Alteration of babassu biodiesel properties through camphor and biodiesel of tung

Alteração das propriedades do biodiesel de babaçu por meio de cânfora e biodiesel de tungue

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Abstract

Babassu oil is extracted from the babassu palm, one of the most important plants in the north and northeast Brazilian regions, and like many biofuels, it does not have adequate properties to be used as pure fuel, especially under low-temperature conditions. Therefore, researches to improve the physical-chemical properties of these biofuels are needed, one of the most common methods is using additives, usually synthetic ones, which are not environmentally friendly. A good alternative would be to try to found natural compounds with this potential. This paper describes the effects of the addition of two natural compounds, tung biodiesel, and camphor, in the physical properties of babassu biodiesel. These additives were select because of their physical-chemical properties, which can potentially improve the babassu biodiesel ones. They were tested separately, the camphor at the 3, 4, 5, 6 % proportions, and the tung biodiesel at 3, 5, 9, 12 %. The results were compared to biodiesel standards, limited by the Brazilian National Agency of Petroleum, Natural Gas, and Biofuels (ANP), and for both additives, the 3 % proportion showed the best suited to the quality standards established at the Brazilian normative. Thus, was observed that the camphor and the tung biodiesel has the potential to be efficient additives in babassu biodiesel.

Keywords: Blends. Biofuel. Natural additives. Freezing point. Viscosity.

Resumo

O óleo de babaçu é extraído da palmeira de babaçu, uma das plantas mais importantes das regiões Norte e Nordeste do Brasil, e como muitos biodieses, o biodiesel de babaçu não possui propriedades adequadas para ser utilizado como combustível puro. Portanto, pesquisas para melhorar as propriedades físico-químicas desses biocombustíveis são necessárias, um dos métodos mais comuns é a utilização de aditivos, geralmente sintéticos, que não são ecologicamente corretos. Uma boa alternativa seria tentar encontrar compósitos naturais que se enquadrem como aditivos para o biodiesel. Este artigo descreve os efeitos da adição de dois compósitos naturais, biodiesel de tungue e cânfora, nas propriedades físicas do biodiesel de babaçu. Estes compósitos foram testados separadamente a cânfora nas proporções de 3, 4, 5, 6 % e o biodiesel de tungue em 3, 5, 9, 12 %. Os resultados foram comparados aos padrões de biodiesel, limitados pela Agência Nacional do Petróleo, Gás Natural e Biocombustíveis (ANP), e para ambos os aditivos, a proporção de 3 % mostrou-se mais adequada a normativa brasileira. Observou-se que a cânfora e o biodiesel de tungue têm potencial para serem aditivos eficientes no biodiesel de babaçu.

Palavras-chave: Blendas. Biocombustível. Aditivos naturais. Ponto de congelamento. Viscosidade.

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Introduction

Automobile fuels are great emitters of greenhouse gases and, therefore, it is important to produce more environmentally-friendly biofuels and to improve the physical-chemical properties of these fuels to make them more efficient biofuels (ATMANLI, 2016; GONÇA; DOBRUCAŁI, 2016; RUHUL et al., 2016; KUMAR; SUBRAMANIAN, 2017; MAGRO et al., 2016).

Biodiesel is a renewable, biodegradable and, non-toxic fuel that can be obtained by transesterification reactions of vegetable oils. However, it has physical-chemical properties that, if not improved, can damage the engines, like viscosity, density and, freezing point. Thus, researches have been conducting to improve these properties, such as mixing additives (ABE et al., 2016; CAMPOS FILHO et al., 2015; ROMAGNOLI et al., 2018; SENRA; MCCARTNEY; SOH, 2019; SECCO et al., 2017; VARATHARAJAN; PUSHPARANI, 2018; VALENGA et al., 2019).

Among the biodiesel physicochemical properties, the freezing point is one that should be improved. Because of the freeze-crystallization, the biofuel can become so compact as to obstruct the fuel supply lines in the engine. Thus, the purpose of this study, and several others, is to perform biodiesel freeze at a much lower temperature, especially in the cold climate region (MONIRUL et al., 2017; SENRA; MCCARTNEY; SOH, 2019; KNOTHE; RAZON, 2017; XUE et al., 2016).

One way to improve these properties without production expenses is by adding substances that change the biodiesel molecular dynamic. The additives are used for many purposes, to prevent deterioration like BHA, BHT, and TBHQ, improve physical properties and improve the freezing points as derived from petroleum products, but usually, these additives are synthetic ones (BORSATO et al., 2014; MAIA et al., 2011; RIZWANUL FATTAH et al., 2014). A more sustainable alternative is to search for additives from natural sources because they provide benefits, as being renewable, non-toxic, and usually cheaper than the synthetic ones (BHARTI; SINGH, 2020; BUOSI et al., 2016).

The babassu palm (Orbignya phalerata, Mart.) is one of the most important palm trees in the north and northeast Brazilian regions because the commercial purpose of wood and straw handicrafts of this plant (OLIVEIRA et al., 2013). The babassu biodiesel has low molecular weight and few double bonds with predominantly of lauric acid (C12: 0), causing it to have low viscosity and inferior freezing properties (SANTOS et al., 2007; SILVA et al., 2010).

Our study’s purpose was to used natural additives as camphor and tung biodiesel to control the babassu biodiesel physical-chemical properties. Camphor is a chemical compound that can be extracted from the camphor plant (Cinnamomum camphora), and tung biodiesel is a fatty acid ester obtained from tung oil transesterification.

Both camphor and tung biodiesel were select to be tested as additives in babassu biodiesel because they chemical structure, cost, and as they have physical-chemical characteristics that can be complements to babassu biodiesel, as good freezing properties and high molecular mass.

Tung biodiesel has predominant alpha Eleostearic acid (C18:3), has CFPP of -11 °C and 9.8 mm/s² viscosity at 40 °C (PARK et al., 2008) these are the main characteristics that lead to test this biodiesel as an additive, was expected that the babassu low viscosity improves the blend viscosity and the tung biodiesel reduce the babassu biodiesel pour point.

Camphor was a tridimensional chemical structure, expected its structure creates difficulties in the biodiesel crystallization process. The main chemical structure of the additives is in Figure 1.

Material and methods

Material

We obtained the babassu oil and the tung oil through Campestre, 2020 company. The camphor and the sodium methoxide (CH3NaO, p.a.) were obtained through the chemistry research group at the Western Paraná State University (UNIOESTE). And all the equipment that we used in this study were provided by the same university.

Production of babassu and tung biodiesel, and the blends babassu/tung and babassu/camphor

The biodiesels were synthesized by methylic route and homogeneous catalyst, using the sodium methoxide (CH3Na, p.a.). The alcohol: oil volume ratio was 1:3 (v/v) and the catalyst concentration of 1 % (v). The system was kept at 60 °C and mechanically stirred for 1 hour. Then, it was transferred to a separator funnel, to separate the glycerin. The purification was performed by three successive washes with distilled water and drying for 1h at 60 °C.
After we produce the biodiesels, we did the blends procedure. To the blends between babassu biodiesel and tung biodiesel were used the proportions of 3, 5, 9, and 12 % (v/v). To the blends between camphor and babassu biodiesel, we described in Table 1.

Table 1 – Quantity of camphor added to babassu biodiesel.

| Percentage of camphor in babassu biodiesel (%) | Camphor added to get the percentage (g) |
|-----------------------------------------------|----------------------------------------|
| Babassu 97% - Camphor 3%                       | 0.75                                   |
| Babassu 96% - Camphor 4%                       | 1.00                                   |
| Babassu 95% - Camphor 5%                       | 1.25                                   |
| Babassu 94% - Camphor 6%                       | 1.50                                   |

We use a Cannon Fenske 75 capillary viscometer. The flow time was writing down and the calculation was made by multiplying the flow time in seconds by the viscometer constant, using a 0.008 mm²/s for the Cannon Fenske 75mL. We performed this procedure at the temperatures 25 °C, 30 °C, 35 °C and 40 °C.

Biodiesels and blends pour point (PP)

Pour point test was performed by the ASTM D97. To this procedure, some modifications were made to obtain a more precise result. Instead of using mercury thermometric, we use a platinum sensor pt-100 term thermometer, with precision measurement of 0.01 °C, and to the low-temperature thermostatic refrigerated bath, the temperature was set up as -15 °C to 5 °C.

Infrared spectrum of tung and babassu oils and biodiesel

The infrared absorption spectra were performed on a Frontier spectrometer, ranging from 4000-400 cm⁻¹, on an ATR accessory.

Statistical analysis

Only basic statistical analysis was used, such as means and standard deviation. All statistical analyzes were performed in the program Microsoft Excel 2016.

Results and discussion

Blends babassu-tung density

The tung biodiesel has a magnifying effect on the babassu biodiesel density, once the samples with higher tung biodiesel proportions, such as 9 % and 12 %, have higher densities. This variation can be explained because tung biodiesel has a higher specific weight.
Figure 2 – Route for babassu biodiesel production and blends with the additives.

(0.934 - 0.943 g cm\(^{-3}\)) than babassu biodiesel (0.903 - 0.924 g cm\(^{-3}\)), and a longer carbon chain (CAMPESTRE, 2020). In Table 2, this effect can be observed.

Although blends had increased the density, none sample was over specification determined by the Brazilian National Petroleum Agency (ANP) standard from 0.85 to 0.90 g mL\(^{-1}\), except for the tung biodiesel (ANP, 2014).

Blends babassu-tung pour point (PP)

In Table 4 is observed the pour point temperatures for biodiesel blends.

According to the data obtained, small amounts of tung biodiesel (3 %) improves the pour temperature and higher concentrations tend to worsen the pour point. Thus, the 3 % blend showed the best result with a temperature of -8.5 °C, improving the pour point of babassu biodiesel.

The study developed by (YUAN et al., 2017) demonstrates the dependence of the cold filter plugging point on the profile of saturated fatty acids present in biodiesel blends.

In case of biodiesel blends which have short saturated fatty acid chains, like babassu biodiesel (C12:0, C14:0), with longer unsaturated fatty acid chains, like tung biodiesel (C18:3), was observed a slight improvement in the cold filter plugging point, until 20 % of long-chain unsaturated fatty acid biodiesel.

For the blend between babassu biodiesel and tung biodiesel, our study shows that this optimal blend percentage to the pour point is lower, around 3 % of the long-chain unsaturated fatty acid biodiesel.
Table 2 – Density of babassu biodiesel blends with tung biodiesel.

| Blends babassu-tung percentage | Blends weight (g) | Blends density (g.mL$^{-1}$) |
|---------------------------------|------------------|-----------------------------|
| Babassu 97% - Tung 3%           | 22.1584          | 0.8732                      |
| Babassu 95% - Tung 5%           | 22.1908          | 0.8745                      |
| Babassu 91% - Tung 9%           | 22.2486          | 0.8768                      |
| Babassu 88% - Tung 12%          | 22.2489          | 0.8769                      |
| Pure Tung biodiesel             | 23.0965          | 0.9102                      |

Source: The authors.

Table 3 – Viscosity (Cst) and standard deviation for babassu biodiesel blends with tung biodiesel.

| T (°C) | Pure Babassu Biodiesel | Babassu 97% - Tung 3% | Babassu 95% - Tung 5% | Babassu 91% - Tung 9% | Babassu 88% - Tung 12% |
|--------|------------------------|-----------------------|-----------------------|-----------------------|------------------------|
| 25 °C  | 4.72±0.21              | 4.85±0.32             | 4.89±0.06             | 5.27±0.02             | 5.53±0.01              |
| 30 °C  | 4.24±0.07              | 4.25±0.01             | 4.34±0.10             | 4.64±0.01             | 4.96±0.01              |
| 35 °C  | 3.74±0.02              | 3.88±0.03             | 3.90±0.02             | 4.14±0.01             | 4.34±0.01              |
| 40 °C  | 3.36±0.02              | 3.48±0.01             | 3.48±0.01             | 3.71±0.01             | 3.90±0.01              |

Source: The authors.

Table 4 – Freeze test temperatures for babassu biodiesel blends with tung biodiesel.

| Blends | T (°C) |
|--------|--------|
| Pure Babassu Biodiesel | -7.87  |
| Babassu 97% - Tung 3%   | -8.50  |
| Babassu 95% - Tung 5%   | -6.90  |
| Babassu 91% - Tung 9%   | -6.50  |
| Babassu 88% - Tung 12%  | -5.00  |
| Pure Tung Biodiesel     | 0.00   |

Source: The authors.

Infrared spectrum of tung and babassu oils and biodiesel

For comparison purposes, besides analyzing the infrared spectrum of babassu and tung biodiesel, also the soybean biodiesel was analyzed, as the respective oils used as raw materials to biodiesel production.

The spectra in Figure 3, can be observed that transesterification occurred, since the band associated with asymmetric vibration of O-C-C does not exist in biodiesel, consequently, the band close to 1100 cm$^{-1}$ does not exist anymore in relation to their respective oil’s spectrum, whereas, in babassu biodiesel, the band close to this wave number decreases markedly when compared to the oil of its raw material. Furthermore, the infrared spectrum can indicate the purity in the biodiesel compositions through the absence of the water and alcohol band in 3500 cm$^{-1}$.

About the composition, both soybean and tung biodiesels show double bonds in their carbon chain, once both biodiesels have a band appears around 3100 cm$^{-1}$. Nevertheless, this band does not appear in the babassu biodiesel spectra, thus indicated that this biodiesel has few unsaturations in its composition.

Blends babassu-camphor density and viscosity

The principal fuel dynamic properties are viscosity and density because of their directly influences the fuel circulation and injection. Therefore, any modifications in these properties should be carefully controlled (GÜLÜM; BILGIN, 2015; KANAVELI; ATZEMI; LOIS, 2017).
Figure 3 – The infrared spectrum of tung, soybean and babassu biodiesel, and their oils.

Source: The authors.

Table 5 shows the effects of camphor addition in the babassu biodiesel density and Table 6 shows the effects of blends in babassu biodiesel viscosity.

The addition of camphor decreases the biodiesel density considerably and all the samples meet the standard set by ANP. A promising result, whereas, which a high biodiesel density, the engine functioning is affected.

Only 3% camphor in babassu biodiesel showed a marked reduction in viscosity compared to babassu biodiesel (0%). Thus, a likely cause is that given the structure of camphor, it induces a breakdown and separation between the carbon chains of biodiesel, reducing its viscosity.

Nevertheless, the higher percentages didn’t present a greater reduction, it can be linked to the effect in the density who also decreases at 3% and doesn’t present a greater decrease in the higher percentages.

Figure 4 presents the graph with the relation temperature and viscosity for the camphor/biodiesel blends.

Viscosity and density are indicatives of the increase/decrease of intermolecular interactions. When viscosity increases became difficult for biofuels to pass through the engines. Therefore, as there was no increase in viscosity results, camphor indicated a potential additive for babassu biodiesel. Also, all the samples were in agreement with the technical regulation established by ANP.

Blends babassu-camphor pour point (PP)

The pour point analysis is observed in Table 7 and shows that the 6% camphor proportion presented the lowest pour point temperature. Nevertheless, there was a small variation between 3% and 6% results, which demonstrates that the 3% solution is more efficient and, consequently, most advantageous.

Researches show that additives affect the physical-chemical properties like freezing points, oxidative stability, heating values, among others. Although some additives improve freezing properties, this addition tends to reduced others, such as density and viscosity (ALI; MAMAT; FAIZAL, 2013).

Usually, researches with antifreeze additives use synthetic additives like alternatives to improve the freezing properties of biodiesels, such as the poly-alpha olefin and methyl polyacrylate (MONIRUL et al., 2017; XUE et al., 2016). A more environmentally friendly alternative would be the use of natural additives, such as camphor, extracted from the Cinnamomum camphora plant.

Monirul et al. (2017) used the methyl polyacrylate additive in blends with coconut biodiesel and diesel, and it obtained an improvement of the cloud point at 3°C.

Xue et al. (2016) used the poly-alpha-olefin blend in biodiesel from reused cooking oil (which has many unsaturations in its carbon chain), obtained an improvement of the biodiesel cloud point in 5°C.
Table 5 – Measurement of density of babassu biodiesel blends with camphor.

| Blends (% ) | Camphor added to babassu biodiesel (g) | Density (g.mL⁻¹) |
|-------------|---------------------------------------|------------------|
| Pure Babassu Biodiesel | 0.00 | 0.8889 |
| Babassu 97% - Camphor 3% | 0.75 | 0.8821 |
| Babassu 96% - Camphor 4% | 1.00 | 0.8825 |
| Babassu 95% - Camphor 5% | 1.25 | 0.8834 |
| Babassu 94% - Camphor 6% | 1.50 | 0.8847 |

Source: The authors.

Table 6 – Viscosity (Cst) and standard deviation for babassu biodiesel blend with camphor.

| T (°C) | Pure Babassu Biodiesel | Babassu 97% - Camphor 3% | Babassu 96% - Camphor 4% | Babassu 95% - Camphor 5% | Babassu 94% - Camphor 6% |
|--------|-------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| 25      | 4.72 ±0.21              | 4.34 ±0.057              | 4.38 ±0.045              | 4.34 ±0.034              | 4.46 ±0.068              |
| 30      | 4.24 ±0.07              | 3.85 ±0.011              | 3.89 ±0.034              | 3.89 ±0.017              | 3.93 ±0.011              |
| 35      | 3.74 ±0.02              | 3.44 ±0.017              | 3.52 ±0.045              | 3.47 ±0.011              | 3.57 ±0.040              |
| 40      | 3.36 ±0.02              | 3.10 ±0.034              | 3.13 ±0.017              | 3.16 ±0.051              | 3.18 ±0.011              |

Source: The authors.

Figure 4 – Graph with viscosity relative to camphor composition added to babassu biodiesel.

Source: The authors.

Camphor, although a natural compound, reduced the babassu biodiesel freezing point at 2 °C, a similar result to the Monirul et al. (2017) research, with coconut biodiesel and methyl polyacrylate as additive. Considering that both biodiesels have similar structural characteristics, the camphor show results to improve biodiesel freezing point similar to synthetic additives.

As described, the camphor had a reductive effect on all the physicochemical properties tested to babassu biodiesel. However, it was possible to observe a trend of increase in density and viscosity from the 3% proportion.
Table 7 – Temperatures of the freezing test of the babassu biodiesel blends with camphor.

| Blends                  | $T$ (°C) |
|-------------------------|----------|
| Pure Babassu Biodiesel  | -7.87    |
| Babassu 97% - Camphor 3%| -9.05    |
| Babassu 96% - Camphor 4%| -9.30    |
| Babassu 95% - Camphor 5%| -9.92    |
| Babassu 94% - Camphor 6%| -10.20   |

Source: The authors.

Conclusion

All the physical-chemical results obtained by the addition of tung biodiesel and camphor are within the biodiesel quality norm established by the Brazilian National Petroleum Agency (ANP) standard.

The 3 % tung biodiesel proportion had the best results in all the evaluated properties using this additive, with a density of 0.8732 g.mL$^{-1}$, viscosity at 40 °C of 3.48 Cst, and pour point of -8.50 °C. Proportion of tung biodiesel greater than 3 % worsened the babassu biodiesel properties.

To camphor, the best pour point improvement was at the 6 % proportion, -10.20 °C. However, the 3 % proportion had the best results for viscosity at 40 °C, 3.10 Cst, and density, 0.8821 g.mL$^{-1}$, and a good pour point improvement too, -9.05 °C.

Camphor was considered a better additive than tung biodiesel, as it improves all the physicochemical properties tested for all the mixtures.

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