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Optimization of Protection Condition on The Stability of Castor (*Ricinuscommunis*) Oil Based Biodiesel using Response Surface Methodology

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Abstract

The effects of designed protection conditions such as different antioxidants (propyl gallate, PG and Pyrogallol, PY), antioxidant concentration (30 – 600 ppm), temperature (30˚C -120˚C) and storage period (3 – 5 days) on the oxidation stability of castor biodiesel were investigated work was to assess the effect of the antioxidants on the oxidative stability of castor biodiesel. Using the American Standard for Testing Materials (ASTM) recommended protocols to determine the changes in the physicochemical properties (acid value, p-anisidine value, peroxide value, totox value, density, kinematic viscosity and refractive index) of the castor biodiesel were measured. The protection conditions were optimized using the Response Surface Methodology (RSM) according to the Box–Behnken Design (Design Expert version 11 Statistical Software). The analysis of variance (ANOVA) of propyl gallate showed concentration levels and temperature as the most important factors in the biodiesel oxidation, whereas the day of storage was one of the lowest factors with the p-value of < 0.05 for most indicated process variables of both linear and quadratic model terms were significant. The changes in some important physicochemical values are indication of degradation occurring in the biodiesel under the set storage condition. The optimal storage conditions were observed in propygallol with the acid value (0.985 mg KOH/g), p-anisidine value (7.650 mg KOH/g) and Totox value 4.005 (mEq/kg) with the overall desirability of 0.923 based on comparatively lower acid, p-anisidine and Totox values, followed by PG. The combined use of PY/PG antioxidants didn't show a synergic or additive result that makes the mixture of those antioxidants unsuitable to boost the biodiesel stability based on their relatively higher Totox Value.

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INTRODUCTION

Biodiesel is an alternative and renewable energy source for the future, but biodiesel prospect has issues of its susceptibility to oxidation during long-term storage than conventional petrodiesel. The challenge can be overcome since biodiesel can be prepared and stored for a period of time under different storage conditions. The physicochemical parameters of edible, non-edible and waste cooking oils such as; refractive index, acid value, *p*-Anisidine value, total oxidation value and percent free fatty acid (% FFA) have direct impacts on the quality of biodiesels that were produced [1-3]. The additional properties of biodiesel such as; cetane number, smoke point, flash point, fire point, pour point and higher heating value can also be measured and improved by antioxidants (pyrogallol (PY), propyl gallate, α-tocopherol etc. at different concentration), storage temperature and days [4-5].

Biodiesel instability primarily happens due to contact with oxygen, but oxidative degradation could occur throughout extended storage and period of transportation to the end user [6-7]. Alternative instabilities of the fuel might occur if the fuel is exposed to air and/or light, higher temperature and the presence of metallic compound that provoke oxidative/thermal degradation

Biodiesel during shipping come in contact with different fuel line component such as fuel lines, feed pump, fuel filter, piston assembly, fuel injector, fuel pump, fuel tank, cylinder etc. impacts pro oxidant tendencies on it. The biodiesel standard specifications of ASTM D6751-12 (USA) and EN 14214 (EU) must therefore be complied to sustain stability The formation of some undesirable species such as gum and sediments cause changes in the biodiesel properties that enhance corrosion of engine parts. The di-electric constant, centane number, refractive index, flash point that are fundamental physicochemical properties that are affected by biodiesel oxidation [9-11]

Numerous monitoring of physicochemical properties such as acid value, iodine value, peroxide value, methyl ester and methods (nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR), pressurized differential scanning calorimetry (PDSC), thermo gravimetric (TG), etc.) have been employed in the biodiesel stability studies [12 – 16].

Many articles targeted on stability of biodiesel without antioxidants optimization to monitor the chemical properties as typically suggested for good storage stability [17-18]. The stability of biodiesel blends with diesel and the fascinating part of antioxidants action is that its action depends on the fatty acids methyl ester (FAME) composition and its fatty-acid is a crucial property of biodiesel stability during extended and it primarily affects biodiesel qualities [17 - 24].

The effect of different antioxidants (BHA, TBHQ, BHT, α-T and PG) with different concentrations (0 – 2000 ppm) sufficiently provided oxidation resistance Ryu*et al.*, [27]. The aim is to investigate the oxidative stability of castor biodiesel (46 - 47% oil yield) doped with different antioxidants at different days and temperature of exposure and hope to provide optimized storage protection conditions against the oxidation process of castor based biodiesel at prolonged storage and higher temperatures that may useful in similar storage application.

MATERIALS AND METHODS

Materials

The raw castor seeds were collected at Oja Oba Ilorin Kwara State, Nigeria. Apparatus and chemicals were supplied by Sigma Aldrich (Gillingham Dorset, UK). Two liters of castor oil extracted by cold oil extraction and the subsequent transesterification reaction and analysis were carried out immediately to keep the properties of the obtained biodiesel according to the American Standard for Testing Materials [28] as recommended protocols, Association of Official Analytical Chemists, [29] and Mustapha *et al*. [30, 31].

Optimizing Biodiesel Stability using Response Surface Method Suited for the Design of Experiment

The relationships between independent variables and response variables are established by the RSM method. Box and Wilson [32] were the pioneers that got a model or optimal response for experimental data, but its industrial application has increased with other techniques to optimize processes. The use of ANOVA for each of the models can be computed to give the P-value. The p-value of < 0.05 for most process variables are favorable when the values were less than 0.0500, indicates model terms were significant. The statistical software used was Design Expert II version, and this was adopted since the software accommodates the three minimum categories of input and response variables that enabled the predicted and experimental values for adequacy check.

Experimental Design

The RSM must form design of experiments (DoE) with the minimum data to create ANOVA models that are accurate. There are many methods that were suggested, but a design matrix (inputs) must be created using a Box–Behnken design (BBD) since BBD designs do not have axial points, thus all design points fall between operating limits. It requires fewer treatment combinations [31]. In this case the input variables (concentration, temperature and days) in number of combination to obtain output variables (refractive index, acid value, p-anisidine value and totox value) were selected. The randomized ranges of experimental factors were: concentration (100, 200, 300, 400, and 600) temperature (30, 60, 90, and 120) and days (1, 3, and 5) were set based on the suggested range of oxidation studies of biodiesel in the literatures [3, 17]. The variable ranges were provided in Table 1 with their responses (outputs).

RESULTS AND DISCUSSION

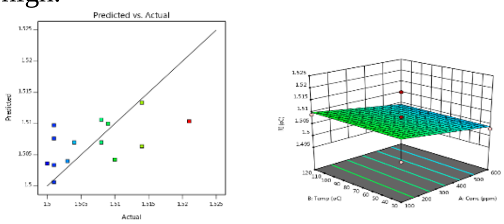
Effect of pyrogallol on the stability of castor biodiesel

The effects of antioxidant (pyrogallol) on the oxidative stability of castor biodiesel, at a concentration range of 100 to 600 ppm at different temperature between 30 – 120ºC for the first five days (1, 3, 5 days). The sample (B100) was used as a blank to compare the results obtained from the degradation process. Table 1 shows the experimental outputs for refractive index (RI), acid value (AV), p-anisidine value (p-ANV) and Totox value (TV) using Box–Behnken DoE design. Each experimental point/run represented different combination of input variables

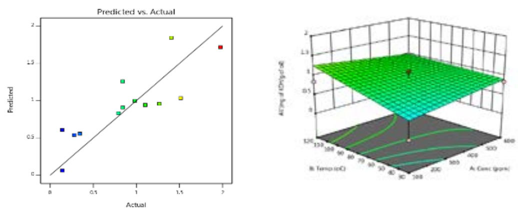
Table 1. Experimental matrix for different pyrogallol concentration and degradation temperature on stability of castor biodiesel for 1 – 5 days

(a)				Responses			
Run	A:Conc (ppm)	B:Temp (°C)	C:Day (d)	RI (°C)	AV	p-AnV	TV
1	100	75	1	1.5	2.75	22.168	9.233
2	600	30	3	1.51	0.096	4.009	3.996
3	600	75	5	1.502	0.14	7.637	1.706
4	350	30	1	1.529	0.968	5.698	6.484
5	100	120	3	1.51	0.988	20.269	5.098
6	350	75	3	1.507	1.873	13.363	2.577
7	100	75	5	1.503	0.142	5.018	2.685
8	350	75	3	1.507	0.187	13.363	2.577
9	600	75	1	1.5	0.983	22.561	5.341
10	100	30	3	1.52	0.983	2.635	3.683
11	350	75	3	1.507	1.873	13.363	2.577
12	600	120	3	1.509	0.14	16.86	1.354
13	350	120	5	1.501	0.271	11.562	1.646
14	350	75	3	1.507	1.873	13.363	2.577
15	350	75	3	1.507	1.873	13.363	2.577
16	350	30	5	1.509	0.095	2.151	2.112
17	350	120	1	1.505	0.632	39.984	4.253

The Design Expert software generated the maximum number of runs based on the three levels of inputs. Figure 1. shows the relationship between the actual values that were obtained experimentally (Table 1) and the predicted different models values of RI (Figure 1a), AV (Figure 1b), AnV (Figure 1c), and TV (Figure 1d). The figures show that these models suffice for the prediction of these values, as the correlations between actual and predicted values were high.



(a)



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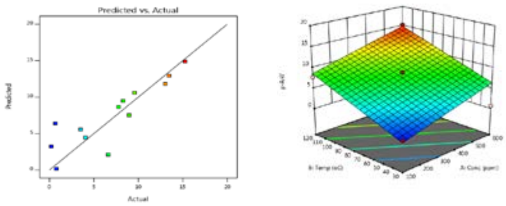

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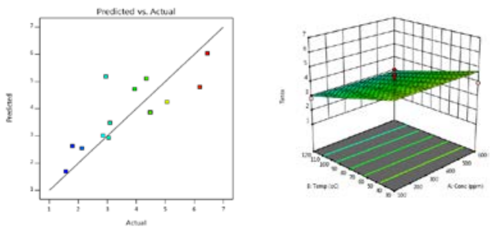


(d)

Figure 1. Scatter diagram (pyrogallol): (a) refractive index (RI); (b) acid value (AV); (c) p – anisidine value (p-AnV); (d) Totox value (TV) with the corresponding 3D surface

The equation in terms of actual factors with the coefficients: concentration; C (ppm), temperature; T (°C), day; D (d) were used for predictions about the response for given levels of each factor. However, these equations with the specified units cannot be used to determine the relative impacts of each factor (RI, AV, p-AnV, Totox), because the coefficients (C, T, D) were scaled to accommodate the units of each factor and the intercept was not at the centre of the design space.

Final Equation in Terms of Actual Factors :

$$RI = +1.51607 - 0.000011\ C + 2.77778E\text{-}06\ T - 0.001750\ D \quad (1)$$

$$AV = +1.21176 + 0.000041\ C + 0.004121T - 0.197344D \quad (2)$$

$$p\text{-}AnV = -2.16293 + 0.012490C + 0.094247\ T - 0.584000D \quad (3)$$

$$Totox = +7.32907 - 0.000158C - 0.019861T - 0.638750D \quad (4)$$

The ANOVA results for each of the models are shown in the Tables 2–5. The p-value of < 0.05 for most process variables were observed in the respective Table.

Table 2. ANOVA Table for the “RI” linear model

Source	SS	df	MS	F-value	P-Value	
Model	0.0002	3	0.0001	1.95	0.01721	significant
A-Conc	0.0001	1	0.0001	2.35	0.1492	
B-Temp	1.250E-07	1	1.250E-07	0.0044	0.9479	
C-Day	0.0001	1	0.0001	3.48	0.0847	
Residual	0.0004	13	0.0000			
Lack of Fit	0.0004	9	0.0000	12.26	0.0140	significant
Pur Error	0.0000	4	3.200E-06			
Cor Total	0.0005	16				

Table 3. ANOVA Table for the “AV” linear model

Source	SS	df	MS	F-value	P-Value	
Model	1.52	3	0.5074	2.70	0.0887	not significant
A-Conc	0.0008	1	0.0008	0.0044	0.9483	
B-Temp	0.2751	1	0.2751	1.46	0.2477	
C-Day	1.25	1	1.25	6.64	0.0230	
Residual	2.44	13	0.1878			`
Lack of Fit	2.44	9	0.2713			
Pur Error	0.0000	4	0.0000			
Cor Total	3.96	16				

Table 4. ANOVA Table for the “P-AnV” for linear model

Source	SS	df	MS	F-value	P-Value	
Model	232.80	3	77.60	12.25	0.0004	significant
A-Conc	77.99	1	77.99	12.32	0.0038	
B-Temp	143.90	1	143.90	22.72	0.0004	
C-Day	10.91	1	10.91	1.72	0.2120	
Residual	82.33	13	6.33			`
Lack of Fit	82.33	9	9.15			
Pur Error	0.0000	4	0.0000			
Cor Total	315.14	16				

Table 5. ANOVA Table for the "TV" for linear model

Source	SS	df	MS	F-value	P-Value	
Model	19.46	3	6.49	7.10	0.0045	significant
A-Conc	0.0125	1	0.0125	0.0137	0.9087	
B-Temp	6.39	1	6.39	7.00	0.0202	
C-Day	13.06	1	13.06	14.30	0.0023	
Residual	11.87	13	0.9129			`
Lack of Fit	11.87	9	1.32			
Pur Error	0.0000	4	0.0000			
Cor Total	31.33	16				

Table 6 show the input variables of pyrogallol concentration (349.99 ppm), temperature (75 °C) and days (2.929 d) were computed during the oxidation/degradation. The treated biodiesel have refractive index of 1.504, p-anisidine value of 7.650 mg KOH/g and Totox value of 4.005 mEq/kg with the overall desirability of 0.923. This indicated the impact of the antioxidant in biodiesel stability against thermal oxidation.

Table 6. Two optimization solutions found using pyrogallol

No	Conc	Temp	Day	RI	AV	p-AnV	Totox	Desirability	
1	349.999	75.000	2.786	1.507	0.985	7.650	4.005	0.923	Selected
2	349.999	75.324	2.776	1.507	0.988	7.686	4.004	0.923	

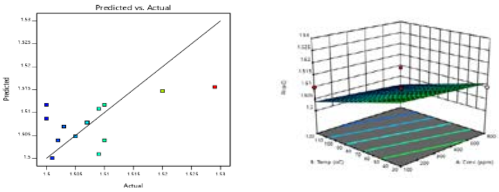
Effect of propyl gallate on the stability of castor biodiesel

The effects of antioxidant (propyl gallate) on the oxidative stability of castor biodiesel, at a concentration range of 100 to 600 ppm at different temperature between 30 – 120°C for the first five days (1, 3, 5 days). Table 7 shows the experimental variables for refractive index (RI), acid value (AV), p-anisidine value (p-ANV) and Totox value (TV) using Box–Behnken DoE design (Table 8 - 11)

Table 7. Experimental matrix for different propyl gallate concentration and degradation temperature on stability of castor biodiesel for 1 – 5 days

(a)				Responses			
Run	A:Conc (ppm)	B:Temp (°C)	C:Day (d)	RI (°C)	AV	p-AnV	TV
1	100	75	1	1.5	2.75	22.168	9.233
2	600	30	3	1.51	0.096	4.009	3.996
3	600	75	5	1.502	0.14	7.637	1.706
4	350	30	1	1.529	0.968	5.698	6.484
5	100	120	3	1.51	0.988	20.269	5.098
6	350	75	3	1.507	1.873	13.363	2.577
7	100	75	5	1.503	0.142	5.018	2.685
8	350	75	3	1.507	0.187	13.363	2.577
9	600	75	1	1.5	0.983	22.561	5.341
10	100	30	3	1.52	0.983	2.635	3.683
11	350	75	3	1.507	1.873	13.363	2.577
12	600	120	3	1.509	0.14	16.86	1.354
13	350	120	5	1.501	0.271	11.562	1.646
14	350	75	3	1.507	1.873	13.363	2.577
15	350	75	3	1.507	1.873	13.363	2.577
16	350	30	5	1.509	0.095	2.151	2.112
17	350	120	1	1.505	0.632	39.984	4.253

The Design Expert software generated the maximum number of runs based on the three levels of inputs. **Figure** 2 shows the relationship between the actual values that were obtained experimentally (Table 7) and the predicted different models values of RI (Figure 2a), AV (Figure 2b), AnV (Figure 2c), and TV (Figure 2d). The figures show that these models suffice for the prediction of these values, as the correlations between actual and predicted values were high.



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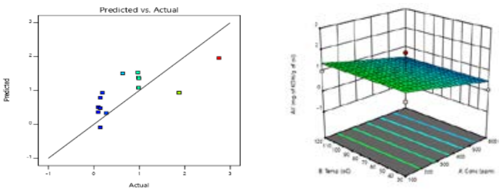

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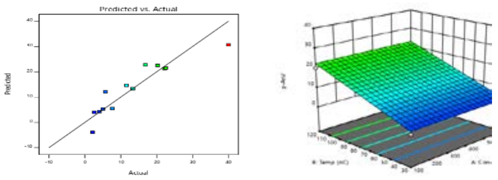
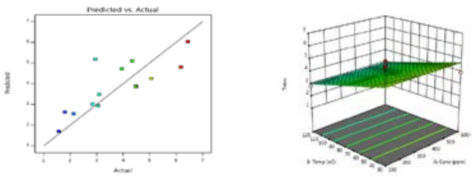


(c)

The ANOVA results for each of the models are shown in the Tables 7–10. The p-value of < 0.05 for most process variables were observed. P-values less than 0.0500 indicate model terms were significant. And values greater than 0.1000 indicate the model terms are not significant.

Table 12 shows the input variables of pyrogallatel



(d)

Figure 2. Scatter diagram (pyrogallate): (a) refractive index (RI); (b) acid value (AV); (c) p – anisidine value (p-AnV); (d) Totox value (TV) with the corresponding 3D surface

The equation in terms of actual factors with the coefficients: concentration; C (ppm), temperature; T (ºC), day; D (d) were used for predictions about the response for given levels of each factor. However, these equations with the specified units cannot be used to determine the relative impacts of each factor (RI, AV, p-AnV, Totox), because the coefficients (C, T, D) were scaled to accommodate the units of each factor and the intercept was not at the centre of the design space.

Final Equation in Terms of Actual Factors :

$$RI = + 1.52244 - 6.00000E - 06\ C - 0.000119\ T - 0.001188\ D \quad (5)$$

$$AV = + 2.44812 - 0.001752\ C - 0.000308\ T - 0.292813\ Day \quad (6)$$

$$p\text{-}AnV = +9.75703 + 0.000489C + 0.206061\ T - 4.00269\ D \quad (7)$$

$$Totox = +5.16935 + 0.001154C - 0.024786T + 0.915375D \quad (8)$$

concentration (349.997 ppm), temperature (75 ºC) and days (2.015 d) that were computed during the oxidation/degradation. The treated biodiesel have refractive index (1.509), acid value (1.222 mg KOH/g), p-anisidine value (17.316 mg KOH/g) and Totox value (4.614 mEq/kg) with the overall desirability of 0.781. This indicated the impact of the antioxidant in biodiesel stability against oxidation.

Table 8. ANOVA Table for the “RI” linear model

Source	SS	df	MS	F-value	P-Value	
Model	4.28	3	1.43	2.67	0.0408	significant
A-Conc	1.53	1	1.53	2.88	0.1137	
B-Temp	0.0015	1	0.0015	0.0029	0.9580	
C-Day	2.74	1	2.74	5.14	0.0411	
Residual	6.94	13	0.5336			
Lack of Fit	4.66	9	0.5181	0.9113	0.5857	
Pur Error	2.27	4	0.5685			
Cor Total	11.22	16				

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Table 9. ANOVA Table for the "AV" linear model

Source	SS	df	MS	F-value	P-Value	
Model	4.28	3	1.43	2.67	0.0408	significant
A-Conc	1.53	1	1.53	2.88	0.1137	
B-Temp	0.0015	1	0.0015	0.0029	0.9580	
C-Day	2.74	1	2.74	5.14	0.0411	
Residual	6.94	13	0.5336			
Lack of Fit	4.66	9	0.5181	0.9113	0.5857	
Pur Error	2.27	4	0.5685			
Cor Total	11.22	16				

Table 10. ANOVA Table for the "AnV" linear model

Source	SS	df	MS	F-value	P-Value	
Model	1200.68	3	400.23	23.36	< 0.0001	significant
A-Conc	0.1193	1	0.1193	0.0070	0.9348	
B-Temp	687.87	1	687.87	40.14	< 0.0001	
C-Day	512.69	1	512.69	29.92	0.0001	
Residual	222.77	13	17.14			
Lack of Fit	222.77	9	24.75			
Pur Error	0.0000	4	0.0000			
Cor Total	1423.45	16				

Table 11. ANOVA Table for the "TV" linear model

Source	SS	df	MS	F-value	P-Value	
Model	47.36	3	15.79	10.66	0.0008	significant
A-Conc	8.62	1	8.62	5.82	0.0314	
B-Temp	1.92	1	1.92	1.30	0.2749	
C-Day	36.82	1	36.82	24.85	0.0002	
Residual	19.26	13	1.48			
Lack of Fit	19.26	9	2.14			
Pur Error	0.0000	4	0.0000			
Cor Total	66.62	16				

Table 12. Two optimization solutions found using pyrogallate

No	Conc	Temp	Day	RI	AV	p-AnV	Totox	Desirability	
1	349.997	75.000	2.015	1.509	1.222	17.316	4.614	0.781	Selected
2	349.992	75.000	2.034	1.509	1.216	17.243	4.594	0.781	

Effect of Pyrogallol/Propyl gallate combination on the stability of biodiesel

The effects of antioxidant (pyrogallol and propyl gallate combination) on the oxidative stability of castor biodiesel, at a concentration range of 100 to 600 ppm at different temperature between 30 – 120ºC for the first five days (1, 3, 5 days). Table 13 shows the experimental variables for refractive index (RI), acid value (AV), p-anisidine value (p-ANV) and Totox value (TV) using the Box–Behnken DoE design.

The equation in terms of actual factors with the coefficients: concentration; C (ppm), temperature; T (ºC), day; D (d) were used for predictions about the response for given levels of each factor. However, these equations with the specified units cannot be used to determine the relative impacts of each factor (RI, AV, p-AnV, Totox), because the coefficients (C, T, D) were scaled to accommodate the units of each factor and the intercept was not at the centre of the design space.

Final Equation in Terms of Actual Factors :

$$RI = + 1.50456 - 2.74366E\text{-}19C - 0.000025\ T + 0.000438\ D \quad (9)$$

$$AV = + 0.719920 + 0.000244C - 0.004265\ T + 0.222594\ D \quad (10)$$

$$P\text{-}AnV = + 455.62405 + 0.008122\ C - 0.014408\ T - 1.78806\ D \quad (11)$$

$$TV = + 5.16935 + 0.001154\ C - 0.024786\ T + 0.915375\ D \quad (12)$$

The ANOVA results for each of the models are shown in the Tables 12–15. The p-value of < 0.05 for most process variables were observed. P-values less than 0.0500 indicate model terms are significant.

Table 13. Experimental matrix for different propyl gallate/progallol concentration and degradation temperature on stability of castor biodiesel for 1 – 5 days

	Factors			Responses			
Run	A:Conc (ppm)	B:Temp (°C)	C:Day (d)	RI (°C)	AV	p-AnV	TV
1	100	75	5	1.501	1.734	0.151	8.285
2	350	30	5	1.504	2.065	1.551	8.582
3	350	75	3	1.506	0.972	1528	6.873
4	350	120	5	1.515	1.247	1.202	6.378
5	100	120	3	1.495	0.842	0.127	4.816
6	600	30	3	1.508	1.44	2.631	8.116
7	100	75	1	1.507	0.793	3.515	2.946
8	600	120	3	1.495	1.143	2.294	6.264
9	600	75	1	1.501	1.404	13.02	4.344
10	350	75	3	1.506	0.972	1528	6.873
11	350	75	3	1.506	0.972	1528	6.873
12	350	75	3	1.506	0.972	1528	6.873
13	600	75	5	1.502	1.553	2.332	8.019
14	350	120	1	1.504	0.6305	6.461	4.016
15	100	30	3	1.503	1.683	0.24	8.387
16	350	30	1	1.503	0.21	10.849	5.312
17	350	75	3	1.506	0.972	1528	6.873

Table 14. ANOVA Table for the "RI" linear model

Source	SS	df	MS	F-value	P-Value
Model	0.0000	0			
Residual	0.0004	16	0.0000		
Lack of Fit	0.0004	12	0.0000		
Pur Error	0.0000	4	0.0000		
Cor Total	0.0004	16			

Table 15. ANOVA Table for the "AV" linear model

Source	SS	df	MS	F-value	P-Value
Model	1.91	3	0.6367	5.88	0.0092
A-Conc	0.0298	1	0.0298	0.2751	0.6088
B-Temp	0.2947	1	0.2947	2.72	0.1228
C-Day	1.59	1	1.59	14.65	0.0021
Residual	1.41	13	0.1082		
Lack of Fit	1.41	9	0.1563		
Pur Error	0.0000	4	0.0000		
Cor Total	3.32	16			

Table 16. ANOVA Table for the "AnV" linear model

Source	SS	df	MS	F-value	P-Value
Model	138.66	3	46.22	0.0001	1.0000
A-Conc	32.98	1	32.98	0.0001	0.9943
B-Temp	3.36	1	3.36	5.331E-06	0.9982
C-Day	102.31	1	102.31	0.0002	0.9900
Residual	8.201E+06	13	6.308E+05		
Lack of Fit	8.201E+06	9	9.112E+05		
Pur Error	0.0000	4	0.0000		
Cor Total					

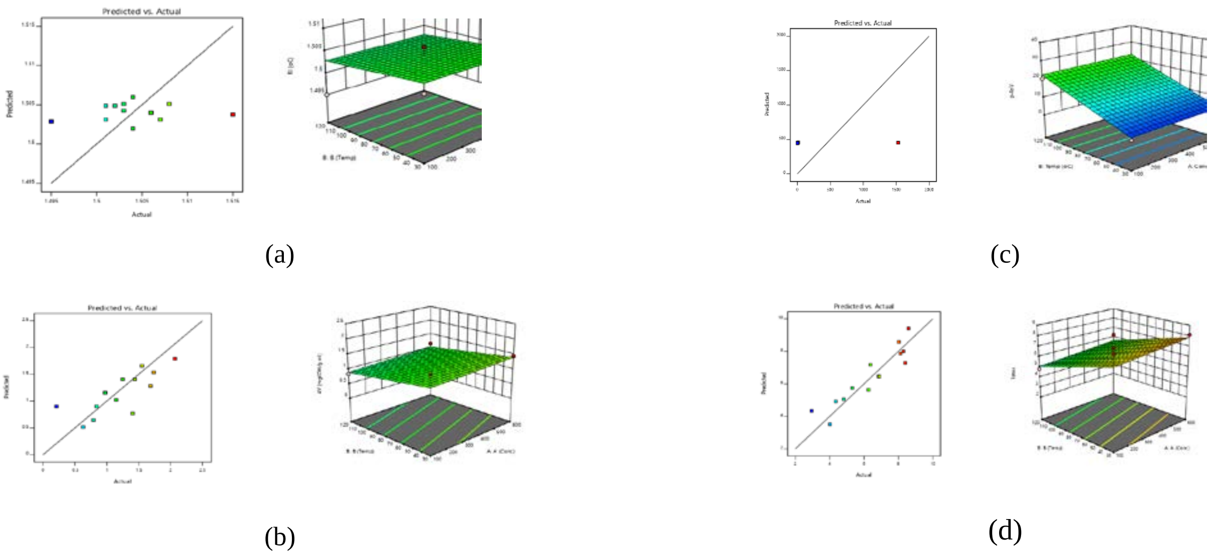

Figure 3. Scatter diagram (pyrogall/pyrog-allate): (a) refractive index (RI); (b) acid value (AV); (c) p– anisidine value (p-AnV); (d) Totox value (TV) with the corresponding 3D surface

Table 17. ANOVA Table for the “TV” linear model

Source	SS	df	MS	F-value	P-Value
Model	37.43	3	12.48	23.16	< 0.0001
A-Conc	0.6664	1	0.6664	1.24	0.2862
B-Temp	9.95	1	9.95	18.47	0.0009
C-Day	26.81	1	26.81	49.76	< 0.0001
Residual	7.00	13	0.5388		
Lack of Fit	7.00	9	0.7783		
Pur Error	0.0000	4	0.0000		
Cor Total	44.44	16			

Table 18. Two optimization solutions found using pyrogallate-pyrogallate combination

No	Conc	Temp	Day	RI	AV	p-AnV	Totox	Desirability	
1	350.000	75.000	2.929	1.504	1.138	452.148	6.396	0.876	Selected
2	350.000	75.000	2.954	1.504	1.143	452.104	6.419	0.876	

Table 19. Experimental outputs obtained according to the three biodiesel optimization scenerios

No	Conc	Temp	Day	RI	AV	p-AnV	Totox	Desirability	
Pyrogallol 1	349.997	75.000	2.015	1.509	1.222	17.316	4.614	0.781	Selected
Pyrogallate 1	349.992	75.000	2.034	1.509	1.216	17.243	4.594	0.781	Selected
Pyrog/Pyrogall	350.000	75.000	2.929	1.504	1.138	452.148	6.396	0.876	Selected

Table 18 show the input variables of pyrogallol/progallate concentration (350.99 ppm), temperature (75 °C) and days (2.929 d) were computed during the oxidation/degradation. The treated biodiesel have refractive index (1.504), acid value (1.138 mg KOH/g), p-anisidine value (452.148 mg KOH/g) and Totox value (6.396 mEq/kg) with the overall desirability of 0.876. This indicated the impact of the antioxidant in biodiesel stability against thermal oxidation.

Tables 19 show the results obtained from the Tables 6, 12 and 18 using various antioxidants (pyrogallOol, propyl gallate and pyrogallol/propyl gallate) and the combination of process that were studied, showing desirability functions from three different criteria. The average input variables such concentration (350 ppm), temperature (75 °C) and days (2.5 d) were computed during the oxidation/degradation for the three processes. The output refractive indices range of 1.504 – 1.509 found were comparable to olive and peanut biodiesel with the lowest refractive index (1.4443 and 1.4448, respectively) whereas soybean and grape biodiesel have highest values (1.4495 and 1.4500, respectively) [34]. Whereas, the average acid values of treated biodiesels for pyrogallol, pyrogallate and pyrogallol/pyrogallate were 0.985; 1.222 and 1.138 mg KOH/g, respectively. These values were higher with the requirements of ASTM D 6751 and EN 14214 [28], which both stipulated a maximum acid number of 0.5 mg KOH/g. Anisidine value is used to assess the secondary oxidation of biodiesel, the lower the p-anisidine value [35], the better the quality of biodiesel. The treated biodiesels have increasing values of p-anisidine using pyrogallol (7.650 mg KOH/g), pyrogallate (17. 316 mg KOH/g), and pyrogallol/pyrogallate (452.148 mg KOH/g), respectively indicating the order of effectiveness of the three antoxidants in biodiesel stability against thermal oxidation. Similarly, the recommended standard Totox values in the three processes were lesser than 19.5 mEq/kg values with pyrogallol, pyrogallate and pyrogallol/pyrogallate treated biodiesel having Totox values of 4.005, 4.614and 6.396 mEq/kg, with corresponding overall desirability 0.923, 0.781 and 0.876.

In this work, the optimal storage conditions were observed in propygallol with the acid value (0.985 mg KOH/g), p-anisidine value (7.650 mg KOH/g) and Totox value 4.005 (mEq/kg) with the overall desirability of 0.923 based on comparatively lower acid, p-anisidine and Totox values. The overall results showed that castor biodiesel could comply with the totox value standard with PY being more effective than PG. The combined use of PY/PG antioxidants didn't show, particularly at low concentrations, a synergic or additive result, that makes the mixture of those antioxidants unsuitable to boost the biodiesel stability based on their relatively higher Totox Value.

CONCLUSION

The effects of antioxidants and storage variables on the biodiesel oxidation were studied using Response surface methodology according to the Box–Behnken design (Design Expert version 11 Statistical Software). The analysis of variance (ANOVA) showed results that indicated the concentration levels, temperature and extended storage period were the most important factors in the biodiesel oxidation (Table 19). In addition, the nature of antioxidants was an important factor for decreasing the oxidation rate. The storage optimal conditions were observed in propygallol with, the acid value mg KOH/g of 0.985, p-anisidine value of 7.650 and Totox of 4.005 mEq/kg with the overall desirability of 0.923 based on comparatively lower acid, p-anisidine and Totox values. The present work showed with the overall desirability of 0.923 based on comparatively lower acid, p-anisidine and Totox values.

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