Korean J. Chem. Eng., 36(8), 1298-1304 (2019)
DOI: 10.1007/s11814-019-0287-x

pISSN: 0256-1115
eISSN: 1975-7220

Cottonseed biodiesel oxidative stability in mixture with natural antioxidants

João Paulo Almeida Freitas*,†, Fernanda Rocha Morais França, Maria Susana Silva***, Richard James Toms****, and Gabriel Francisco da Silva*****

*Chemical Engineering Department, Federal University of Sergipe, Sergipe, Brazil
**Chemical Engineering Department, Federal University of Alagoas, Alagoas, Brazil
***Oil and Gas Research Center, Chemical Engineering Department, Federal University of Sergipe, Sergipe, Brazil
****Centre for Environment and Sustainability, University of Surrey, Surrey, United Kingdom
*****Laboratory of Alternative Technologies, Chemical Engineering Department, Federal University of Sergipe, Sergipe, Brazil
(*Received 21 February 2019 • accepted 27 April 2019*)

Abstract−We evaluated the antioxidant power of the natural extracts catechin, curcumin and quercetin on the oxidative stability of methylic cottonseed oil biodiesel by applying the simplex-centroid augmented mixture experimental design, in addition to verifying the existence and the type of synergy among the extracts. The oxidative stability was measured using Rancimat method (EN 14112) for biodiesel added with 1,000, 2,000 and 3,000 ppm of additives, and compared with the commercial synthetic antioxidant butyl hydroxyanisole at the same concentrations. All additives had a positive effect on biodiesel oxidative stability; in addition, catechin and quercetin proved to be more efficient than the synthetic antioxidant, whereas curcumin showed similar results. The results also revealed that the interactions among the extracts varied not only with the proportion in which they were added to the biodiesel, but also with the total concentration, so that the increase in concentration reduced the magnitude of the synergistic effect.

Keywords: Antioxidant, Biodiesel, Biofuel, Experimental Design, Oxidative Stability

INTRODUCTION

Biodiesel is a renewable, biodegradable and non-toxic fuel that is generally synthesized by alkali or acid transesterification reaction of vegetable oils with short-chain alcohols [1]. Its properties resemble those of petroleum diesel and they are miscible in any proportions [2].

The unsaturated bonds in the fatty acids chain are susceptible to oxidation. The same occurs with biodiesel, which directly affects its long-term storage and consequently its quality and efficiency [3]. The oxidation proceeds at different rates depending on the number and position of the unsaturated bonds. The positions allylic to the double bonds in the fatty acid chains are those susceptible to oxidation. Bis-allylic are even more susceptible to oxidation than allylic positions [2].

Simic [4] defines three steps for the oxidative process: initiation →free radicals are formed due to the withdrawal of a hydrogen atom molecule by an atomic oxygen, an excited state or another free radical (X in Eq. (1)). Then, oxygen and the free radical react to form a peroxy radical (Eqs. (1) and (2)); propagation→The radicals formed in Eqs. (1) and (2) withdraw hydrogen from other molecules to form more free radicals and hydroperoxides, primary oxidation products (ROOH) (Eq. (3)). The chain reaction can be long, once a sigle free radical can form many hydroperoxide molecules; termination→A free radical reacts with another free radical to form a stable compound (Eq. (4)). The reaction between a peroxy radical and an antioxidant is a particular termination reaction.

$$X+RH_2 \rightarrow \bullet RH+XH \quad (1)$$

$$O_2+\bullet RH \rightarrow HROO\bullet \quad (2)$$

$$HROO\bullet+RH_2 \rightarrow HROOH+\bullet RH \quad (3)$$

$$2HROO\bullet \rightarrow HROORH+O_2 \quad (4)$$

The use of antioxidants helps to reduce or inhibit the oxidative process, avoiding chain reaction propagation. Furthermore, some of these additives when used together and in certain proportions may have different effects than when used separately, the so-called synergistic effect. It can be positive when one antioxidant contributes to the action of the other; negative, when one inhibits the other; or additive when there is no combined effect [5]. When positive, it is possible to reduce costs by using a mixture of additives which may be able to meet the required specifications at lower concentrations. However, it is not easy to determine the ideal proportions for each combination. Studies have been developed to optimize the proportions and concentrations to maximize the synergistic effect among specific antioxidants [6-8].

Commercially, synthetic antioxidants, although generally toxic and non-biodegradable, are widely used in biodiesel to increase its oxidative stability. Yet, natural antioxidants have also been investigated as possible substituents since they are biodegradable and non-toxic [9,10]. Examples of such natural antioxidants are catechin (CAT), curcumin (CUR) and quercetin (QUE), all with a polyphenolic structure and proven antioxidant activity in living beings.

†To whom correspondence should be addressed.
E-mail: jp_a_f@outlook.com
Postal address: Marechal Rondon Avenue, Jardim Rosa Elze, São Cristóvão-SE, zip code: 49100-000, Brazil

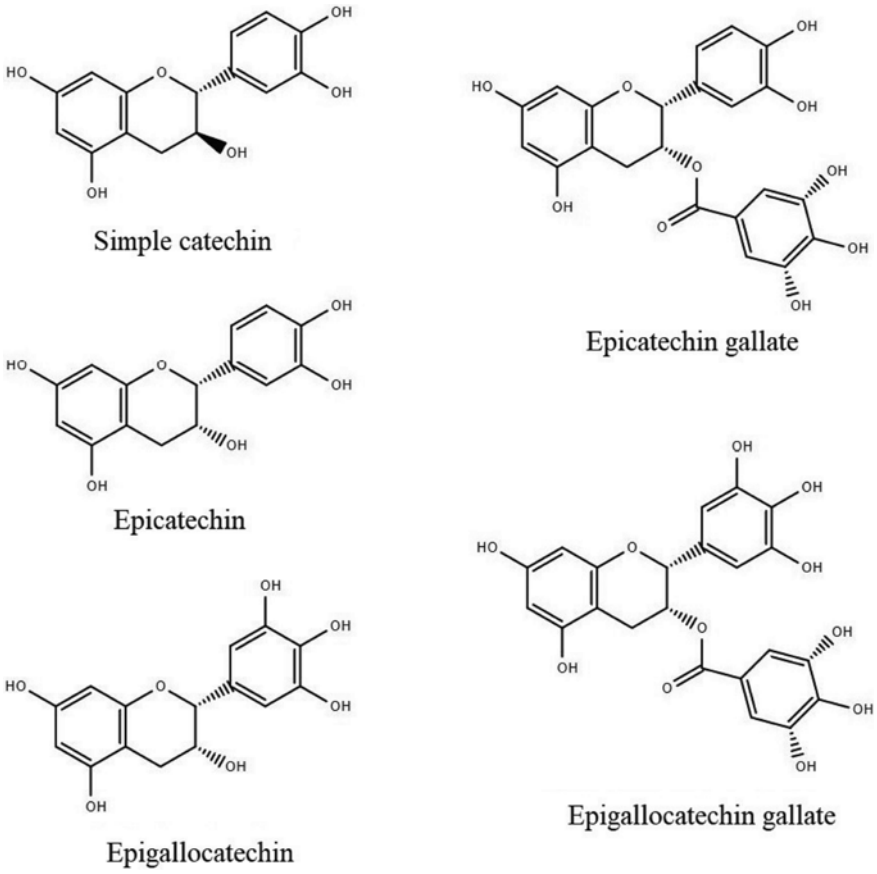

Fig. 1. Chemical structure of the five types of CAT.

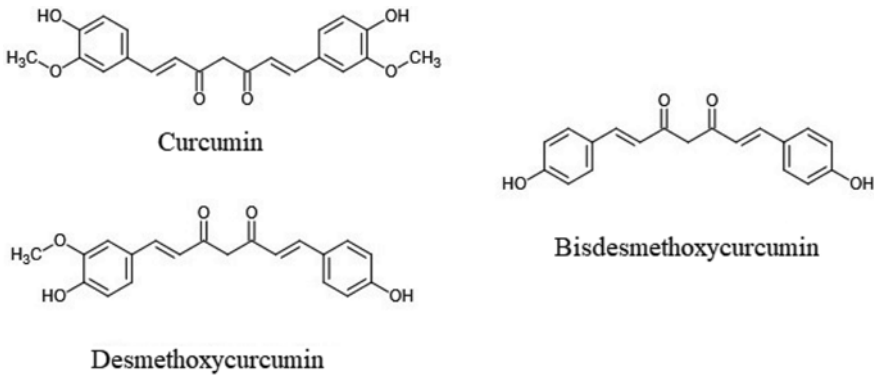

Fig. 2. Chemical structure of the main curcuminoids in *Curcuma longa L.*.

However, their use within the biodiesel industry is scarce [11-13].

CAT belongs to a group of polyphenols that are a powerful antioxidant and free metal scavenger. Its main sources are green tea, dark chocolate, blackberries and black tea [14-16]. There are five types of catechin (Fig. 1), all of them comprising a similar molecular structure that enables them to stabilize free radicals and inhibit oxidative process. The use of CAT as an antioxidant in biodiesel has not yet been reported in the literature. However, studies have identified that its presence within moringa plant extracts demonstrates its potential to be used as an antioxidant additive in biodiesel [17].

CUR occurs naturally in *Curcuma longa L.* and, in its powdered form, is better known as turmeric [18]. It is composed of curcumin (59-71%), desmethoxycurcumin (25-29%) and bisdesmethoxycurcumin (4-12%) (Fig. 2), all of them with antioxidant potential [19]. Due to their phenolic nature, curcuminoids have been studied as antioxidant additives in various systems [12]. Use in biodiesel has been little reported, despite the antioxidant potential being already proven [9].

QUE is one of the most present flavonoids in the human diet and it can be found in onions, broccoli and apples [20,21]. Although there are few studies on the antioxidant power of QUE,

one can infer, by its molecular structure, that its antioxidant properties can also be used in biofuels [22]. Its use to inhibit oxidation in vegetable oils has been reported in the literature [23]. Yet, despite this evidence, its use as an antioxidant for biodiesel has not yet been explicitly documented.

Despite the scarcity of studies on the application of these natural extracts in biodiesel, the results presented so far suggest that all three of the aforementioned extracts show great potential as an additive to improve biodiesel oxidative stability and to replace synthetic antioxidants. In addition, the combination of the three antioxidants can also improve their activity in inhibiting oxidative process by synergistic effect. To the best of our knowledge, this is the first time the synergistic effect among three antioxidants in biodiesel has been reported in the literature.

The objective of this study was to evaluate the antioxidant power of CAT, CUR and QUE separately and in binary and ternary assemblies at 1,000, 2,000 and 3,000 ppm of total concentration, using the simplex-centroid augmented experimental design, as well as verifying the existence and type of synergy between the extracts and compare the results to commercial synthetic antioxidant butyl hydroxyanisole (BHA).

MATERIAL AND METHODS

1. Biodiesel Synthesis and Purification

The biodiesel was synthesized via transesterification reaction of cottonseed oil using analytical grade methanol and potassium hydroxide as catalyst. Cottonseed oil was obtained in the local market. Reaction conditions were based on the optimization study of Onukwuly et al. [24] using 6 : 1 methanol/oil molar ratio and 0.6% (mass) of potassium hydroxide. The reaction mixture was heated under 55 °C and slowly stirred for one hour. Biodiesel was separated from glycerol by decantation in a separatory funnel. After separation, the esters were washed with deionized water at 90 °C to remove remaining methanol and catalyst until neutral pH was achieved. Biodiesel was dried at 100 °C for 3 hours to remove water.

2. Antioxidants

The three natural extracts were obtained from a local compounding pharmacy to ensure high purity: CAT (72.7%, 52.6% are epigallocatechin gallate); CUR (96.68% of curcuminoids); and QUER (97.22%), all produced by Florien. BHA (Merck) was used to compare the results.

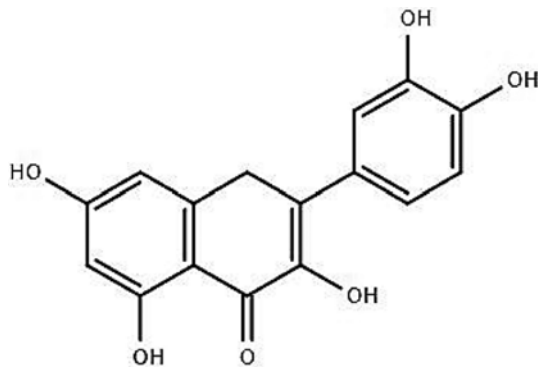

Fig. 3. Chemical structure of QUE.

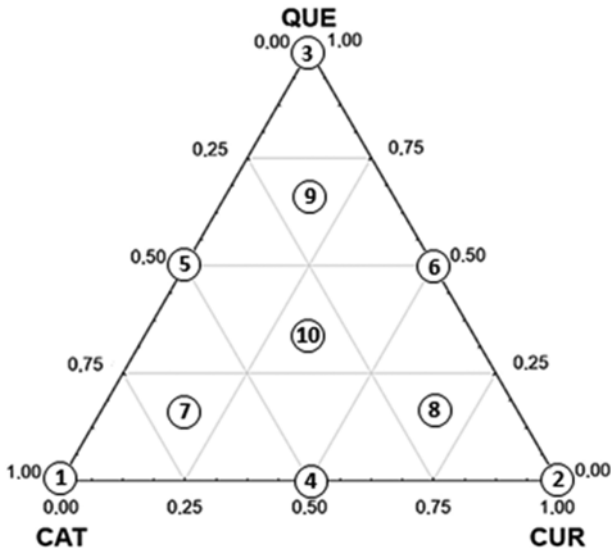

Fig. 4. Simplex-centroid augmented experimental design for three components.

3. Oxidative Stability Tests

The tests were carried out at 110 °C according to European standard EN 14112 for neat biodiesel and biodiesel added with antioxidants. The concentration for each run was according to experimental design at 1,000, 2,000 and 3,000 ppm (total).

4. Mixture Experimental Design

The simplex-centroid augmented design (Fig. 4) was used with three replicates in the central point.

5. Synergy Calculation

The synergistic effect was calculated based on the equation developed by Frankel [5] (Eq. (5)) using the individual effect of each antioxidant. Neat biodiesel was used as control.

$$\%\mathrm{Syn} = \frac{\Delta \mathrm{IP}_{mix} - \Sigma_{i=1}^{n} \Delta \mathrm{IP}_{i}}{\Sigma_{i=1}^{n} \Delta \mathrm{IP}_{i}} \cdot 100 \quad (5)$$

where ΔIP_{mix} is the difference between the sample induction period (IP) (with antioxidants) (IP_{sample}) and the control sample IP ($IP_{control}$) (Eq. (6)); and ΔIP_i is the difference between biodiesel IP with one antioxidant at the same fraction of concentration ($IP_{individual}$) and the IP of the control sample ($IP_{control}$) (Eq. (7)). For

$$\Delta \mathrm{IP}_{mix} = \mathrm{IP}_{sample} - \mathrm{IP}_{control} \quad (6)$$

$$\Delta \mathrm{IP}_{i} = \mathrm{IP}_{individual} - \mathrm{IP}_{control} \quad (7)$$

Thus, it was necessary to perform experiments with the fractions of concentrations of each design (166.67, 333.33, 500, 666.67, 1,333.33 and 1,500 ppm) to determine the antioxidants individual effects in each run.

6. Statistical Analysis

Statistica v.10.0 software was used to analyze data and calculate the coefficients of determination and analysis of variance [25] using a confidence level of 95%. The cubic mathematical model (Eq. (8)) was used for all designs since it takes into account both binary and ternary interactions.

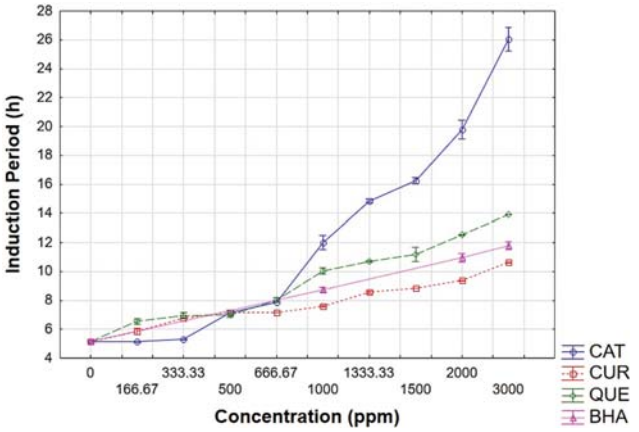

Fig. 5. Results of biodiesel IP (h) for antioxidants used individually.

$$IP=\gamma_1 x+\gamma_2 y+\gamma_3 z+\gamma_4 xy+\gamma_5 xz+\gamma_6 yz+\gamma_7 xyz \quad (8)$$

where IP is the biodiesel IP (hours); x, y and z represent the fractions of CAT, CUR and QUE added to biodiesel, respectively; and γ_i is the coefficients of each term.

RESULTS AND DISCUSSION

1. Antioxidants' Individual Effect on Biodiesel IP

The increase in concentration caused the increase of oxidative stability for all the additives used, as can be observed in Fig. 5.

All three extracts showed antioxidant activity, what was already expected due to their chemical structures and analysis of other studies presented in literature with different systems.

In general, the order of antioxidant power was CAT>QUE> BHA>CUR, which is consistent with their chemical structures (Fig. 1, Fig. 2, Fig. 3 and Fig. 6). The presence of activating groups (electron donors) *ortho* and/or *para* to the hydroxyl group of phenol enhances the antioxidant activity of the compound by inductive effect. Thus, the more electronegative the substituent, the greater the inductive effect in benefit of the antioxidant activity. On the other hand, branched alkyl groups *ortho* to the hydroxyl group of phenol decreases the antioxidant activity, since it enables the molecule to create a stable resonance structure that makes it difficult for the antioxidant to participate in the propagation reactions of the oxidative process [26].

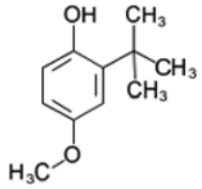

Fig. 6. Chemical structure of BHA.

Thus, in addition to BHA having less hydroxyls than CAT and QUE, it has an *ortho* branched alkyl radical, which reduces its antioxidant activity. CAT, on the other hand, in addition to having the largest number of hydroxyls attached to the aromatic ring among the antioxidants used, it also has some of these hydroxyls in *ortho* position, increasing its antioxidant power. Regarding CUR, it has a *para* deactivating radical, which may justify its lower antioxidant action when compared to the BHA.

Therefore, it is verified that the antioxidant power of CAT, CUR and QUE, which has already been proven in studies with living organisms and in natural extracts for application in biofuels [11-13,27,28], can also be used to inhibit the oxidation process in methylic cottonseed biodiesel. The results revealed that the extracts have great potential for commercial use and possible replacement of synthetic antioxidants.

2. Antioxidants' Combined Effect on Biodiesel IP

Table 2 shows the results for IP and synergy obtained through the simplex-centroid augmented mixture design. It is important to emphasize that the synergistic interaction mechanisms among antioxidants are expected to be complex [29] and their elucidation is

Table 1. Results for IP (h) and synergy (%) obtained through the simplex-centroid augmented experiment design

Assay	Mixtures[a]	1,000 ppm		2,000 ppm		3,000 ppm	
		IP (h)	%Syn	IP (h)	%Syn	IP (h)	%Syn
1	(1; 0; 0)	12.00	-	19.79	-	26.04	-
2	(0; 1; 0)	7.60	-	9.39	-	10.63	-
3	(0; 0; 1)	10.06	-	12.54	-	13.92	-
4	(1/2; 1/2; 0)	6.29	−71.88	14.21	−2.43	18.89	−7.08
5	(1/2; 0; 1/2)	7.41	−41.15	11.43	−14.58	12.75	−22.09
6	(0; 1/2; 1/2)	8.84	−4.29	18.54	14.02	21.86	−2.42
7	(2/3; 1/6; 1/6)	8.59	−28.35	15.08	−24.42	24.66	5.75
8	(1/6; 2/3; 1/6)	8.25	−9.00	9.39	−20.71	13.72	5.94
9	(1/6; 1/6; 2/3)	10.30	45.26	11.72	−10.45	15.98	−4.92
10	(1/3; 1/3; 1/3)	9.98	34.83	12.11	−8.61	18.33	−7.09
11	(1/3; 1/3; 1/3)	9.71	27.27	11.75	−13.35	17.97	−9.63
12	(1/3; 1/3; 1/3)	9.86	31.47	12.03	−9.67	18.21	−7.94
Control	-			5.16			

[a](%CAT; %CUR; %QUE)

Table 2. Relative error (%) of each design based on the cubic mathematical model

Assay	Mixtures[a]	1,000 ppm	2,000 ppm	3,000 ppm
1	(1; 0; 0)	2.82	0.76	1.96
2	(0; 1; 0)	1.39	1.18	2.25
3	(0; 0; 1)	2.05	1.25	1.36
4	(1/2; 1/2; 0)	3.66	1.85	1.50
5	(1/2; 0; 1/2)	4.11	2.36	3.42
6	(0; 1/2; 1/2)	1.36	1.66	1.51
7	(2/3; 1/6; 1/6)	10.41	5.39	7.24
8	(1/6; 2/3; 1/6)	3.90	7.31	4.21
9	(1/6; 1/6; 2/3)	6.40	6.96	2.81
10	(1/3; 1/3; 1/3)	1.44	4.84	3.30
11	(1/3; 1/3; 1/3)	1.30	1.73	1.27
12	(1/3; 1/3; 1/3)	0.22	4.15	2.62
Average relative error		3.25	3.29	2.38
Standard deviation		2.82	2.34	1.91

[a](%CAT; %CUR; %QUE)

beyond the scope of the present work. Although, we will present inferences base on other results as discussed in the literature.

The results obtained with the 1,000 ppm design (Table 1) show that regarding the combined effects, only assays 4 and 5 did not reach the minimum value for oxidative stability of 8 hours for IP required by standard EN 14214. These were also the assays that presented the lowest synergy magnitudes. Still, only the assays with individual effects and positive synergy had better results than synthetic antioxidant BHA (8.75 h), CUR excluded. Both facts point to the importance in choosing the additives and their concentration used in biofuels in order to optimize their properties.

Moreover, the three binary combinations (assays 4, 5 and 6) presented negative synergies, with emphasis on the combinations CAT-CUR (assay 4) and QUE-CUR (assay 5). Assays 7 and 8 also presented negative synergy (emphasis particularly on assay 7), where the amount of CAT was the highest between the aforementioned experiments. It shows that the effect of CAT combined with the other extracts may be opposite to that desired for this concentration, like the findings of Sousa, Moura, Oliveira and Moura [9], who observed that β-carotene had its antioxidant activity reduced by 15% when combined with CUR. Also, regarding assays 9 and 10, where QUE was in greater quantity in the former and equivalent to the other components in the latter, there was positive synergy. Studies have reported the positive synergistic effect of QUE in other systems [30,31], indicating that it may have contributed to this result. Also, another factor that may contribute to the positive synergy is the regeneration of one antioxidant by the other. It happens when the antioxidant with less activity restores the hydrogens donated by the most effective antioxidant, which increases the overall antioxidant activity [32].

All combinations tested in 2,000 ppm design reached the minimum value for oxidative stability established in the resolution (Table 1). However, except for assay 6, all the assays presented negative synergy, with lower magnitude than 1,000 ppm design. Also, among the combined effects, only assay 8 resulted in lower IP than the synthetic antioxidant BHA (10.97 h). Assay 6 showed positive synergy and resulted in IP almost twice as high as BHA's. Thus, although CAT alone had the highest antioxidant effect, it is possible to achieve almost the same result using a combination of CAT and QUE in equal proportions. Yin et al. [33], in consonance with the study of Jia et al. [34], found that CAT compounds, especially epigallocatechin gallate, when used in association with α-tocopherol acts way to prevent its degeneration. They related this result to a possible regeneration of α-tocoferoxil radicals by epigallocatechin gallate. A similar situation may have occurred to result in positive synergy between CAT and QUE.

Regarding 3,000 ppm design, all the combinations reached the minimum value established in norm for oxidative stability, although the majority of the cases had resulted in negative synergy. In addition, it is observed again that the synergistic effect magnitude was smaller than the previous experiments. Thus, one can infer that the increase of concentration reduces the synergetic effect magnitude, which can be related to the saturation of antioxidants in the bulk [9]. Moreover, all the assays presented better results than the synthetic antioxidant BHA (11.80 h), particularly assays 6 and 7, where the IP was two-times higher.

By applying the simplex-centroid augmented experimental design, the cubic models for 1,000, 2,000 and 3,000 ppm designs (Fig. 7, Fig. 8 and Fig. 9 respectively), represented by Eq. (9), Eq. (10) and Eq. (11) respectively, were obtained and the coefficients of determination (R^2) were 93.07%, 97.48% and 98.29% respectively.

$$IP_{1000}=11.67x^{*}+7.71y^{*}+10.27z^{*}-14.49xy^{*}-8.99xz^{*}-5.07yz+84.49xyz \quad (9)$$

$$IP_{2000}=19.64x^{*}+9.28y^{*}+12.38z^{*}-2.03xy+8.91xz+1.34yz-84.50xyz \quad (10)$$

$$IP_{3000}=26.56x^{*}+10.40y^{*}+13.73z^{*}+2.79xy+8.20xz+1.04yz+1.07xyz \quad (11)$$

The terms with asterisks are significant at the level of 95%, according to ANOVA. All linear terms presented positive coefficients, indicating that the extracts positively influence biodiesel's IP. This result shows that x (CAT), y (CUR) and z (QUE) increase

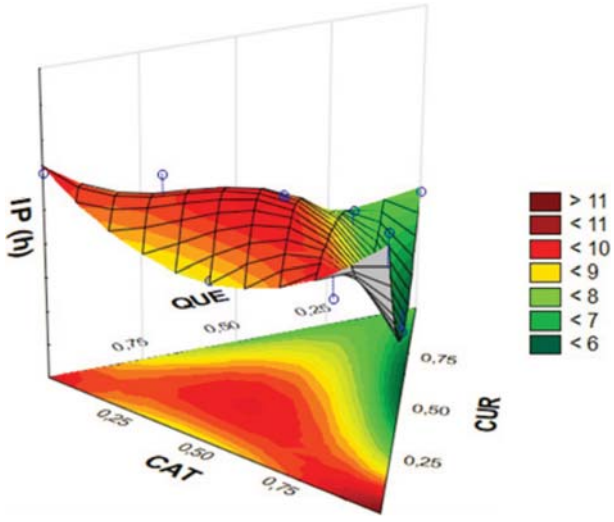

Fig. 7. Region of combination among the extracts CAT, CUR and QUE obtained through Eq. (9) for the induction periods at 1,000 ppm.

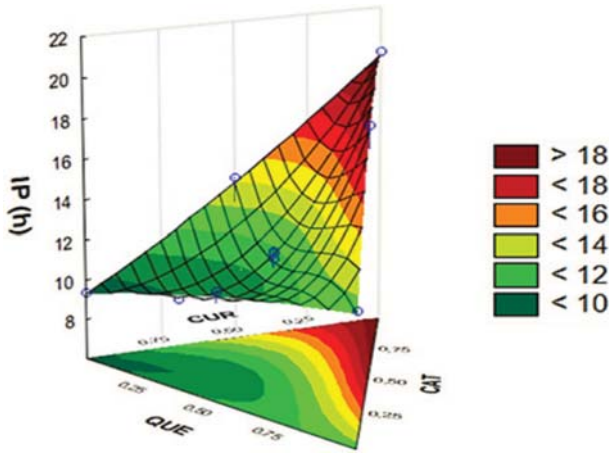

Fig. 8. Region of combination among the extracts CAT, CUR and QUE obtained through Eq. (10) for the induction periods at 2,000 ppm.

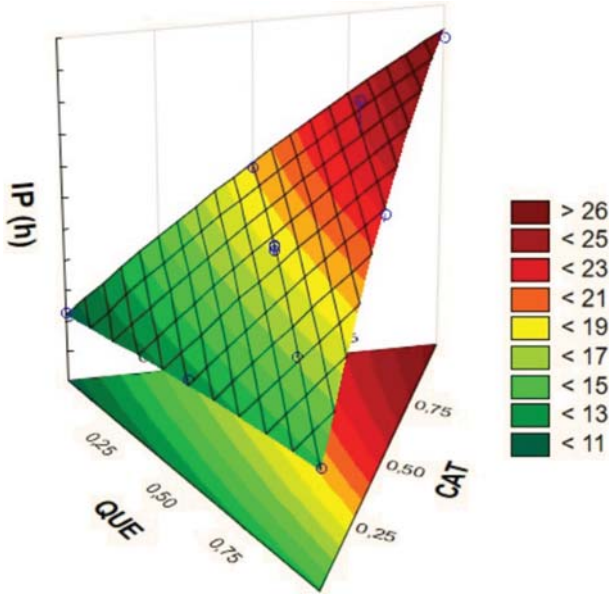

Fig. 9. Region of combination among the extracts CAT, CUR and QUE obtained through Eq. (11) for the induction periods at 3,000 ppm.

biodiesel's oxidative stability when added individually.

Regarding 1,000 ppm design, one can observe that the region of the response surface (Fig. 7) with the highest IP is the upper concentration limit of CAT (12 hours). However, both the central region and the upper concentration limit of QUE also reach high values for IP. Also, the lowest IPs (dark green region) are related to CUR, with emphasis on the binary region CUR-QUE, which showed the lowest value. This behavior indicates, once again, the negative effect of CUR-CAT and CUR-QUE interactions, with emphasis on the latter, which is in agreement with the inference previously explained and also corroborates the studies of Sousa, Moura, Oliveira and Moura [9], who observed negative synergy between CUR and β-carotene. In addition, the negative signals in the coefficients of the binary interactions CAT-CUR and CAT-QUE in Eq. (9) show that such combinations reduce the biodiesel oxidative stability. Conversely, the ternary combination has a positive effect on the oxidative stability, indicating a positive synergy when the three extracts are used together, even though it is not statistically significant.

Regarding 2,000 ppm design, only the ternary combination had synergistic effect relevant at the level of 95%. However, such combination decreased the IP of the biodiesel studied, as it can be observed by the negative signal of the ternary term in Eq. (10). Once again, the region with the highest CAT concentration resulted in the highest IP (~20 hours). Response surface analysis (Fig. 8) shows once again the synergy magnitude reduction for a higher concentration.

The response surface obtained for 3,000 ppm design (Fig. 9) shows a linear behavior, which is in agreement with Eq. (11), where only the linear terms were statistically significant at a level of 95%. This result points to the additive synergistic effect among the extracts for 3,000 ppm total. This type of synergy occurs when there is little or no interaction among the additives, so that they act only in order to regenerate the radicals formed by the hydrogen donation [35]. Sousa, Moura, Oliveira and Moura [9] also observed that the synergistic effect reduced at higher concentrations of antioxidants. The saturation of antioxidant may suppress its regeneration power, which reduces the total antioxidant activity [9]. Although the synergy calculations did not result in nullity as predicted by additivism, it is observed that all values ranged from −10 to 6%, which can be considered low to characterize the synergistic effect, except for assay 5.

By using the equation obtained for each design (Eq. (9), Eq. (10) and Eq. (11)) it is possible to obtain the theoretical IP and thus calculate the relative error for each assay (Table 2). One can observe that the average relative error is low for all three designs. This result corroborates the models' good fit to the experimental data, represented by R^2. Note that most of the assays resulted in relative error lower than 3%. All these results show that the centroid simplex augmented design can represent the system satisfactorily with good predictivity.

By comparing the three designs, one can conclude that the increase in total concentration reduced the synergy magnitude among the additives. It is observed that only one interaction was not significant for the 1,000 ppm design; only one interaction showed statistical significance for the 2,000 ppm design; and none was significant for the 3,000-ppm design. These results show that, for this system, synergistic interactions depend not only on the proportion in which they were added but also on the total concentration, which is in accordance with the findings of Rawat et al. [32]. In addition, by increasing total concentration, the synergistic effect magnitude is reduced, which corroborates the study of Sousa, Moura, Oliveira and Moura [9]. Moreover, even in the cases where the synergistic effect was negative, the extracts presented, in general, higher antioxidant activity than BHA, especially for higher concentrations.

In practical use, this study shows that 1,000 ppm is enough to reach the minimum value for oxidative stability (8 h) or commercial biodiesel. Besides, it is possible to reach IP higher than 10 hours by using 1/6, 1/6 and 2/3 of CAT, CUR and QUE, respectively, for the same concentration. This result shows that a lower

amount of antioxidants would be enough to meet the specification and thus could reduce the costs related to these additives. However, an additional study is suggested to verify the antioxidant's stability over a long-term storage, which could lead to using higher antioxidant concentrations to compensate for their degradation over time.

CONCLUSIONS

All three extracts showed antioxidant activity for cottonseed biodiesel. By increasing antioxidant concentration, biodiesel IP also increased. Nearly all combinations tested reached the minimum value required by European standard. CAT showed the highest antioxidant activity, followed by QUE and finally CUR. CAT and QUE showed higher antioxidant activity than BHA, whereas CUR was equivalent.

A synergistic phenomenon was more noticeable at lower concentrations. There was no combination effect for the 3,000 ppm design. We conclude that synergy varies with proportion and total concentration of antioxidants added to biodiesel.

AKCNOWLEDGEMENTS

To CAPES for the Master's scholarship.

REFERENCES

1. M. C. G. Albuquerque, Y. L. Machado, A. E. B. Torres, D. C. S. Azevedo, C. L. Cavalcante Jr., L. R. Firmiano and E. J. S. Parente Jr., *Renew. Energy*, **34**, 857 (2009).
2. G. Knothe, J. V. Gerpen and J. Krajl, The biodiesel handbook, AOCS Press, Campaign (2010).
3. E. Christensen and R. L. Mccormick, *Fuel Process. Technol.*, **128**, 339 (2014).
4. M. G. Simic, *J. Chem. Educ.*, **58**, 125 (1981).
5. E. N. Frankel, Lipid oxidantion, Woodhead Publishing, Filadélfia (2012).
6. D. Borsato, D. Galvan, J. L. Pereira, J. R. Orives, K. G. Angilelli and R. L. Coppo, *J. Braz. Chem. Soc.*, **25**, 1984 (2014).
7. E. C. R. Maia, D. Borsato, I. Moreira, K. R. Spacino, P. R. P. Rodrigues and A. L. Gallina, *Fuel Process. Technol.*, **92**, 1750 (2011).
8. D. S. Rawat, G. Joshi, B. Y. Lamba, A. K. Tiwari and P. Kumar, *Energy*, **84**, 643 (2015).
9. L. S. Sousa, C. V. R. Moura, J. E. Oliveira and E. M. Moura, *Fuel*, **134**, 420 (2014).
10. D. F. Pereira, A. P. D. Silva, V. M. Vasconcelos, D. a. G. Aranda and G. F. D. Silva, *Rev. Tecnol.*, **33**, 156 (2012).
11. J. Huang, Y. Wang, Z. Xie, Y. Zhou, Y. Zhang and X. Wan, *Eur. J. Clin. Nutr.*, **68**, 1075 (2014).
12. V. Sueth-Santiago, G. P. Mendes-Silva, D. Decoté-Ricardo and M. E. F. Lima, *Quim. Nova*, **38**, 538 (2015).
13. F. Gerin, U. Sener, H. Erman, A. Yilmaz, B. Aydin, F. Armutcu and A. Gurel, *Inflammation*, **39**, 700 (2016).
14. Sfgate, Foods high in catechins, http://healthyeating.sfgate.com/foods-high-catechins-4512.html (accessed 04 april 2017).
15. G. J. Du, Z. Zhang, X. D. Wen, C. Yu, T. Calway, C. S. Yuan and C. Z. Wang, *Nutrients*, **4** (2012).
16. S. Matsubara and D. B. Rodriguez-Amaya, *Food Sci. Technol. (Campinas)*, **26**, 401 (2006).
17. F. R. M. França, D. S. Menezes, J. J. S. Moreira, G. F. Silva and S. T. Brandão, Potencial da moringa oleifera lam (moringaceae) como fonte de antioxidante natural para biocombustível, *Congresso Brasileiro de Engenharia Química*, Florianópolis, 1 (2014).
18. S. K. Borra, P. Gurumurthy, J. Mahendra, K. M. Jayamathi, C. N. Cherian and R. Chand, *J. Med. Plant Res.*, **7**, 2680 (2013).
19. L. Péret-Almeida, C. D. C. Naghetini, E. D. A. Nunan, R. G. Junqueira and M. B. A. Glória, *Ciência e Agrotecnologia*, **32**, 875 (2008).
20. Sociedade Brasileira De Química, Química nova interativa - quercetina, http://qnint.sbq.org.br/qni/popup_visualizarMolecula.php?id=6NuC9uLNPgID7hAidXH8Q1lvow3lBbwociTinYJvz60jIaFjMH8EPPds5i7BO5NDxBRUmAGjRhwKEcm4mDXSQQ== (accessed 28 march 2017).
21. J. Mlcek, T. Jurikova, S. Skrovankova and J. Sochor, *Molecules*, **21** (2016).
22. I. R. Lima, M. R. G. Pedrosa and C. B. Pereira, Avaliação do potencial antioxidante de produtos naturais em diferentes biodieseis submetidos ao aquecimento, *Simpósio Brasileiro de Educação Química*, Terezina (2013).
23. R. Kowalski, *J. Food Qual.*, **33**, 269 (2010).
24. D. O. Onukwuli, L. N. Emembolu, C. N. Ude, S. O. Aliozo and M. C. Menkiti, *Egypt J. Pet.*, **26**, 103 (2017).
25. A. Morales-Sillero, A. G. Pérez, L. Casanova and J. M. García, *Food Chem.*, **237**, 1216 (2017).
26. P. K. J. P. D. Wanasundara and F. Shahidi, Antioxidants: Science, technology, and applications, Wiley-Interscience, New Jersey (2005).
27. F. R. M. França, L. Dos Santos Freitas, A. L. D. Ramos, G. F. Da Silva and S. T. Brandão, *Fuel*, **203**, 627 (2017).
28. M. Kobori, Y. Takahashi, Y. Akimoto, M. Sakurai, I. Matsunaga, H. Nishimuro, K. Ippoushi, H. Oike and M. Ohnishi-Kameyama, *J. Funct. Foods*, **15**, 551 (2015).
29. I. Van Der Westhuizen and W. W. Focke, *Fuel*, **219**, 126 (2018).
30. D. Liu, Y. Li, Y. Qian, Y. Xiao, S. Du and X. Qiu, *ACS Sustainable Chem. Eng.*, **5**, 8424 (2017).
31. P. Pedrielli and L. H. Skibsted, *J. Agric. Food Chem.*, **50**, 7138 (2002).
32. D. S. Rawat, G. Joshi, J. K. Pandey, B. Y. Lamba and P. Kumar, *Fuel*, **214**, 471 (2018).
33. J. Yin, E. M. Becker, M. L. Andersen and L. H. Skibsted, *Food Chem.*, **135**, 2195 (2012).
34. Z.-S. Jia, B. Zhou, L. Yang, L.-M. Wu and Z.-L. Liu, *J. Chem. Soc., Perkin Trans.*, **2**, 911 (1998).
35. M. R. Jesus, T. D. C. Soares, P. R. M. Silva, G. A. Romeiro, M. G. Fonseca and L. N. Batista, *Sustainable Energy Fuels*, **1**, 56 (2017).