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Article

Application of Full Factorial Design to Evaluate the Effect of Different Variables on the Stability of Biodiesel:Diesel Blends under Storage Conditions

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Biodiesel is obtained from a renewable source and has been used as an alternative to fossil fuels. It has unsaturated fatty acid methyl esters that can degrade due to oxidation of the double bonds. The instability of biodiesel during storage may cause problems regarding the maintenance and operation of motors. This work evaluated the effect of several variables on the storage conditions of biodiesel:diesel blends. The study was performed using an experimental design, and the variables were water content in biodiesel (0.01, 0.05 and 0.09%), biodiesel content in diesel (5.0, 7.5 and 10.0%), time (15, 30 and 45 days) and temperature (30, 40 and 50 °C). The levels simulated actual Brazilian storage conditions. The degradation was evaluated based on direct measurement of methyl linoleate and methyl oleate in the blends by gas chromatography-mass spectrometry. These unsaturated fatty acid methyl esters are target compounds in the oxidation process. All experiments were carried out in sealed flasks. The results suggest that the restriction of oxygen limited the degradation of biodiesel in blends with higher percentage of the biofuel. The variables temperature, time and water content in biodiesel individually did not affect the degradation process within the range investigated at 95% confidence interval.

Keywords: biodiesel:diesel blends, biodiesel storage, degradation of biodiesel, factorial design

Introduction

The gradual depletion of fossil fuel has increased the need to look for alternatives. Biodiesel has been used as an alternative fuel for diesel engines.[1] It is renewable, biodegradable and non-toxic, has a low emission profile and can be used directly or blended with diesel.[2-6] Despite the many advantages, the composition of biodiesel makes it more susceptible to oxidation than diesel during storage. Because of this, storage stability is an important aspect of the commercialization of biofuel.[7-9] The stability of biodiesel depends on the raw material, the presence of natural antioxidants and the storage conditions.[10-12]

Several studies have been conducted on the degradation of biodiesel and biodiesel:diesel blends. Some attempted to estimate the efficiency of antioxidants under accelerated and storage conditions.[13-19] Other studies evaluated the degradation of biofuel in specific conditions.[7,20-24] Methods for evaluating oxidative stability in accelerated conditions have restricted validity, because the mechanism of oxidation changes as the sample is submitted to heat, light or metal contact.[25] Some experiments that involved the storage period of biodiesel using the Rancimat method and an oven showed that there is a significant difference between the methods and the oven was more suitable for determining storage time.[26]

Most of the research available in the literature focused on the stability of pure biodiesel. Few studies have simulated the usual storage conditions of biodiesel:diesel blends in order to evaluate their degradation. Berrios *et al.*[7] reported the stability of B20 (20% v/v of biodiesel in diesel) samples stored in opaque glass bottles or stainless steel bottles, in the absence of light, with little air turnover, at 15 and 25 °C for 6 months. The authors used a 2^2 factorial experimental design, and the variables selected were temperature and bottle material. The methyl ester content and the fatty acid composition were determined by gas chromatography with a method in accordance with EN 14103.[7] Yang *et al.*[22] performed experiments with B5 and B20 biodiesel:diesel blends with air exposure, in a dark chamber at 22 ± 2 °C for approximately 6 months. The fatty acid methyl ester composition of the samples was periodically analyzed by gas chromatography/mass spectrometry (GC/MS) after the fractionation of the blends on a silica gel column using

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hexane and dichloromethane as the eluent.[22] Recently, the same authors studied the effect of water and copper as impurities in B20 blends at 15 and 40 °C for 12 months.[23]

As far as we know, no studies in the literature have evaluated simultaneously how the variables involved in the degradation process of biodiesel:diesel blends may affect it in storage conditions. The use of a full factorial design may elucidate the significance of the variables and show whether there are interactions between the variables. Therefore, the aim of the present study was the application of a full factorial design to evaluate the effect of different variables on the stability of soybean-derived biodiesel:diesel blends under storage conditions similar to those found in Brazilian real situations. It is important to emphasize that the studied conditions were distinct from those described in the literature. The samples were not exposed to air turnover or light. The degradation was evaluated based on the direct measurement of methyl linoleate and methyl oleate in the blends by GC/MS using the selective ion monitoring (SIM) mode. These unsaturated fatty acid methyl esters are target compounds in the oxidation process. The use of GC/MS as analytical method together with the use of a factorial design approach can help us understand how the biodiesel degradation process is affected and how to mitigate it.

Experimental

Materials

Potassium hydroxide (85% purity) and sodium sulfate (99% purity) were purchased from Vetec (Brazil). Ethyl acetate and methanol (99.9% purity) were purchased from Tedia (Brazil), and deuterated chloroform (99.8% purity) was purchased from Cambridge Isotope Laboratories, Inc. (USA). Soybean oil was purchased at a commercial establishment. The 5 Å molecular sieve was from Prolabo (USA). The S50 diesel was provided by the Laboratory of Fuel and Oil Products of the Federal University of Rio de Janeiro (LABCOM).

The flasks used for sample storage were pretreated at 450 °C for 4 h. The S50 diesel was stored with 5 Å molecular sieve at –20 °C. The thermometers used to control the oven temperature and the syringes used for the sample preparation and for the analytical curves were calibrated.

The standards methyl linoleate, methyl oleate and methyl palmitate were purchased from Sigma-Aldrich (USA) (99% purity). Pentadecanoyl propanoate (the internal standard) was synthesized, purified and characterized as previously reported by our research group.[27]

Synthesis of biodiesel

Biodiesel was synthesized using 300 mL of soybean oil, 105 mL of methanol and about 3 g of catalyst (potassium hydroxide). Soybean biodiesel was chosen because it represents approximately 80% of the Brazilian biodiesel production.[28] This biodiesel has about 53% methyl linoleate, an ester with two double bonds in its structure. The mixture was stirred at 45 °C for 2 h. After 24 h of standing, two phases were observed: the upper layer containing the methyl esters (biodiesel) and the lower layer containing glycerin. The glycerin phase was removed, and the biodiesel was neutralized with 0.5% v/v of HCl solution. Then, the biodiesel was washed with NaCl-saturated solution and with water. The organic layer was dried over anhydrous Na_2SO_4, maintaining the suspension under constant stirring for 2 h. The product was stored with a 5 Å molecular sieve previously activated at 200 °C.

Analysis of water content in biodiesel by coulometric Karl Fischer method

The residual water content in biodiesel was determined by ASTM method D6304:2008[29] using a coulometric Karl Fischer analyzer (Metrohm, model 756KF). The biodiesel sample was analyzed in triplicate.

Analysis of biodiesel by ^1H NMR

The proton nuclear magnetic resonance (^1H NMR) spectroscopic measurements were carried out at 298 K using a Bruker DPX-200 spectrometer (Germany), operating at 200 MHz in hydrogen frequency. The sample was prepared by dissolving 10 mg of biodiesel in 0.6 mL $CDCl_3$. The spectra were referenced to tetramethylsilane (TMS). The relative areas of the signals were obtained with electronic integration. The percentage conversion (%C) of vegetable oil in biodiesel is given by equation $\%C = 100 \times (2A_1 / 3A_2)$, where A_1 is the area obtained in the NMR spectrum at 3.7 ppm related to the three hydrogens of the methoxy groups ($-OCH_3$), and A_2 is the area obtained at 2.3 ppm related to the two hydrogens of α-carbonyl methylene groups ($-CH_2CO$).[30]

Experimental design

The effect of the variables on the stability of the biodiesel:diesel blends was investigated by using a 2^4 factorial design with three center points (Table 1). The variables were the biodiesel content in diesel, the water content in biodiesel, temperature and time.

Table 1. Experimental design of the storage conditions (2^4 factorial design with 3 center points)

Sample	X_1	X_2	X_3	X_4
1	–1	–1	–1	–1
2	–1	–1	+1	–1
3	–1	+1	–1	–1
4	–1	+1	+1	–1
5	+1	–1	–1	–1
6	+1	–1	+1	–1
7	+1	+1	–1	–1
8	+1	+1	+1	–1
9	–1	–1	–1	+1
10	–1	–1	+1	+1
11	–1	+1	–1	+1
12	–1	+1	+1	+1
13	+1	–1	–1	+1
14	+1	–1	+1	+1
15	+1	+1	–1	+1
16	+1	+1	+1	+1
17	0	0	0	0
18	0	0	0	0
19	0	0	0	0

The variable levels are summarized in Table 2. The levels of the biodiesel content in diesel were chosen according to the current level regulated by the Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP). The minimum water content level was below the maximum established by the ANP. The central point and the maximum level were set above the values allowed by the ANP in order to evaluate whether higher water content, above the recommended level, would significantly affect the fuel degradation. The temperature levels were selected based on the temperature range that could be observed in a closed tank, taking into account the storage temperature regulated by the ANP via ASTM D4625.[31] The time levels were chosen based on the maximum length of fuel storage recommended by the ANP. The suggested period for biodiesel and its blends was 30 days.

The prepared biodiesel:diesel blends were maintained in a 15 mL sealed flask containing 10.0 mL of the sample. The storage was performed simultaneously in three ovens with temperatures according to the experimental design. The temperature variation was ± 1 °C. Each experiment was performed in triplicate, and a control sample of each experiment was kept in a freezer at –20 °C.

Standard solutions

A standard stock solution was prepared by weighting 15.0 mg of methyl linoleate, 8.0 mg of methyl oleate and 3.0 mg of methyl palmitate in a 10.0 mL volumetric flask and completing with ethyl acetate. The stock solution was then stored at –20 °C. Standard diesel solutions were prepared from this stock solution in the range of approximately 0.40-5.30 g L^{-1} of methyl linoleate, 0.20-3.10 g L^{-1} of methyl oleate and 0.10-1.00 g L^{-1} of methyl palmitate. The standard diesel solutions were prepared by mixing a known volume (15, 40, 65, 90, 115, 140, 165 and 190 µL) of the standard stock solution, 50 µL of diesel and 100 µL of a 3.10 g L^{-1} pentadecanoyl propanoate solution as the internal standard. The volume was completed to 500 µL with ethyl acetate.

The ester concentrations were selected in order to construct standard curves equivalent to 1.0, 2.5, 4.0, 5.5, 7.0, 8.5, 10.0 and 11.0% of biodiesel in diesel and an internal standard at 0.60 g L^{-1}. All points were obtained in triplicate and were randomly injected.

GC/MS-SIM analysis

The biodiesel content in diesel was determined via GC/MS using the selected ion monitoring (SIM) mode according to a method previously developed and validated by our research group.[32] Recently, it has been used in the determination of biodiesel content in blends aged under accelerated oxidation conditions.[28]

GC/MS analyses were performed on an Agilent Technologies 6890A gas chromatography coupled to an Agilent Technologies 5973 mass spectrometer. Electron ionization at 70 eV ionization energy was used. A DB-1HT (100% methyl polysiloxane) capillary column (J&W, USA) with 30 m, 0.25 mm i.d. and 0.10 µm d_f was used. The carrier gas was helium at a flow rate of 1.5 mL min^{-1}. The temperature program was 80 °C, at 10 °C min^{-1} to 150 °C, then at 5 °C min^{-1} to 180 °C, followed by 25 °C min^{-1} to

Table 2. Variables and levels of factorial design

Variable	Level of variables		
	Low level (–1)	Central point (0)	High level (+1)
(X_1) Biodiesel content in diesel / (% v/v)	5	7.5	10
(X_2) Water content in biodiesel / (% v/v)	0.01	0.05	0.09
(X_3) Temperature / °C	30	40	50
(X_4) time / days	15	30	45

300 °C, and an isothermal period of 5 min. The injection volume was 1.0 µL in split mode and with the 1:20 split ratio. The injector temperature was 290 °C, and the transfer line, ion source, and MS quadrupole analyzer were held at 300 °C. All samples were analyzed in the SIM mode. The selected characteristic ions are summarized in Table 3. The injection samples were prepared by mixing 50 µL of the storage sample, 100 µL of the IS solution and 350 µL of ethyl acetate.

Table 3. Selected compound characteristic ions (*m/z*)

Ester	Characteristic ions (*m/z*)
Methyl palmitate	74, **143**, 239
Methyl linoleate	220, **263**, 294
Methyl oleate	74, **264**, 296
IS	182, 210, **255**

Ions for quantitative analysis are shown in bold.

Statistical analysis

The significance of the effects of each variable was evaluated with analysis of variance (ANOVA) using the statistical software Statistica 12 (Statsoft, Brazil). A p value of less than 0.05 was considered significant. ANOVA was performed at the 95% confidence interval to assess the significance of the statistical test results.

Results and Discussion

Synthesized biodiesel

The analysis of the synthesized biodiesel by ^{1}H NMR showed the conversion of 97% of the soybean oil in methyl esters. This value is in accordance with the minimum percentage regulated by the ANP, which is 96.5%.

The water content in biodiesel was determined only in the samples before storage, because the process of oxidative degradation produces carboxylic acids and aldehydes that cause interference in the Karl Fischer method.[33] The analysis of the synthesized biodiesel showed the presence of 0.01% (v/v) water in the sample. From this biodiesel, two new samples were prepared with 0.05 and 0.09% water. Analysis with the Karl Fischer method confirmed the water content.

Analytical curves

The standard solutions were analyzed, and each analytical curve was built using the diagnostic ions *m/z* 255, 143, 263 and 264 for the quantitative determination of pentadecanoyl propanoate, methyl palmitate, methyl linoleate and methyl oleate, respectively. Previously, pure diesel was analyzed by GC/MS-SIM, and the result showed that pure diesel does not have compounds with these ions near the retention time of the esters used for quantification. Mass chromatograms of pure diesel and diesel fortified with the standard esters are illustrated in Figure 1. The standard calibration parameters are summarized in Table 4. The calculated confidence intervals for the linear coefficients (CI) showed no bias in the regressions.

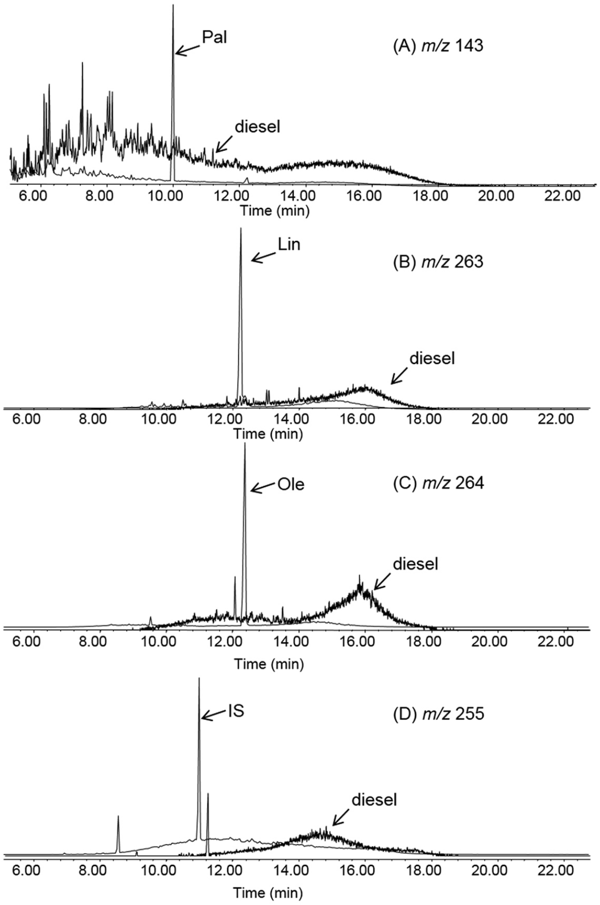

Figure 1. GC/MS-SIM mass chromatograms of pure diesel and diesel fortified with ester: (A) *m/z* 143; (B) *m/z* 263; (C) *m/z* 264 and (D) *m/z* 255.

Evaluation of the degradation of biodiesel:diesel blends in storage conditions

The experimental conditions used to study the significance of the variables in the degradation process of biodiesel:diesel blends, as well as their interactions, were similar to actual Brazilian storage conditions. The levels used in this study were selected according to the storage regulations recommended by the ANP. Brightness was not considered as a variable because the biodiesel:diesel blend

Table 4. Parameters of the standard solution analytical equation

Ester	Equation	R^2	CI
Methyl palmitate	$y = 4.62x + 0.202$	0.991	0.202 ± 0.238
Methyl linoleate	$y = 0.64x + 0.155$	0.967	0.155 ± 0.398
Methyl oleate	$y = 3.31x - 0.085$	0.991	-0.085 ± 0.702

CI: Confidence interval for the linear coefficient.

was stored in the dark, as recommended by the ANP. In this study, the samples were stored in the dark to minimize possible photodegradation.

The immediate GC/MS-SIM analyses of the prepared samples confirmed the percentage of biodiesel in diesel that was actually added. Control samples were kept in a freezer over the 45-day trial, and the GC/MS-SIM analyses also showed no change in the initial biodiesel content.

The percentages of biodiesel in the samples from the experimental design are presented in Table 5. The results showed that the samples underwent degradation in all storage conditions. Even so, samples 1, 5, 6, 15, 17, 18 and 19 presented biodiesel content within the variation range allowed by the ANP (± 0.5%).

The Pareto chart (Figure 2) showed that the percentage of biodiesel in diesel (variable 1 in the chart) and the interaction between time and water content in biodiesel (2by4 in the chart) are significant factors for sample degradation. According to the chart, the intensity of the degradation process is inversely proportional to the biodiesel content in diesel. This result requires a very careful interpretation because the experiments were carried out in sealed flasks and in the absence of light. Considering that the volume of all samples from the experimental design was the same (10.0 mL), the detection of less oxidative degradation even increasing the amount of biodiesel in diesel could be linked to the amount of oxygen present in the flask. In the studied conditions, the biodiesel can suffer only auto-oxidation. There was no possibility of degradation by photo-oxidation. Auto-oxidative degradation of biodiesel occurs via radical chain reaction. During the initial biodiesel oxidation stages, the allylic and

Table 5. Average percentages (%) of biodiesel in the samples after storage for 15, 30 and 45 days

Sample	Biodiesel in diesel / %	Water content / %	Temperature / °C	time / days	Biodiesel in diesel after storage / %	Response / %
1	5.0	0.01	30	15	**4.5**	0.5
2	5.0	0.01	50	15	3.9	1.1
3	5.0	0.09	30	15	3.9	1.1
4	5.0	0.09	50	15	4.1	0.9
5	10.0	0.01	30	15	**9.7**	0.3
6	10.0	0.01	50	15	**9.6**	0.4
7	10.0	0.09	30	15	9.4	0.6
8	10.0	0.09	50	15	9.0	1.0
9	5.0	0.01	30	45	4.0	1.0
10	5.0	0.01	50	45	4.1	0.9
11	5.0	0.09	30	45	4.1	0.9
12	5.0	0.09	50	45	4.1	0.9
13	10.0	0.01	30	45	9.1	0.9
14	10.0	0.01	50	45	9.1	0.9
15	10.0	0.09	30	45	**9.5**	0.5
16	10.0	0.09	50	45	9.2	0.8
17	7.5	0.05	40	30	**7.2**	0.3
18	7.5	0.05	40	30	**7.1**	0.4
19	7.5	0.05	40	30	**7.0**	0.5

Response = (initial percentage of biodiesel in diesel) – (percentage of biodiesel in diesel after storage). Standard deviation of 0.2, based on replicates of the central point. Samples in accordance with ANP specification are shown in bold.

bis-allylic methylene groups to the double bonds are more active and hydrogen radicals ($H^{\bullet}$) are abstracted by radical initiators. The resultant radicals interact with oxygen, which results in peroxide formation for the propagation step.[34] Thus, the restriction of oxygen is a limiting factor of the oxidative process.

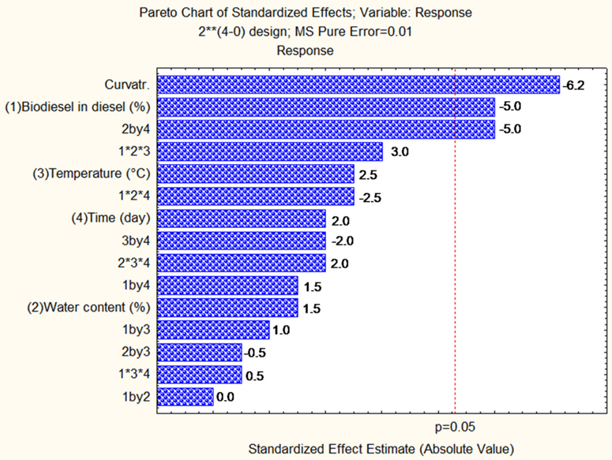

Figure 2. Pareto chart from 2^4 factorial design.

Some studies have provided support for this hypothesis.[35,36] Du Plessis *et al.*[35] concluded that the exclusion of air slows the oxidation of pure biodiesel, regardless of the temperature, if the storage stability is tested at or above 30 °C. Recently, Kovács *et al.*[36] monitored the absorption of oxygen in biodiesel samples for 120 days at 35 and 20 °C. The results showed that the absorption of oxygen from the headspace compartment was higher at 35 °C than at 20 °C. However, the authors also reported that there was no sharp increase in the amount of absorbed oxygen.

The results presented by these two studies[35,36] also provide support for a second discussion. Hydrocarbons with higher vapor pressure present in diesel certainly migrate to the vapor phase establishing an equilibrium within the flask. The presence of hydrocarbons in the headspace could cause an increase in the absorption of oxygen in the liquid phase. If this is possible, it could explain the higher degradation observed in samples with higher diesel volume, i.e., less biodiesel content. A more in-depth study of how the amount of oxygen affects the autoxidation process of biodiesel should be carried out. But these results are a new important contribution to the knowledge of the stability of biodiesel:diesel blends. As an example, Karavalakis *et al.*[10] evaluated the effect of different characteristics of diesel fuel on the blends' oxidation stability. The authors suggested that stability may also be affected by certain characteristics of the diesel fuel. Their results revealed that additional studies must be carried out to fully evaluate the actual mechanisms that may affect the oxidation stability of biodiesel:diesel blends and to investigate the impact of diesel fuel composition on this process.[10]

As far as we know, all the studies reported in the literature showed that raising the concentration of biodiesel in diesel also increases the oxidative degradation of the sample. It is worth mentioning that the experiments were performed under favorable conditions of oxidative degradation such as exposure to air, sunlight or accelerated oxidation conditions. Our experiments, on the other hand, simulated ideal storage conditions.

The Pareto chart also showed that the interaction between time and water content in biodiesel has a significant effect on the degradation process. Although, individually, the variables water content in biodiesel and time were not significant within the range evaluated, at the 95% confidence interval. The replicates provided reliability to the result obtained and the interpretation is not trivial. It may be associated with changes in the water content throughout the storage period due to the establishment of a vapor-liquid equilibrium in the sealed flask. The probability of migration of hydrocarbons to the vapor phase associated to the possibility of absorption of oxygen in the liquid phase make this discussion even more complex.

In a previous study, the authors showed that there was no accelerated effect on the degradation of biodiesel sample due to increased water levels.[21] Our experimental design indicated that the presence of 0.09% v/v of water in biodiesel does not significantly affect the fuel degradation. This concentration is above the maximum limit allowed by the ANP (0.02% v/v). Although the percentage of water was not shown to be statistically significant for the degradation process within the range studied, this result does not mean that the water content should not be monitored and controlled. The results showed that the interaction of water content with others variables, like time for example, can affect the stability of the fuel. Biodiesel is hygroscopic, and water can cause ester hydrolysis, which changes the fuel composition and property as well. Therefore, the water content is an important issue.[11] Another factor that must be considered is that the water content can affect the performance and durability of the motor.

The ANOVA data (Table 6) showed that the model is well adjusted. The p value of the lack of fit was higher than α (0.05 at the 95% confidence interval). The ANOVA results also indicated that the significant variables were the biodiesel content in diesel (variable 1, Table 6) and the interaction between time and the water content in biodiesel (2by4, Table 6). This result was verified with the p value and the F value. The ANOVA results are in agreement with those on the Pareto chart (Figure 2).

Table 6. ANOVA results based on the average of the response values

Source	Sum of squares (SS)	Degree of freedom (df)	Mean square (MS)	F-Value (F)	*p*-Value
Curvature	0.392636	1	0.392636	40.90821	0.023584
(1) Biodiesel content in diesel / %	0.250893	1	0.250893	26.14015	0.036191
(2) Water content in biodiesel / %	0.039123	1	0.039123	4.07612	0.180950
(3) Temperature / °C	0.103289	1	0.103289	10.76149	0.081698
(4) time / days	0.052756	1	0.052756	5.49653	0.143723
1 by 2	0.003349	1	0.003349	0.34897	0.614562
1 by 3	0.024072	1	0.024072	2.50804	0.254112
1 by 4	0.031971	1	0.031971	3.33098	0.209535
2 by 3	0.000928	1	0.000928	0.09666	0.785285
2 by 4	0.265925	1	0.265925	27.70638	0.034249
3 by 4	0.036912	1	0.036912	3.84576	0.188907
1*2*3	0.126244	1	0.126244	13.15322	0.068327
1*2*4	0.050984	1	0.050984	5.31195	0.147665
1*3*4	0.006398	1	0.006398	0.66660	0.500017
2*3*4	0.037815	1	0.037815	3.93987	0.185572
Lack of fit	0.057650	1	0.057650	6.00650	0.133857
Pure error	0.019196	2	0.009598		
Total SS	1.500141	18			

ANOVA; Var.:Response; R-sqr=.94877; Adj:.69264 2^4 design; MS Pure Error=.009598.

Figure 3 shows the mean plots obtained from the relations among the variables biodiesel content in diesel, water content in biodiesel and time. According to the plot, the highest degradation response was obtained for lower biodiesel content in diesel. A variation can be observed in the degradation response with time and the amount of water, as corroborated by the ANOVA data and by the Pareto chart values.

Other statistical evaluations that corroborate the previous discussion are presented in Figures 4, 5 and 6. Figure 4 shows the response surface of the relation between the variable time, the variable water content in biodiesel and the response [(initial percentage of biodiesel in diesel) – (percentage of biodiesel in diesel after storage)]. The graphic shows that a higher degree of degradation is attained when one variable is at its lowest level and the other is at its highest level simultaneously. This is consistent with that observed in the means plots, and the negative significance of this interaction appears on the Pareto chart and ANOVA.

Figure 5 shows the response surface for degradation of the relation between the variables time and biodiesel content in diesel. The graphic shows that response increases as the biodiesel content decreases, confirming the results obtained with ANOVA and the values generated by the Pareto chart.

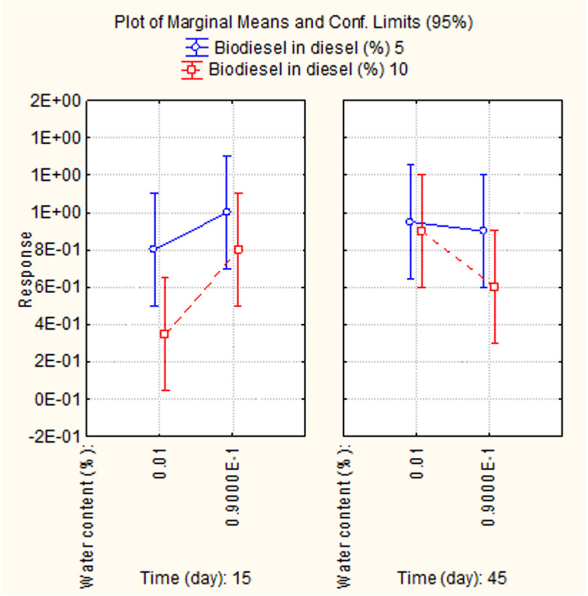

Figure 3. Mean plots between the variables biodiesel content in diesel and water content in biodiesel for 15 and 45 days.

Figure 6 shows the response surface of the relation between the variables water content in biodiesel and biodiesel content in diesel. The variation in the response is mainly affected by the biodiesel content in diesel, corroborating the previous discussion. The full factorial

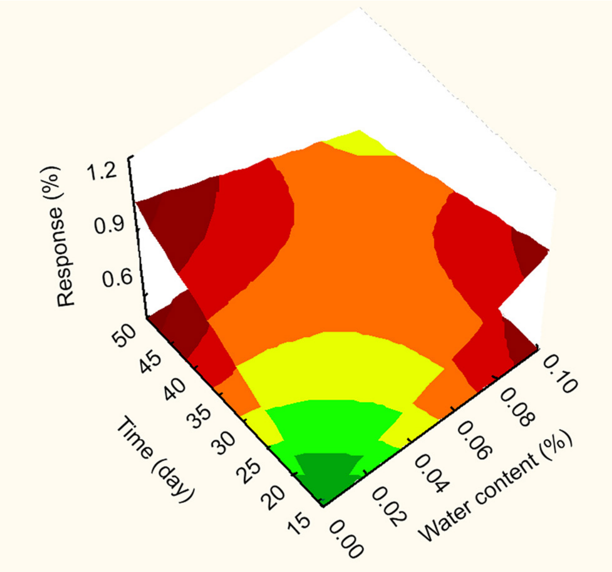

Figure 4. Response surface of biodiesel degradation highlighting the interaction between the variables time and water content in biodiesel (biodiesel content in diesel: 7.5% v/v; temperature: 40 °C).

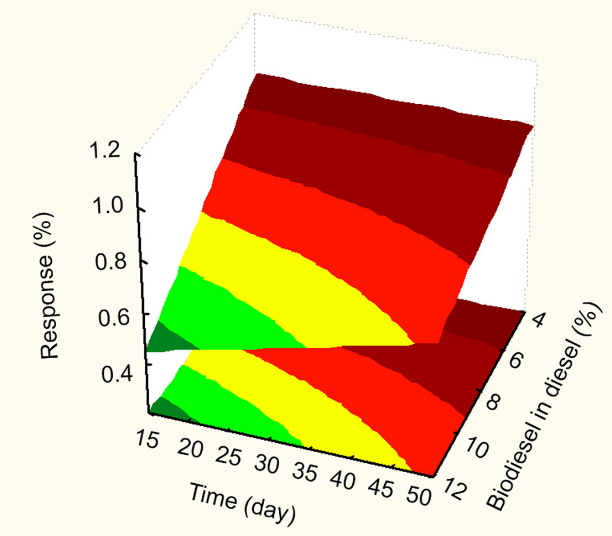

Figure 5. Response surface of biodiesel degradation highlighting the interaction between the variables time and biodiesel content in diesel (water content in biodiesel: 0.05% v/v; temperature: 40 °C).

design allowed the analysis of the behavior of the variables. None of the graphics shows higher degradation, only trends within the range investigated.

Conclusions

The stability of biodiesel:diesel blends is a complex process that is affected by various factors. The present study used a full factorial design to assess the significance of several variables related to the storage conditions of soybean biodiesel:diesel blends. Sample degradation was evaluated based on the direct measurement of methyl linoleate and methyl oleate, which are the target compounds in the oxidation process.

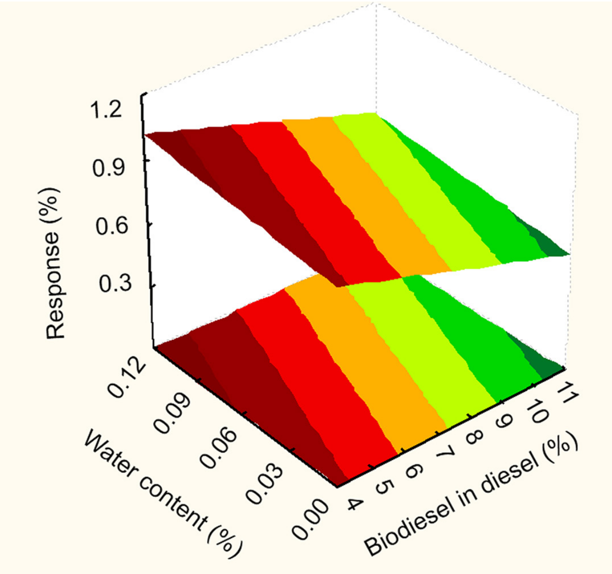

Figure 6. Response surface of biodiesel degradation highlighting the interaction between the variables biodiesel content in diesel and water content in biodiesel (time: 30 days; temperature: 40 °C).

Our experiments simulated ideal storage conditions, different from the studies described in the literature. The results indicate that the restriction of oxygen turnover in the samples limited the degradation of biodiesel in blends with higher percentage of the biofuel. Further studies are needed to elucidate the effect of the amount of oxygen on this process. The variables water content in biodiesel, temperature and time did not significantly affect the degradation process within the range investigated and at the 95% confidence interval. Although the water content in biodiesel did not affect the degradation process, it is an important variable to control. There is no doubt that these results are a new important contribution to the knowledge of the stability of biodiesel:diesel blends.

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