reaction time, the reaction was conducted for 4 h and the
179 acid value was monitored at different time intervals, by removing 2 mL of sample from
180 the reactor each time and further analyzing the acid value (2.2.3). After the end of the
181 reaction, the products were poured into a separation funnel to separate the oil phase

182 from the water/acid/alcohol phase; settling lasted 12 h. The oily phase, named mixture
183 (mixture of *Jatropha curcas* oil and biodiesel) was then submitted to vacuum
184 distillation (using a rotary evaporator) at 65 ˚C, using a maximum vacuum of 200 mbar,
185 to recover the excess of methanol used. The acid value was determined to confirm the
186 effectiveness of the reaction and the absence of residual sulphuric acid.
187
188 2.2.2 Transesterification of the mixture
189 The reaction flask and setup was similar to the one used for the acid esterification
190 (2.2.1). Sodium hydroxide (1% w/w) was dissolved in methanol (6:1 molar ratio relative
191 to oil) and then poured into the reactor that already had the mixture that resulted from
192 2.2.1. Reaction was performed at 60 ˚C, during 90 min, using vigorous stirring, taking
193 into account the results from Encinar et al. [25] and Dias et al. [10]. After the end of the
194 reaction, the products were poured into the separation funnel to separate the biodiesel
195 phase and the glycerol phase; settling lasted 2 h. The removal of methanol in excess
196 both from the biodiesel and the glycerol phase was also performed by vacuum
197 distillation at 65 ˚C, at a maximum vacuum of 200 mbar (using a rotary evaporator).
198 Biodiesel was further purified by acid and water washing and dried using an anhydrous
199 salt as follows. Biodiesel was washed one time using 50% V/V (relative to oil) of an
200 hydrochloric acid solution (0.5% V/V), to neutralize the catalyst, and then repeatedly
201 with 100% V/V (relative to oil) of distilled water until the pH of the washing water was
202 close to the pH of the distilled water (clear water). Small amounts of sodium chloride
203 were slowly added to break the emulsion, when appeared during washing, being
204 removed in the subsequent water washing step. After water washing, the residual
205 biodiesel water was absorbed by using 25 % w/w of anhydrous sodium sulfate, that was

206 added to the product, vigorous stirred during 10 min and left settling overnight. The
207 biodiesel was finally filtered by vacuum to obtain the final product. To prevent
208 oxidation, the product was left in the freezer at -20 ºC.
209
210 2.2.3. Oil and biodiesel characterization
211 *Jatropha curcas* oil was characterized considering: the acid value, by volumetric
212 titration as reported in NP EN ISO 660:2002; the water content, by coulometric Karl
213 Fischer titration, according to ISO 8534:996; the iodine value, by volumetric titration
214 using Wijs reagent, according to the standard ISO 3961:1996; and, oxidation stability at
215 110 °C (using 837 Biodiesel Rancimat® from Metrohm). Oil composition was obtained
216 from the methyl ester profile evaluated by GC analysis (DANI 1000 Gas
217 Chromatography) according to NP EN 5508:1996 and EN 14103:2003.
218 The following quality parameters were determined in the biodiesel product: density, by
219 a hydrometer method, according to ISO 3675:1998; kinematic viscosity, using capillary
220 viscometers, according to ISO 3104:1994; flash point, using a rapid equilibrium closed
221 cup tester, according to ISO 2160:1998; methyl ester content, using GC analysis
222 according to EN 14103:2003; acid value, according to EN 14104:2003 and oxidation
223 stability at 110 ºC, according to EN 14112:2003 (using 837 Biodiesel Rancimat® from
224 Metrohm).
225 All the results are presented as mean values with relative percentage differences always
226 less than 2 % of the mean.
227
228 2.2.4. Influence of synthetic antioxidants on the oxidation stability of biodiesel
229 The following antioxidants were used: Pyrogallol (PY), Tert-Butyl Hydroquinone
230 (TBHQ), Propyl Gallate (PG), and Butylated hydroxytoluene (BHT).

231 The antioxidant was accurately weighted, added to 100 mL of the biodiesel obtained
232 from 2.2.2 and dissolved by mixing to obtain the concentrated solutions (up to 2500
233 ppm, depending upon the antioxidant). The solutions were further diluted with biodiesel
234 to obtain the range of antioxidant concentrations studied (100 – 2500 ppm).
235 In agreement with the standard EN 14104:2003, 3 g of sample were used in all cases to
236 measure the oxidation stability. The measurement was conducted in duplicate for each
237 antioxidant, at each concentration. Following the study, linear correlations were found
238 between the concentration of antioxidant and the induction period. For each correlation,
239 the linear regression statistical parameters were determined, including the determination
240 coefficient (r^2) and the probability value (p), using an F test.
241 To validate the results obtained from the models, experiments were also performed in
242 duplicate.

243

244

245 **3 Results and discussion**

246 3.1 Oil characterization

247

248 The initial acid value of *Jatropha curcas* oil was 35.36 mg KOH/g sample (around 18%
249 w/w of free fatty acids), the iodine value was 99.3 g I_2/100 g and the water content was
250 0.252 % w/w. Taking into account the very high acid value, a pre-treatment was
251 required in order to enable biodiesel production through alkali methanolysis. The iodine
252 value relates to oil composition and indicates the fulfillment of the biodiesel standard
253 that imposes a value < 120 g I_2/100 g. Since acid esterification was performed as pre-
254 treatment, no dehydration of the oil was performed.

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

263 It can be observed that *Jatropha curcas* oil composition is dominated by unsaturated
264 fatty acids, mostly oleic and linoleic fatty acids, which represent 76.5% of the oil. The
265 high unsaturated degree contributes for the low oxidation stability, together with the
266 high FFA content, since it is known that FFA can significantly affect the oxidation
267 stability of the oil [15]. Comparing to others studies (Table 1), the fatty acid content of
268 the Indonesian *Jatropha curcas* oil was found to be similar to the one from Malaysia
269 [27], Nigeria [4] and Brazil [28].

270

271 3.2. Acid oil esterification

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

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

279 After conducting the esterification reaction, removing the acid by settling and the excess
280 alcohol by vacuum distillation, the product presented an acid value of 1.6 mg KOH/g
281 sample which is equivalent to 0.8 % w/w FFA, being within the requirements to
282 conduct alkali transesterification. The results are in agreement with the ones of Kumar
283 Tiwari et al. [13]. The analysis of the esterified oil by Gas Chromatography showed
284 that, after the esterification, the oil contained 32.5 % w/w of Fatty Acid Methyl Esters,
285 meaning that both acid esterification and transesterification occurred.
286
287 3.3 Biodiesel quality
288 Following the esterification, the product was submitted to alkali transesterification to
289 obtain the final biodiesel product. After purification, the product was characterized to
290 evaluate its quality, considering 8 key quality parameters; the results are presented in
291 Table 2.
292 From the results we can observe that three properties, namely, the methyl ester content,
293 the acid value and the oxidation stability, do not agree with the European biodiesel
294 quality standard. The other 5 properties evaluated show a good quality product and
295 agree with the results presented by Sarin et al. [24].
296 In what concerns the product purity, inferred by the methyl ester content, we can see
297 that it is less than 3% lower than required for a high quality product. Since this is raw
298 oil, and no additional pre-treatment steps were performed rather than acid esterification,
299 it is likely that residual impurities might have led to the results obtained. Note that for
300 raw oil this is a very good result, if we compare with the maximum purity of 83.4 %
301 w/w obtained after optimization studies on transesterification using raw castor oil, in a
302 study by Dias et al.[3].

303 Regarding the acid value, in fact, higher values than the limit were also observed; such
304 trends were also verified by Dias et al. [3], where the range of results for this parameter
305 was from 0.92 to 1.87 mg KOH/g using raw oil, being explained by the presence of
306 impurities that difficult the washing stage, causing an increase in the product acid value.
307 The parameter that caused the greatest concern regarding the product quality was in fact
308 the oxidation stability (IP = 1.37) since the product was very far from achieving the
309 required quality (IP > 8 h). The results agree with the ones obtained in several other
310 studies on biodiesel production from oils with high unsaturated fatty acid content [29].
311 Tang et al. [30] showed values of oxidation stability of biodiesel from different oil
312 sources such as soybean oil (IP = 3.52), cottonseed oil (IP = 6.57), poultry fat (IP =
313 0.67) and yellow grease (IP = 2.25). In what relates *Jatropha curcas* oil biodiesel, Sarin
314 et al. [24] found an induction period of 3.95 h for this product, which although higher
315 than the one found in the present study, is still much lower than desirable. The
316 difference found is expected since in the mentioned study the oil presented a much
317 higher quality, with a low free fatty acid content, that allowed direct alkali
318 transesterification. The study by Jain and Sharma [19] showed an oxidation stability of
319 jatropha biodiesel of 3.27; in this study, the oil presented a high free fatty acid content
320 (15.4 wt.). The higher FFA content of the oil studied in the present work and the
321 different oil composition and biodiesel properties might explain the variation between
322 the results obtained.
323
324 3.4. Influence of synthetic antioxidants on the oxidation stability of biodiesel
325 In order to determine which would be the best antioxidant and at which concentration, to
326 improve the quality of the biodiesel obtained using raw *Jatropha curcas* oil, a set of
327 experiments was conducted using the 4 most used and effective synthetic antioxidants

328 according to the literature review [15, 31]. Due to the lower effectiveness of the natural
329 antioxidants previously reported, compared to the synthetic ones [15], they were not
330 considered in the present study. The study started by evaluating the effectiveness of the
331 antioxidants at a concentration up to 1000 ppm, in agreement to the literature review [15],
332 but due to the fact that some of the antioxidants required higher concentrations, the range
333 of concentrations studied was adjusted, taking into account their effectiveness and
334 behavior towards the increase of the oxidation stability of the product. Therefore, PY
335 concentrations studied varied from 100 to 1000 ppm, TBHQ concentrations studied
336 varied from 500 to 2500 ppm, PG concentrations studied varied from 100 to 1000 ppm
337 and BHT concentrations varied from 500 to 2000 ppm. All the experiments were
338 performed in duplicate.
339 The results presented in Fig. 2 show that Pyrogallol (PY) was the most effective
340 antioxidant, allowing the fulfillment of the biodiesel quality (IP = 8 h) at the lowest
341 concentration, close to 200 ppm. The order of effectiveness was PY > PG > BHT >
342 TBHQ. For all the antioxidants studied, a linear correlation was found between the
343 antioxidant concentration and the induction period. In agreement, predictive models
344 with high coefficients of determination (r^2), varying from 0.9105 to 0.9862 were
345 obtained (Fig. 2); all the regressions were statistically significant, with p value < 0.02,
346 using an F test. To achieve an IP of 8 h, the models estimate that the following
347 concentrations are required for each antioxidant: 204 ppm for PY, 354 ppm for PG,
348 1722 ppm for BHT and 2047 ppm for TBHQ. The effectiveness of the antioxidant
349 concentration can also be expressed by the "stabilization factor" - F, where $F = IP_x/IP_0$
350 (IP_x – induction period when the antioxidant is present and IP_0, IP when antioxidant is
351 absent), as referred by the review of Fattah et al. [31] and expressed in the study by Loh
352 et al. [32]. If we take into consideration the use of 204 ppm (the minimum optimum

353 concentration for PY) and calculating the respective IP for each antioxidant using the
354 linear correlations obtained (IP_x), we can also show the effectiveness of the antioxidants
355 by showing the respective F values at such concentrations, which would be: 5.84 for
356 PY, 4.06 for PG, 1.85 for BHT and 0.85 for TBHQ.
357 In the review by Jain and Sharma [15], where no studies are reported on *Jatropha*
358 *curcas* biodiesel oxidation stability, different results for several other sources of oil are
359 presented and most use 1000 ppm of antioxidant aiming the previously imposed limit of
360 6 h IP; at that concentration, a significant amount of studies also report PY as the best
361 antioxidant.
362 The results presented by Sarin et al. [17] showed that BHT (although not exactly the
363 same reagent as the one used in the present study) was the most effective antioxidant, at
364 200 ppm, to increase the oxidation stability to an IP of 6 h (previous requirement of
365 EN14214) of different types of biodiesel, including the one from Jatropha (initial IP =
366 3.95 h) and also that the use of blends with palm oil biodiesel could considerably reduce
367 the antioxidant concentration required. The present study showed that it is possible to
368 use effectively PY as antioxidant at much lower concentrations (< 41%, considering the
369 predicted value for the IP of 6 h), without any other blend. A further study by Jain and
370 Sharma [19] showed the need to use 100 ppm to reach an IP of 6 h using jatropha
371 biodiesel with an IP of 3.27; in this case the model predicts that a close concentration,
372 of 118 ppm, would be required to achieve the previous 6 h specification. This is a very
373 good result if we take into consideration the significantly lower initial IP of the studied
374 biodiesel (1.37).
375 The good results obtained with PY agree with what is reported by Rizwanul Fattah et al.
376 [31], being attributed to its higher number of labile hydrogen compared to other less
377 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.

Conclusions

Biodiesel was produced from high free fatty acid raw *Jatropha 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.

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 *Jatropha 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 *Jatropha 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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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

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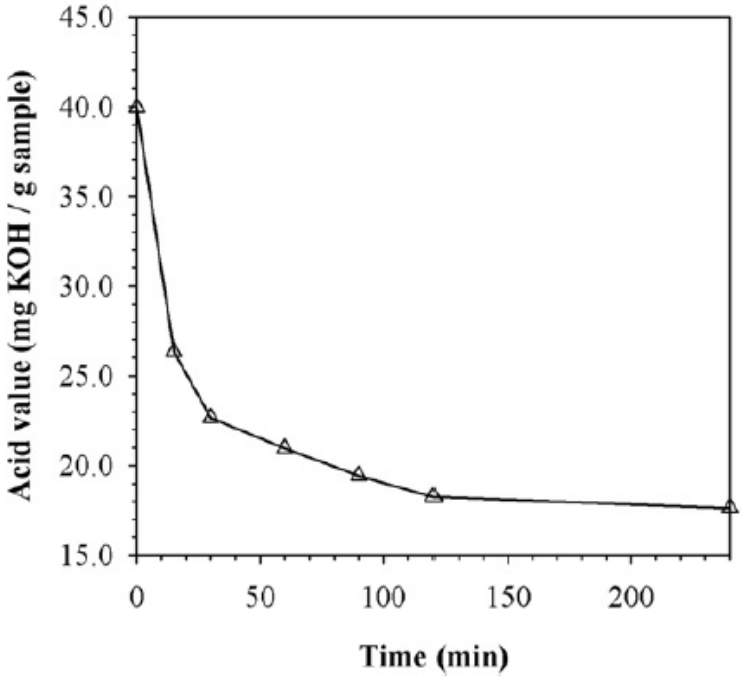
500 Fig.1. Primary oxidation reaction mechanism.



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

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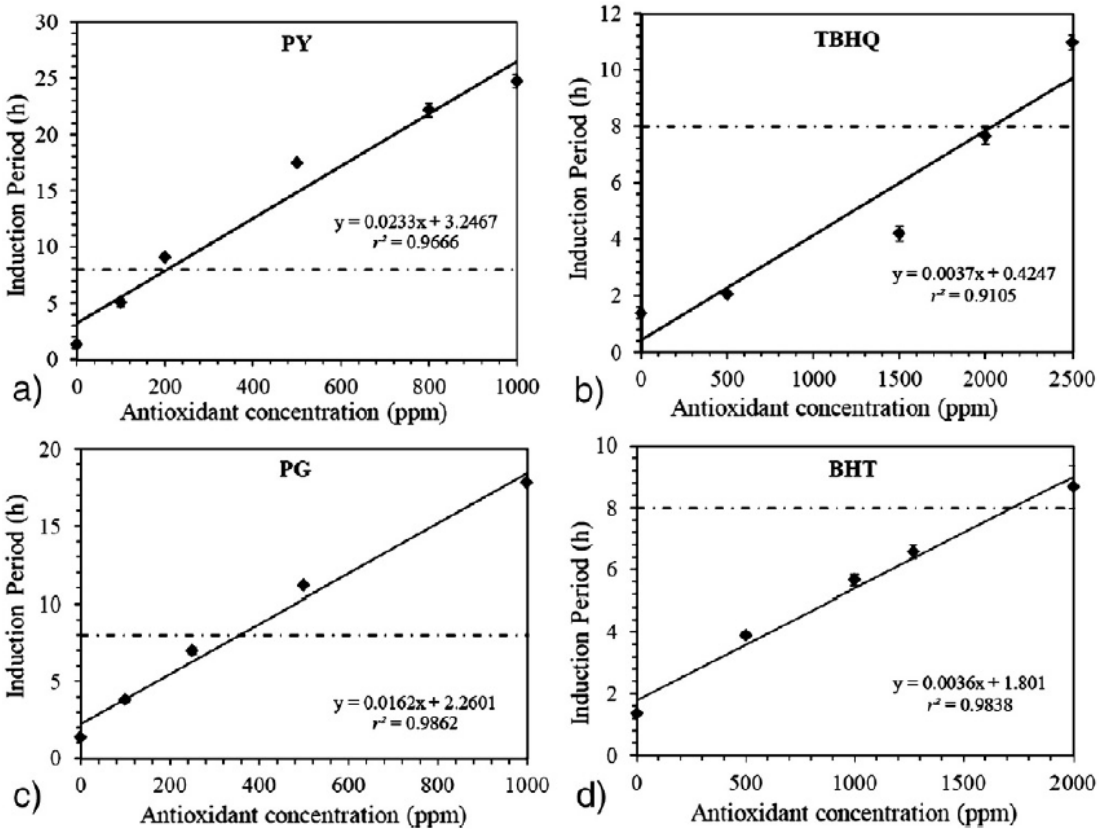

Fig.3. Influence of antioxidant concentration on biodiesel oxidation stability and linear correlations. Dashed line indicates minimum IP according to EN 14214. a) PY – Pyrogallol; b) TBHQ – Tert-butyl hydroquinone; c) PG – Propyl Gallate; and, d) BHT - Butylated hydroxytoluene

517 Table 1 Composition and other properties of raw Jatropha curcas oil and comparison
518 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 available.

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520 Table 2 Quality parameters of the biodiesel product and requirements according
521 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.

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527 Table 3 Validation of the model: experimental and predicted IP values for each
528 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.

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