CHEMIOMETRIC STUDY ON THE INFLUENCE OF CAROTENOIDS AND SATURATED FATTY ACIDS IN BIODIESEL STORAGE STABILITY

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ABSTRACT

Biodiesel is a fuel derived from renewable raw materials with the potential to change the world's energy matrix, and reduce the damage caused by fossil fuels to the environment and human health. The disadvantage of biodiesel is its low oxidative stability which affects its storage time. In this study, experimental biodiesel blends were used to identify the influences of carotenoid and free fatty acid contents on storage stability by using UV-VIS spectroscopy. Binary biodiesel blends were prepared blending buriti biodiesel contents ranging from 30% (v/v), 60% (v/v), and 90% (v/v) with soybean, sunflower, and beef tallow biodiesel. The blends were stored up to 45 days to compare the oxidative stabilities. The binary biodiesel blend composed by 90% buriti biodiesel and 10% beef tallow one presented the highest oxidative stability during the evaluated storage time.

KEYWORDS

biodiesel; oxidative stability; buriti; beef tallow; storage time

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1. INTRODUCTION

As a fuel alternative to diesel oil, biodiesel has gained space in the world's energy scenario since it comes from renewable sources with sustainable social, environmental and economic production (Ferrari et al., 2005; Sousa-Aguiar et al., 2014). Biodiesel production has increased due to its use as a pure fuel or in biodiesel/diesel blends to replace a portion of the fossil fuel. As a consequence, a more rigorous quality control is required throughout the production process, as well as in its storage stability.

Biodiesel consists of alkyl esters of fatty acids that may exhibit one or more unsaturations along the chain. The number of carbons and unsaturations, as well as their positions, varies according to the plant species from which the oil was extracted. Some vegetable oils (soybean, sunflower, and canola) used in the production of biodiesel are composed by triacylglycerides with polyunsaturated fatty acids, and in the transesterification reaction there is no modification in the fatty acid chain. Hydrogen in the allylic position at the instauration is acidic, and deprotonation is the beginning of a radical auto-oxidation mechanism. The oxidation process passes through unstable products until it is completed with the formation of neutral molecules, generally polymeric ones, which affect important biodiesel properties such as viscosity (Mendonça et al., 2011; Lôbo et al., 2009).

One of the disadvantages of biodiesel compared to fossil diesel is related to its oxidation stability, which directly affects the storage time (Carvalho et al., 2013; Pinto et al. 2005). Knowledge of the oxidative stability is a fundamental condition for the quality control of biodiesel (Carvalho et al., 2013). The lower oxidative stability of biodiesel, when compared to fossil diesel, is due to external factors such as: temperature, light, impurities, and contact with atmospheric oxygen, as well as intrinsic factors to its chemical composition (Carvalho et al., 2013). As the presence of external factors is inevitable, the intrinsic factors become highly relevant. Thus, the oxidative degradation of biodiesel depends on the degree of esterification, the process chosen for its production, the humidity, the presence of intrinsic antioxidants such as carotenes, and the nature of the fatty acids used in its production, because the amount of

unsaturated fatty acids of oils and fats favor the development of oxidative rancidity, mainly of oleic acid (C18:1), linoleic acid (C18:2) and linolenic acid (C18:3) (Ferrari & Souza, 2009; Stavinoha & Howell, 1999).

In this sense, it is possible to detach some raw materials such as animal tallow and vegetable fats that have a strong saturated character, which represents a delay in the oxidative degradation of biodiesel. In addition, many oleaginous plants have biomolecules that act in the defense of the plant, and remain in the oil, such as the phenolic compounds (Rodrigues et al., 2009), and the carotenoids that have antioxidant properties. Thus, fuel performance and storage capacity can be improved without the aid of synthetic antioxidants that can compromise environmental and socioeconomic benefits of biodiesel's production and use.

One possibility to increase stability and improve final fuel quality is to use biodiesel blends derived from different raw materials. For example, beef tallow biodiesel increases stability during storage, once its composition includes highly saturated fatty acids. Due to that, the degradation can occur more slowly (Prado et al., 2015). Another raw material that improves the stability of the final product is buriti (*Mauritia flexuosa*) oil, which was used in this work (Albuquerque et al., 2005). This fruit originated from the Amazon region, abundant in the Brazilian cerrado, is rich in monounsaturated fatty acids and carotenoids (β -carotene) (Rodrigues et al., 2009).

One of the challenges in the production of biodiesel from the buriti oil is related to the lack of fruit availability throughout the year. On the other hand, it does not require the deforestation of large areas, generating social, environmental, and economic benefits. It also has no competition for food, when compared to other crops such as soybean. The buriti fruit is rich in oil, both in the pulp and in the nut. Two fatty acids are more prominent in its oil composition: oleic acid (75%, C18:1) and palmitic acid (18%, C16:0) (Albuquerque et al., 2005). Pulp oil has a high content of β -carotene, one of the main carotenoids with medicinal value (healing) and antioxidant properties (Prado et al., 2015). Carotenoids have antioxidant properties due to their high capacity to sequester free radicals, and to deactivate reactive

oxygen species. The antioxidant potential of β -carotene is due to the number of conjugated double bonds, which give the molecule high chemical reactivity (Rodrigues et al., 2009). In the structure of the carotenoids, the presence of conjugated double bonds contributes to its pigmentation, absorption of radiation in the UV-VIS range, and antioxidant activity.

In this work, it was investigated how the intrinsic factors, such as the chemical composition of biodiesel (contents of carotenoids and saturated fatty acids), affect its storage stability. The experiment monitored the ester decomposition, and the formation of primary and secondary oxidation products during the storage of binary biodiesel blends from soybean, sunflower, beef tallow, and buriti via UV-VIS spectroscopy.

2. MATERIALS AND METHODS

2.1 Vegetable oils and beef tallow

In this work, it was used vegetable oils (buriti, sunflower, and soybean) and animal fat (beef tallow) to produce biodiesel blend. The buriti oil used in the study was extracted by means of the cooking process from the pulp acquired in the city of Mateiros (Tocantins - Brazil). The sunflower and soybean oils were bought at the supermarket in the city of Gurupi (Tocantins - Brazil). The beef tallow was supplied by a municipal slaughterhouse from the city of Gurupi (Tocantins - Brazil).

2.2 Purification and characterization

Initially, the crude oil from buriti and beef tallow were submitted to degumming treatment, using 40 g of oil for every 40 g of warm water at (90 °C). The oil/water mixture

was stirred on a hot plate (Thelga, TMA 10CFI) with magnetic stirring. Then, a new stirring was made in an automatic orbital shaker table (Biofoco Equipamentos para laboratório, BF2 MAOR 200) under 180 rpm rotation at room temperature (27 °C), for 1 hour. The mixture was subjected to phase separation using a separating funnel, and dried in an oven at 110°C for 1 hour. At the end, the following measurements were made in the oil and fat: pH (MERCK, pH-Indikatorstäbchen nicht blutend pH 0-14 Universalindikator), acid number - AOCS method (Osawa et al., 2006), saponification - AOCS method (Toscano et al., 2012), and viscosity through the analog rotary viscometer (EDUTECH, EEQ-9031 NDJ-4).

2.3 Biodiesel production

Biodiesel was produced using 140 g of each vegetable oil or animal fat at a 9:1 methanol/oil molar ratio and 2% w/w of catalyst (KOH) (Prado et al., 2015). After biodiesel production, the samples were done in triplicate and, then, submitted to acidity index and saponification index physicochemical analysis. In this work, the average parameters were used and their relative deviation was very small. After, binary biodiesel blend samples were obtained in accordance with Table 1.

The samples were stored under normal conditions of temperature and pressure in glass bottles protected from light. The storage stability control was performed by using UV/Vis spectroscopy (PG Instruments, T60 Spectrometer UV-vis). The samples were prepared in 10-mL volumetric flasks by diluting the blends in dichloromethane (1:10, v/v). The absorbance for esters and carboxylic acids was

Table 1. Binary biodiesel blends used in this work (v/v).

Blend A Buriti / Soybean		Blend B Buriti / Sunflower		Blend C Buriti / Beef tallow	
A1	30 % / 70 %	B1	30 % / 70 %	C1	30 % / 70 %
A2	60 % / 40 %	B2	60 % / 40 %	C2	60 % / 40 %
A3	90 % / 10 %	B3	90 % / 10 %	C3	90 % / 10 %

monitored at 205 nm, and for the primary oxidation compounds and secondary oxidation compounds, at 232 and 268 nm, respectively.

2.4 Statistical analysis

The statistical analysis of data obtained by chemical analyses was conducted by Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA). The PCA uses a linear transformation of data in multidimensional space, i.e. the original correlated variables are converted into a set of values of linearly uncorrelated variables called principal components (Long & Valder, 2011). For this method the data were analyzed with SciLab software (SciLab, 2012). The hierarchical clustering or hierarchical cluster analysis (HCA) is a method of cluster analysis which seeks to build a hierarchy of clusters. This analysis was developed for clustering correlation matrixes with the goal of building a dendrogram that assembles all elements into a single tree. The software XLStat was used to do the dendrogram (XLstat, 2017).

3. RESULTS AND DISCUSSION

3.1 Characterization of the raw materials and biodiesel

The oils were characterized in terms of acid value, saponification value, appearance, and kinematic viscosity, according to the data presented in Table 2.

As expected, the refined soybean and sunflower oils presented a clear/impurity-free appearance, unlike beef tallow and crude buriti oil. On the other hand, the acidity value found for sunflower oil was significantly higher than the specification (0.3 mg KOH/g oil) for edible refined oils (Toscano et al., 2012). Beef tallow also stands out because of its high acid value (10.5 mg KOH/g of fat), considering that it is a gross residual raw material. Acid value reflects the state of conservation of oils and fats and therefore a quality parameter for edible oils. Thus, beef tallow and sunflower oil do not present adequate edible oil characteristics and cannot be used directly in biodiesel production via basic transesterification (Sampaio & Carrazza, 2012). The degradation reactions of the triacylglycerides, constituents of the oils and fats, formed as free fatty acid products, have the concentration determined by the acidity index (Paucar-Menacho et al., 2007). For biodiesel production, the high content of these free fatty acids is undesirable because they can favor the saponification reaction, lowering the efficiency of the transesterification reaction. To avoid this problem, an acid esterification step prior to transesterification is usually included. In this case, the free fatty acids are converted to methyl esters, which allow a transesterification reaction with high yield, and simple phase separation (Sampaio & Carrazza, 2012; Ramadhas et al., 2005).

The values of the saponification index for buriti, soybean, and sunflower oils were lower than those described in the literature (Murugessan et al., 2009; Berchmans & Hirata, 2008). It can be inferred that the oils have a reasonable unsaponifiable content, and cannot be converted into esters and, therefore, decrease the yield of the synthesis. However, beef tallow presented a

Table 2. Physicochemical properties of the raw materials and biodiesel (FAME).

Parameters*	Buriti		Soybean		Sunflower		Beef Tallow	
	Oil	FAME	Oil	FAME	Oil	FAME	Oil	FAME
Kin. Visc. (mm ² /s)	5.23	4.42	4.50	–	4.30	–	–	–
SV (mg KOH/g oil)	68.4	86.9	62.9	78.6	60.2	204.9	126.0	197.0
AV (mg KOH/g oil)	0.034	0.047	0.258	0.017	1.13	0.052	10.5	0.513
Aspect**	POM	LFI	LFI	LFI	LFI	LFI	POM	LFI

* Fatty acid methyl esters (FAME) Specifications (ANP, 2014): Kinematic viscosity (Kin. Visc.) – 3.0 to 6.0 mm²/s; Saponification value (SV) – not required; Acid value (AV) – 0.50 mg KOH/g of oil; Aspect – Limpid and free of impurities (LFI)

** Aspect – Presence of organic material (POM); Limpid and free of impurities (LFI)

saponification index closer to that described by other authors, and leading one to believe that its chemical composition is highly favorable to the saponification reaction (Silva et al., 2009).

After the transesterification reaction, the values found were in accordance with standards for acid value and appearance for all samples of methyl esters (Jovanovic et al., 1998). The saponification value of the biodiesel was higher than the ones for respective oils and fats, demonstrating that the transesterification reaction was efficient, since biodiesel is composed of methyl esters of fatty acids, and they are a highly saponifiable matter (Ma & Hanna, 1999).

3.2 UV-vis spectroscopy analysis

The chemical changes related to degradation during the storage period of the biodiesel samples were monitored with the specific wavelengths of the UV-vis: 205 nm (carboxylic acids), 232 nm (primary oxidation compounds), 268 nm (secondary oxidation compounds). To verify the influence of the chemical composition on the stability during the storage, it was used binary blends containing different percentages of biodiesel from buriti, soybean, beef tallow, or sunflower biodiesels. The absorbances at 205 nm

were measured and the results for the binary blends are shown in Figure 1.

One could verify that, up to 21 days of storage, the absorbance at 205 nm abruptly decreases, showing an oxidation apex for samples A1, A2, B1, and B2. After 30 days, absorbance begins to increase mainly for samples A1, A2, B1, B2, B3, C1, C2, and C3. This behavior is perceived because at this wavelength the absorbance of esters and carboxylic acids occur.

The expected behavior during the oxidation process is that the esters degrade rapidly after the start of the reaction and this reflects in the absorbance. After that, the carboxylic acids are formed, according to the auto-oxidation mechanism (Jain & Sharma, 2010; Knothe, 2006; Vasconcelos & Godinho, 2002), and an increase in absorbance is observed at 205 nm. So, the longer it takes to determine this oxidation peak, the greater is the storage stability of the biofuel. In the sample with soybean biodiesel with higher buriti content (A3), as well as in samples containing beef tallow biodiesel (C1, C2, and C3), this oxidation peak is milder because oxidation occurs more slowly, since buriti is rich in natural antioxidants and beef tallow has a high content of saturated fatty acids. The increase in oxidation observed after 30 days was

Figure 1. UV-vis data of biodiesel at 205 nm during the days of storage.

Figure 2. The deterioration degree "k" for biodiesel blends during storage.

smaller for buriti biodiesel, due to the influence of the natural antioxidants present in the buriti oil that reduce the formation of the free fatty acids and retard the oxidation process.

It was also found that blends with higher buriti content (A3 and B3) and buriti blends with beef tallow (C1, C2, and C3) showed a decrease in the absorbance at 205 nm on the twenty-first day, due to a possible synergistic effect of two intrinsic factors of the samples: natural antioxidant content and saturated fatty acid content.

Additionally, the variation of the chemical composition was also accompanied by the intensity of the absorbance at 232 nm and 268 nm wavelengths, where the formation of primary and secondary oxidation products was observed. When the degradation reaction begins, radical species that react in chains are formed. As the degradation evolves, more stable secondary products are formed and, thus, biodiesel in advanced degradation is observed. The higher the formation rate of these secondary compounds, the faster the deterioration of the essential characteristics of biodiesel as fuel, such as viscosity. The "k" value is the ratio between absorbance at 268 nm and 232 nm, and it gives the increase in the deterioration degree of biodiesel, as shown in Figure 2.

As it was observed with the variations of absorbance at 205 nm, the samples composed by

biodiesels blends of buriti and beef tallow present minimal formation of degradation products. It means that during the days of storage, the formation of secondary products proportional to the primary ones is more intense in samples A and B. From Figure 2, it is highlighted the abrupt increase of "k" on the twenty-first day of storage in these samples, indicating the maximum storage period in consonance with what was observed at 205 nm. The behavior of B3 sample, with the highest percentage of buriti biodiesel (90%), shows the effect of the presence of carotenoids on storage stability, inhibiting low oxidation degree during 45 days of storage.

To verify the influence of the characteristics of the beef tallow biodiesel and buriti biodiesel, such as carotenoids and saturated fatty acids, in the storage stability, the principal component was used to analyze the samples. The results of UV absorption parameters during 45 days of storage were organized in a 6:55 matrix containing absorbance in 205 nm, "k", and percentage of tallow and buriti biodiesel. A centralization and reduction of the original data matrix was performed, and the data were analyzed with SciLab 5.5.2 software (SciLab, 2012).

The correlation matrix (Pearson) presented in Table 3 shows a significant positive correlation between storage days and absorbance at 205 nm,

Table 3. Principal Component Analysis - Matrix of correlation (Pearson).

	Days	abs 205 nm	K	% buriti	% beef tallow
Days	1	0.333	-0.044	-5.9×10^{-17}	1.161×10^{-17}
abs 205 nm	0.333	1	0.224	-0.181	-0.116
K	-0.0044	0.225	1	-0.185	-0.653
% buriti	-2.978×10^{-17}	-0.191	-0.185	1	-0.346
% beef tallow	9.672×10^{-18}	-0.116	-0.653	-0.346	1

as well as between absorbance at 205 nm and “k”. As it was observed experimentally, the absorbance at 205 nm increases with the storage time of biodiesel. The “k” value shows a weak negative correlation with the days of storage. This presents a peak of maximum concentration of secondary oxidation products, and then begins to decrease for the formation of compounds, such as polymers.

Moreover, there is a negative correlation between % buriti, % beef tallow, absorbance values at 205 nm, and “k”. Buriti oil has high levels of carotenoids that act as natural antioxidants, and beef tallow has a higher amount of saturated fatty acids, and therefore could influence to degrade the samples for a long time. Thus, during the storage, the samples constituted of higher concentration of buriti biodiesel and tallow biodiesel do not show an increase in the absorbance values.

Both carotenoids and saturated fatty acids play important roles in the delay of auto oxidation, but what is not known is the degree of higher

influence, the presence of natural antioxidants or a higher degree of saturation. Analysis of the correlation matrix shows that there is a greater negative correlation between the absorbance at 205 nm and the percentage of buriti than between this absorbance and the percentage of beef tallow. The presence of carotenoids seems to prevent the initial stage of auto oxidation of the esters in the formation of free fatty acids. But it was also possible to note an even greater negative correlation value between the percentage of beef tallow and “k”. Thus, one can be notice that the higher content of saturated fatty acids in the composition of biodiesel delays the formation of secondary oxidation compounds more effectively than carotenoids. Therefore, both carotenoids and the content of alkyl esters of saturated fatty acids in the biodiesel composition had an important influence for the antioxidant role. However, these factors act differently in this case.

In Figure 3 one can see the results of PCA that show the behavior of the first two principal

Figure 3. Results of the first two principal components (PC1 and PC2).

Figure 4. Dendrogram obtained from hierarchical cluster analysis.

components, which explain 62.9% of the total variance of data. Principal components 1 and 2 (PC1 and PC2) represent 34.9% and 28%, respectively, of the total variance. It is possible to observe that there is a strong correlation between the storage days and the absorbance intensity at 205 nm. This indicates that the longer period of storage of the biodiesel sample highly influences the degradation of the esters in the formation of free fatty acids that absorb in this region. A correlation between storage days, absorbance at 205 nm, and the “k” value was also observed. The samples classified in the first quadrant showed higher degradation during storage.

The percentage of buriti and absorbance at 205 nm and the days of storage explain the negative correlation with each other in PC2. The absorbance at 205 nm has a small increase and the result is the low formation of free fatty acids to the detriment of the esters. Samples with a higher percentage of buriti biodiesel take more time to degrade, in relation to the production of free fatty acids and in the formation of by-products oxidation process. The best samples are those in the fourth quadrant, as they suffer less degradation over the storage period. These samples are samples composed of buriti and beef tallow.

A hierarchical cluster analysis was used to verify the influence of the percentage of sunflower and soybean. The data was obtained from a matrix similar to the previous one with an addition of only

of two columns: % of sunflower and % of soybean for the classification into groups. Figure 4 shows the dendrogram resulting from HCA in which the percentages of sunflower and soybean were included. It is possible to separate them into three main groups: G1, G2, and G3. The G1 group is composed of samples that contain a higher percentage of sunflower biodiesel. This group presented the worst performance during the storage, with a significant increase in absorbance at 205 nm and in “k” value (ratio 268/232 nm). The second group G2 is composed by the samples with the highest percentage of soybean biodiesel, with an intermediate stability. The third group G3 is composed by the samples that less degraded during the storage, for example, samples with biodiesel of beef tallow and 90% of buriti biodiesel.

The G3 group, which had the lowest deterioration during the 45 days of storage, consisted of a blend of a highly saturated biodiesel (beef tallow) with a biodiesel rich in carotenoids (buriti). It is possible, however, to notice a subdivision in this group between the samples that contain beef tallow at a greater percentage, and that contains buriti at a greater percentage. All binary beef tallow: buriti blends less degraded during storage compared to the others. Based on the above, one can conclude that blends C1 and C2 represent the best blends, in which there is less formation of free fatty acids and oxidation of the by-products from oxidation process.

4. CONCLUSIONS

The quality of biodiesel is essential to avoid the modification of its physicochemical characteristics between production and application. The chemical composition of biodiesel, rich in unsaturated fatty acids, implies in a lower storage stability compared to mineral oil diesel. The proper selection of raw material, in terms of chemical composition, can change this scenario. In this work, binary biodiesel blends from four raw materials: soybean oil, sunflower oil, beef tallow, and buriti oil; were tested in relation of the storage stability.

One could verify that the amount of unsaturated fatty acids influences the storage stability strongly through the UV-vis absorbance at 232 and 268 nm. On the other hand, the use of highly saturated raw materials, such as beef tallow, is insufficient to avoid the formation of free fatty acids, due to the degradation of the methyl esters.

Also, the use of raw materials rich in carotenoids and natural antioxidants, such as buriti, can significantly decrease the degradation of esters to form free fatty acids. When the raw materials were highly unsaturated, like sunflower oil, the carotenoids reduced the oxidation reaction. But when the effects could be combined, the degradation of the esters to form free fatty acids and formation of secondary oxidation compounds could be avoided for at least 45 days (C1, C2, and C3). The oxidation could be inhibited for up to 45 days with the use of binary blends of beef tallow and buriti, minimizing the use of synthetic antioxidants.

The intrinsic effects of the raw material influenced strongly the behavior during the biodiesel storage. The saturated fatty acid and the carotenoid contents had important effects on the degradation of the esters and the formation of degradation products.

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