Agronomy Research **19**(S1), 721–738, 2021
https://doi.org/10.15159/AR.21.050

Productive efficiency and density and viscosity studies of biodiesels from vegetable oil mixtures

R.C.B. Correia[1], F.C. Silva[1,*], M.M. Barros[2], A.C.L. Maria[1], D. Cecchin[1], L.A. Souza[1] and D.F. Carmo[1]

[1]Federal Fluminense University, Agricultural and Environmental Engineering Department, 156 Rua Passos da Pátria 156, bloco D, sala 235, BR24210-240 Niterói, Brasil
[2]Federal Rural University of Rio de Janeiro, Engineering Department, Rodovia BR 465, Km 07, s/n Zona Rural, 23890-000, Seropédica, Brasil
[*]Correspondence: flaviocastro@id.uff.br

Received: January 31st, 2021; Accepted: April 10th, 2021; Published: April 29th, 2021

Abstract. Currently in Brazil the minimum content of biodiesel in mixtures is 11% and, according to Brazilian laws, the goal is to reach 15% in volume in diesel fuel available for final consumers by 2023. Therefore, studies about different matrices of biodiesel and distinct mixtures are essential. The present work had two goals, the first one was to analyse physico-chemical properties of 16 biofuels produced from soybean and cotton oils, using S10 diesel, in mixtures B8, B10, B20 and B30. The second goal was to verify the vantages and disadvantages of biodiesel production through prior mixing of the oils, before and after the transesterification process. All biofuels produced presented results of specific mass values at 20 °C and kinematic viscosity at 40 °C within the limits established by ANP Resolution no 30/2016 and International Resolutions. The soybean B20 biofuel showed the best overall results, with the second highest production yield of 65.36%, the fifth lowest kinematic viscosity with 3.48 mm s^{-1}. The mixture of soybean and cotton oils before the transesterification process presented the highest production yield when compared with the production from a single oil or biodiesel mixtures. The results found proved to be satisfactory and corroborate to continue with the increase of biodiesel in the mixture with diesel to B15 until 2023 and support the possibility of planning for a gradual increase of this mixture in the following years.

Key words: transesterification, biodiesel, physical characterization, yield, mechanical performance.

INTRODUCTION

The energy produced for human consumption on the planet is largely dependent on fossil fuels that have limited sources of raw material and are considered to be the main causes of the increase in global warming and emissions of gases harmful to our health during their burning (Abed et al., 2019). According to Manaf et al. (2019), among the worst consequences of global warming, it is possible to highlight the increase in the concentration of CO_2 in the atmosphere, the increase in the acidity of sea water and the

temperature of the sea surface, which generate serious consequences for society and reinforce that one of the ways to reduce these harmful emissions is using renewable energies.

According to Dantas et al. (2016), the use of biomass has been gaining relevance in the world scenario because it can be applied to the use in the production of heat for industrial thermal use or even for the generation of electric energy. Among the alternative energy sources, biodiesel, as it is a derivative of renewable materials, has become an increasingly used and studied substitute for diesel oil. Among the raw materials that can be used to produce biodiesel, vegetable oils and animal fats can be highlighted and they both result in a biofuel presenting mainly low emission of polluting gases, promoting a more sustainable energy production (Ambat et al., 2018).

According to Knothe et al. (2006), biodiesel can be obtained through different technologies, namely transesterification, esterification and cracking. The transesterification process occurs naturally when you mix vegetable oil with alcohol. In order to accelerate the process, in addition to the use of catalysts, which can be basic or acidic, magnetic stirrers and sonifiers are generally used at laboratory level, helping to reaction speed and minimizing the total time of the transesterification process as highlighted by Rockembach et al. (2014).

The biofuel manufacturing route is related to the type of alcohol used during the production process, which may be the methyl or ethyl route, the first being used due to its lower cost (Knothe et al., 2006). According to Meneghetti et al. (2013) in transesterification, basic or acid catalysts can be used, however the difference occurs when opting to use acid catalysts and we can see that there is an increase in corrosion of industrial equipment during the biodiesel production process and lower rates of reaction conversion. The basic catalysts, most used in the transesterification process, are sodium and potassium hydroxides.

When assessing the environmental impact of burning fuels, it can be said that when using biodiesel, lower amounts of carbon dioxide (CO_2), sulfur dioxide (SO_2), carbon monoxide (CO) and hydrocarbons are released compared to when using diesel, and that these emissions are proportional and lower the higher the percentage of biodiesel in the mixture (Perin et al., 2015).

For Silva et al. (2019) assessing the emission of exhaust gases from different biodiesel mixtures, concluded that the lowest SO_2 emissions were obtained with fuels containing higher biodiesel percentages and operating at higher rotation speeds and nitrous oxides and carbon dioxide emissions decrease with higher engine rotation speed. Overall, higher percentages of biodiesel in the fuel mixture result in a less polluting fuel.

According to ANP (2019) Brazil, together with the United States, leads the world ranking of the largest biodiesel producers nowadays. The biodiesel production capacity in Brazil reached 8.76 billion liters in 2019 and a total of 5.89 billion liters were produced. Among the raw materials used to produce biodiesel in Brazil, soybean stands out, which in 2019 was responsible for approximately 70% of all production.

According to Knothe (2006), the physical-chemical characterization of biodiesel is an essential process to qualify and evaluate the biofuel, to ensure that it presents a complete combustion, and helps in the proper functioning of the engine, guaranteeing its useful life. The characteristics usually calculated and addressed in didactic studies are the specific mass at 20 °C and the kinematic viscosity at 40 °C. This mass must be in accordance with the norms established by the ANP in its resolution 30/2016, where limit

values are established for some characteristics of the mixtures of BX to B30, where X indicates the amount of biodiesel in the mixture, and which method should be used to determine each characteristic of the mixture (Brasil, 2016).

The amount of Biodiesel produced in Brazil has been increasing along with the mandatory percentage of biodiesel in the mixture with diesel stipulated by the Government for commercialization. Nowadays, in Brazil, the minimum biodiesel content established in the mixture is 11% according to Law 13.263/2016, this percentage increased by 1 percentage point in September of the year 2019, and may have an addition percentage of up to 15% in volume from biodiesel to diesel oil sold to the final consumer, and the minimum percentage must comply with the schedule provided for in CNPE Resolution No. 16, of 2018 (ANP, 2019). The schedule approved by the National Energy Policy Council (CNPE) in October 2019 in Resolution CNPE on 05/2018 establishes a gradual increase of 1 percentage point per year until 2023 to achieve a mixture with 15% biodiesel with diesel (MME, 2019).

Aiming to optimize the production of biodiesel through methyl route using basic NaOH catalyst, the present work sought to carry out the production of biodiesel through previous mixtures of soybean and cotton oils, before and after the transesterification process, and to measure the amount of production and its physical characteristics, in different proportions of mixtures of B8, B10, B20 and B30 with diesel.

MATERIAL AND METHODS

The work was divided into four stages, the first being the production of biodiesel from soybean and cotton oils by means of transesterification via methyl route using an alkaline catalyst. The second stage began with the mixing of unitary biodiesel to obtain binary biodiesel.

In the third stage, the pure biodiesel produced with S10 diesel was mixed in four proportions, in order to obtain samples of B8, B10, B20 and B30 from each of them, totaling 16 biodiesels. These first three stages were carried out at the Agricultural Machinery Laboratory - LABMAQ of the Department of Agricultural and Environmental Engineering (TER) at the Federal Fluminense University (UFF).

In the fourth stage, the physical characterization of the produced biodiesels began, carried out at the Rheology Laboratory - LARE of the Mechanical Engineering Department (TEM) of the Federal Fluminense University (UFF).

The diesel used in this work was pure S10, that is, considered as B0 which is also called petrodiesel, without the addition of biodiesel and additives. This diesel was donated by 'Empresa Ipiranga S/A'.

Biodiesel production

The biodiesels studied in the present work were produced from soybean and cotton oils and in four distinct stages.

The first step was the production of unitary biodiesels of soybean and cotton by means of a methyl route from the transesterification process of each vegetable oil individually.

Soon after, the production of biodiesels from the mixture of soybean and cotton oils was carried out in two different ways. Mixing before the transesterification process and

after the transesterification process. Then there was the production of biodiesel from the binary mixture of two previously produced biodiesels, after the transesterification process.

Finally, mixtures of each biodiesel produced with diesel S10 were carried out in different proportions giving rise to the biodiesels: B8, B10, B20 and B30.

Production of unitary biodiesel

The unit biodiesel was produced from refined soybean and refined cottonseed oil through batches with 100 mL of oil, 30 mL of methanol and 1% of the NaOH (Sodium Hydroxide) catalyst. The production process followed the proportions of 1.0 mol of vegetable oil to 6.0 moles of methyl alcohol P.A (99.7%) as established by Tomasevic & Marinknov (2003).

This process was carried out for each of the two oils, soybean and cotton, resulting in pure unitary biodiesels.

Production of biodiesel from the oil mixture before the transesterification process

The Biodiesel from the binary mixture of soybean and cotton oils was produced in batches with equal molar proportions, with 0.5 mol of refined soybean oil and 0.5 mol of refined cottonseed oil. This mixture was carried out before the transesterification process with the addition of the oils, preheated to 45 °C, simultaneously inside the Erlenmeyer that was already containing the mixture of methanol + NaOH on the action of the magnetic stirrer.

Afterwards, the transesterification stage was the same as that performed in the production process of unitary biodiesels, occurring at 45 °C, with 1% NaOH P.A and magnetic stirring for 45 minutes. After this process, the mixture was transferred to the decantation funnel where it remained for 24 hours so that there was a complete separation of the phases involved. Afterwards, the biodiesel was washed and then dried in the greenhouse for two hours so that it could be stored.

Production of biodiesel from the oil mixture after the transesterification process

The biodiesel was produced from the binary mixture of soybean and cotton biodiesels after the transesterification process. To create it, the mixture was made in the same molar ratio of two biodiesel already produced, thus obtaining a new biodiesel containing 50% molar of each one. To produce this fuel, 1 mol of pure soybean biodiesel was mixed with 1 mol of pure cottonseed biodiesel, thus originating B soybean + B cotton.

Production of biodiesels in different proportions with S10 diesel

After the production of the pure biodiesel (B100), mixtures of these with the S10 diesel started. The mixtures occurred with each of the four types previously produced, namely: B soybean, B cotton, B soybean + cotton before transesterification (B soybean + cotton) and B soybean + cotton after transesterification (B soybean + B cotton). The proportions chosen and realized were: 8% biodiesel with 92% diesel (B8), 10% biodiesel with 90% diesel (B10), 20% biodiesel with 80% diesel (B20), 30% biodiesel with 70% diesel (B30) in each of the four pure biodiesels previously produced, resulting in a total of sixteen samples.

It is important to note that after the records the biodiesels were kept in opaque glassware and protected from heat and sunlight.

Production yield

The yield of each treatment was obtained through Equation 1, used by Ambat et al. (2018), just evaluating the values of the oil mass and the clean biodiesel mass produced in each batch.

$$\text{Yield} = \frac{biodiesel\ mass}{soybean\ mass} \quad (1)$$

Physical characterization

The physical characterization process took place in four different parts, namely: analysis of the specific mass at 20 °C and, later, at 40 °C with the use of pycnometer; verification of dynamic viscosity using a rheometer and calculation of the kinematic viscosity from the data found in the previous steps.

Table 1 identifies the physical-chemical properties that were used as a reference in this work to characterize and compare the biodiesel produced. Table 1 shows the standards for each characteristic, according to ANP No. 45/2014 resolution.

Table 1. Chemical physical property and corresponding pattern

Chemical physical property	Pattern
Kinematic viscosity at 40 °C	NBR 10.441 ASTM D 445 EN/ISO 3.104
Specific mass at 20 °C	NBR 7.148 NBR 14.065 ASTM D 1.298 ASTM D 4.052 EN/ISO 3.675 EN/ISO 12.185

Source: Resolution adaptation nº 45/2014 of ANP.

Specific Mass

The specific mass was determined by the pycnometer and the thermostatic bath that was used to maintain the temperature of the biodiesel analyzed at 20 °C. The pycnometer used to measure the specific mass was previously calibrated by analyzing the distilled water at 20 °C before the tests with the biodiesels were started.

To measure the specific mass, the pycnometer was initially weighed on an analytical balance. Subsequently, 50 mL of biodiesel was added to the pycnometer, which was fixed to a support that left it submerged in a thermostatic bath, thus ensuring that the sample contained in it stabilized its temperature at 20 °C. With the aid of a digital thermometer, you can have precise control of the temperature of the thermostatic bath.

In addition to the biofuel present in the pycnometer, the fuel that was being characterized was placed together with the other samples of biodiesel, which would then be analyzed in 100 mL beakers in the same thermostatic bath in which the pycnometer was located. This situation facilitated the measurement of the temperature of each biofuel and ensured that the samples stabilized at 20 °C. After stabilizing the pycnometer's interior temperature, it was removed from the thermostatic bath and weighed on the analytical balance with the biodiesel sample inside.

With the weight of the empty pycnometer, and then the measurement when it was filled with biodiesel, it was possible to calculate the specific mass of the sample using Eq. 2:

$$\rho = \frac{Pp\backslash b - Pp}{Vp} \cdot 1{,}000 \qquad (2)$$

where ρ – specific mass of biodiesel (kg m^{-3}); $Pp\backslash b$ – weight of the pycnometer-biodiesel set (g); Pp – weight of the pycnometer (g); Vp – volume of the pycnometer (mL).

The specific mass was calculated for all biodiesel samples, five repetitions were performed for each one. With the average of the five repetitions, it was possible to find the most precise value of the specific mass of each biodiesel sample.

After the specific mass at 20 °C was found, the test was carried out again with the temperature of the biodiesel stabilized at 40 °C. This new measurement was necessary so that the kinematic viscosity at 40 °C could be found from the dynamic viscosity calculated with the same temperature.

Dynamic viscosity

To determine the dynamic viscosity at 40 °C, the RS 50 RheoStress rheometer from Precitech Instrumental LTDA was used with the coupled thermostatic bath to ensure that the experiment was carried out at a constant temperature previously established. The DG41Ti concentric cylinder was used for the measurement of biofuels because it ensures that during the experiment there is no loss of the sample and that it can be reused afterwards. The rheology tests were carried out at the Rheology Laboratory (LARE) of the Mechanical Engineering Department (TEM) of the Federal Fluminense University (UFF).

For the sake of carrying out the analysis on the rheometer, the data that was intended to be obtained through the equipment's RheoWin Pro 2.97 software, previously installed on the computer and attached to the rheometer, were previously inserted. A constant temperature of 40 °C was established for the execution of the experiment. The software itself creates a graph based on the data collected, which were previously selected to be measured, they are: dynamic viscosity versus shear rate (flow curve) and shear rate versus shear stress, both with temperature constant of 40 °C.

The rheometer test consists of turning the upper cup inside the lower one, applying a shear stress to the biodiesel present internally. This applied stress varied and increased over time, generating a shear rate corresponding to this variation.

This analysis was performed twice for each sample, with the results being tabulated and displayed graphically, to minimize possible errors.

The dynamic viscosity found was used to obtain the kinematic viscosity of biodiesel, a technical characteristic regulated by ANP standards.

In a rheological study, the fundamental parameter that must be investigated is viscosity. In these studies, the flow properties are usually illustrated by using graphs indicating the shear stress and viscosity as a function of the shear rate. These graphical representations of the flow and viscosity curves help to verify the behavior of the fluid to analyze whether it is considered a Newtonian fluid, since the functional relationship between the shear rate and the deformation rate is a line whose extension passes through the source.

Kinematic viscosity - Direct method

To determine the kinematic viscosity at 40 °C, the values found for the specific mass and dynamic viscosity at the same temperature were used. From these values, Eq. 3 was used to find the kinematic viscosity of each sample.

$$v = \frac{\mu}{p} \quad (3)$$

where v – kinematic viscosity of biodiesel (mm² s^{-1}); ρ – specific mass of biodiesel (kg m^{-3}); μ – dynamic viscosity of biodiesel (Pa s^{-1}).

Kinematic viscosity - Capillary viscometer method

To determine the kinematic viscosity at 40 °C of pure S10 diesel (B0) and pure biodiesels (B100), the Cannon-Fenske capillary viscometer was used as well as a thermostatic bath of the brand Nova Ética model N480, necessary so that the fuel at constant temperature could be measured. A transparent thermostat from the Schott model CT52 was also used.

Initially the temperature of the thermostatic bath was fixed at 40 °C and then a small amount of diesel was introduced in the viscometer to fill 2/3 of the larger bulb located at the bottom of the viscometer. Subsequently, the viscometer was placed in the thermostatic bath and 30 minutes was waited for the fuel temperature inside the viscometer to stabilize at 40 °C. To finish the experiment, the time taken for the B0 to go through the marks located on the viscometer was measured.

In order to measure the kinematic viscosity from the flow rate of B0 inside the viscometer, Eq. 4 below was used.

$$v = t \times c \quad (4)$$

where v – kinematic viscosity of biodiesel (mm² s^{-1}); t – time spent for biodiesel to flow between the capillary viscometer marks (s); c – capillary viscometer constant (mm² s^{-2}).

The capillary viscometer measures the flow rate of the fluid through a glass capillary, which is measured by the time it takes for the liquid to flow between two marks on the viscometer. This type of viscometer is widely used for Newtonian liquids, which have low viscosity, as in the case of biodiesels, however, they have limitations when used for non-Newtonian fluids, since they do not allow shear stress variation.

The results found for specific mass at 20 °C and 40 °C and kinematic viscosity at 40 °C and dynamics at 40 °C, were tabulated in two large groups so that the results could be analyzed, and the statistical test of Tukey applied at 5% significance. The first group of tables considering the source of triglyceride (B soybean, B cotton, B soybean + cotton and B soybean + B cotton) and in each table the results of their proportions with diesel (B8, B10, B20, B30). In a second group, four new tables were built, but considering first the percentage of mixture (B8, B10, B20, B30) and in each one the biofuels (B soybean, B cotton, B soybean + cotton and B soybean + B cotton) in this proportion.

It is important to emphasize that the specific mass at 40 °C and the dynamic viscosity at 40 °C are not parameters that have a lower and upper limit determined by ANP resolution no. mandatory biodiesel specifications in the standard. However, the tests to determine these values were carried out for each of the biodiesels produced to use them in the direct calculation to determine the kinematic viscosity at 40 °C of the biofuels produced.

Statistical analysis

For the statistical analysis, the program SISVAR version 5.3 (Ferreira, 2014) was used, applying the Tukey test at the significance level of 5%. The statistical analysis was performed using the experimental data obtained in the present study, with all

observations, estimating the effects on the biodiesel production yield of the studied variables, source of triglycerides and their interactions. The same test was applied to verify whether there was any differentiation in the physical-chemical characterization parameters.

RESULTS AND DISCUSSION

Production yield

Analyzing the general production yield of biodiesel, with a focus on the amount of product that was used and the amount of biodiesel generated, it can be seen from Table 2 that regardless of the type of biodiesel studied, there was no statistical variation, using Tukey's test at the 5% level of significance in the production.

These results demonstrate the viability for the production of biodiesel from different sources of triglycerides. Thus, it is possible to use different sources together (blend) without causing a reduction in efficiency in the production of biodiesel.

Table 2. Results of the production of biodiesels according to the source of triglycerides

Biodiesel	Amount of production (%)
B cotton	64.53 a
B soybean + B cotton	64.95 a
B soybean	65.36 a
B soybean + cotton	65.49 a

Averages followed by the same letter do not differ by Tukey's test at the 5% level of significance.

Regardless of the mixture of biodiesels, there was no variation in the amount of product generated. Thus, considering only this variable, regardless of the matrix, we will have the same amount of biodiesel produced. The average amount value of all mixtures was 65.08%.

Physical characterization of biodiesel

The specific mass at 20 °C and the kinematic viscosity at 40 °C were initially measured using the capillary viscometer of the B100 produced before mixing with the S10 diesel. The results obtained for the B100 produced from different sources and mixtures can be found in Table 3.

When analyzing the values found, it can be seen that all results of specific mass at 20 °C and kinematic viscosity at 40 °C remained within the limits pre-established by ANP No. 45/2014, being 850 to 900 kg m^{-3} and from 3.0 to 6.0 mm^2 s^{-1}, respectively (Brasil, 2014).

Table 3. Physical characterization of B100 biodiesels produced from different sources

Source	Specific mass (kg m^{-3})	Kinematic viscosity (mm^2 s^{-1})
B soybean	883.10 bc	4.24 b
B cotton	882.93 b	4.22 b
B soybean + cotton	883.11 c	4.32 c
B soybean + B cotton	882.54 a	4.13 a

Averages followed by the same letter do not differ at the 5% level of significance using the Tukey test.

Analyzing the results presented, it appears that the B soybean + B cotton showed the lowest specific mass values at 20 °C and kinematic viscosity at 40 °C, being 882.54 kg m^{-3} and 4.13 mm^2 s^{-1}, respectively. The pure biodiesel with the highest specific mass values at 20 °C and kinematic viscosity at 40 °C was B soybean + cotton with 883.11 kg m^{-3} and 4.32 mm^2 s^{-1}, respectively.

For the kinematic viscosity at 40 °C the biofuels B soybean and B cotton did not vary significantly by the Tukey test at the level of 5% significance, unlike B soybean + cotton and B soybean + B cotton which varied significantly between them by the applied statistical test. For the specific mass at 20 °C, all the biofuels analyzed varied significantly between themselves by the Tukey test at the level of 5% of significance.

These physical variations are related to the composition of each oil (source of triglycerides) used in the transesterification process, as described by Gonçalves et al., (2019).

The specific mass at 20 °C and the kinematic viscosity at 40 °C were also measured using the capillary viscometer of the S10 diesel used to produce the biofuels B8, B10, B20 and B30. The results found for B0 can be seen in Table 4 and it can be noted that the values found for specific mass at 20 °C and kinematic viscosity at 40 °C remained within the lower and upper limits established by Resolution 46/2012 of the ANP that regulates the characteristics of the S10 diesel (BRASIL, 2014), being 820.00 to 850.00 kg m^{-3} and 2.0 to 4.5 mm^2 s^{-1}, respectively. Note that the specific mass and kinematic viscosity measured for B0 are lower than the values found for pure biodiesels (B100).

Table 4. Physical characterization of B0 S10

Fuel	Specific mass (kg m^{-3})	Kinematic viscosity (mm^2 s^{-1})
B0	830.28	2.85

According to ANP Resolution No. 30/2016, which determines the lower and upper limits for BX to B30 biodiesel, the value calculated for specific mass at 20 °C must be between 817.80 and 865.00 kg m^{-3} when used diesel S10 in mixtures. For the kinematic viscosity at 40 °C, the regulation determines that the value must be within the range of 1.9 to 4.1 mm^2 s^{-1} (Brasil, 2016).

Table 5 below shows the results of kinematic Viscosity (.10^{-3} mm^2 s^{-1}) at 40 °C according to ANP Resolution No. 30/2016. It can be observed that the biofuel that showed the highest value of kinematic viscosity at 40 °C, among all the tested samples, was the B 30 of B soybean + B cotton with a value of 3.94 mm^2 s^{-1} and that showed a significant difference when compared to the values of other biofuels from other sources of triglycerides in the same proportion (B30), in addition it differs significantly when comparing with other proportions from the same source. This value is 15.88% higher than the lowest result of kinematic viscosity at 40 °C found in the analyzes. The lowest value calculated was for B10 of cotton biodiesel, with a value of 3.40 mm^2 s^{-1}.

Table 5. Kinematic viscosity (.10^{-3} mm^2 s^{-1}) at 40 °C of biodiesels produced from different sources of triglycerides

Source	Biodiesel			
	B8	B10	B20	B30
Soybean	3.44 Ab	3.41 Ba	3.48 Ac	3.54 Ad
Cotton	3.55 Db	3.40 Aa	3.67 Cc	3.72 Cd
B soybean + cotton	3.54 Cb	3.42 Ca	3.91 Dd	3.61 Bc
B soybean + B cotton	3.50 Ba	3.58 Db	3.64 Bc	3.94 Dd

Averages followed by the same letter, uppercase in the column and lowercase in the row, do not differ at the 5% level of significance by the Tukey test.

It is worth mentioning that for the analyzed results of kinematic viscosity at 40 °C, all values varied significantly in each other, whether in the column between different sources of triglycerides in the same ratio of biodiesel to diesel (BX), or in the line for the same source triglycerides and comparing the different proportions B8, B10, B20 and B30.

A pattern of increase in kinematic viscosity values was observed at 40 °C in the following order B10, B8, B20 and B30. Only for source B soybean + B cotton the value B8 was lower than B10, presenting a gradual increase as the amount of biodiesel in the mixture with diesel increased. Observing the behavior of the soybean source, the B30 showed the highest kinematic viscosity value, being $2.94.10^{-3}$ mm^2 s^{-1} and 4.25% higher than the value found for B8 in the same triglyceride source.

The only source that did not show the highest value of kinematic viscosity at 40 °C in the B30 mixture was B soybean + B cotton.

Table 6 below shows the results of specific mass at 20 °C according to ANP Resolution No. 30/2016.

Table 6. Specific mass (kg m^{-3}) at 20 °C biodiesels produced from different sources of triglycerides

Source	Biodiesel			
	B8	B10	B20	B30
Soybean	832.78 Aa	833.86 Ab	838.55 Ac	843.50 Bd
Cotton	833.82 Ba	834.57 BCb	839.43 Bc	844.55 Cd
B soybean + cotton	833.44 Ba	835.02 Cb	839.67 Bc	844.38 Cd
B soybean + B cotton	833.73 Ba	834.11 ABa	838.80 ABa	841.83 Ac

Averages followed by the same letter, uppercase in the column and lowercase in the row, do not differ at the 5% level of significance by the Tukey test.

Among the values found for specific mass at 20 °C, it can be noted that the B30 of cotton and B soybean + cotton were the ones that presented the highest results when compared to the others, being respectively 844.55 and 844.38 kg m^{-3}.

For all sources except B soybean + B cotton there was an increase in specific mass directly proportional to the increase in the percentage of the mixture

The lowest value found for specific mass at 20 °C was for soybean B8, 832.78 kg m^{-3}, which was 1.38% lower than the highest result, found for cotton B30. The result of soybean B8 varied significantly if compared to the other results found for the same source of triglyceride in the other mixing proportions, that is, for B10, B20 and B30, and also varied significantly when compared with the other triglyceride sources in the same proportion. It is worth mentioning that for the B8 mixture, the other samples produced from other sources of triglycerides did not vary significantly among themselves.

The results found for the specific mass at 20 °C and for kinematic viscosity at 40 °C, as well as the tendency to increase the value of the specific mass as the amount of biodiesel in the mixture with diesel increases, this issue found for most results in this work, confirm the results found by Lahane et al. (2015) and by Silva et al. (2019).

It can be seen that for the specific mass at 20 °C, there is a tendency to increase as the percentage of biodiesel in the mixture with diesel increased, presenting the highest values generally for mixtures B30 and the lowest for B8. The increase in specific mass indicates that a greater amount of biodiesel will be injected into the combustion chamber of the engine when analyzing the same control volume (combustion chamber). This characteristic contributes to a greater energy potential and, therefore, less loss of power

in the engine when it is operating with biofuels in high mixtures, since biodiesel presents a lower calorific power when compared to pure diesel (B0) that presented the lowest specific mass when compared to the biofuels produced in this work.

The upward trend, both in specific mass and viscosity in different mixtures, is related to the higher molecular weight of methyl and ethyl esters of fatty acids, when compared to fossil diesel. Unsaturation and heteroatoms in the chains of the trichylglycerides induce a higher viscosity in biodiesel (Candeia, 2008). This behavior was also found in the study by Cunha (2011) when analyzing a total of 6 samples of biodiesel in proportions from B5 to B100.

The behavior found of the tendency to increase both the specific mass at 20 °C and the kinematic viscosity at 40 °C as the proportion of biodiesel in the mixture with diesel increased, also confirms the results found by Cavalcanti (2013) when performing rheological tests and determining the specific mass and viscosity of biofuels from castor oil, cotton and beef tallow by methyl route in proportions from B2 to B50.

Observing the results of the cotton source, all values found for this biofuel showed an increase as the proportion of biodiesel in the mixture with diesel increased. Thus, B8 had the lowest specific mass at 20 °C calculated, of 833.82 kg m^{-3}, while B30 had a 1.29% higher result, 844.55 kg m^{-3}.

When analyzing the behavior of the kinematic viscosity from B10, where the values increase as the proportion of biodiesel in the mixture with diesel increases, the behavior of the calculated data confirms the results found by Klajn (2016), in his study where the difference in viscosity of biofuels in proportions of B7, B10, B15 and B20 was analyzed. The lowest value of kinematic viscosity found in the study was for B8, being 3.55 mm^2 s^{-1}, this being 4.57% lower than the result found for B30 of 3.72 mm^2 s^{-1}, the greater value for the study in question.

The values found for cotton biodiesel for specific mass at 20 °C confirm to the result found by Cavalcanti (2008) when analyzing the physical characteristics of mixtures from B2 to B50 for biodiesel produced from cotton oil, castor, bovine and octane oil.

For the Bsoybean + cotton source, the highest specific mass value at 20 °C occurred for the B30 with 844.38 kg m^{-3}, this being 1.31% higher than the B8 value of 833.44 kg m^{-3}, this being the lowest result found. All specific mass values at 20 °C showed a significant difference between them by the Tukey test at 5%.

This behavior does not confirm to that analyzed in the results found by Fagundes et al. (2007) who identified a gradual increase in kinematic viscosity in their 9 samples of biodiesels analyzed in different proportions between B0 and B100. Differently from the behavior found between B8 and B10 of B soybean + Cotton, the behavior of the other values maintained the tendency to increase according to the increase in biodiesel in the mixture with diesel.

The results found for the specific mass at 20 °C of all biodiesel produced in different proportions with diesel can be seen in Fig. 1 where the limits, lower and upper, established by ANP in the range comprising 817.80 are indicated by vertical lines. at 865.00 kg m^{-3}. Analyzing Fig. 1, it is possible to identify that all the results found for the biofuels produced presented the specific mass within the technical specifications.

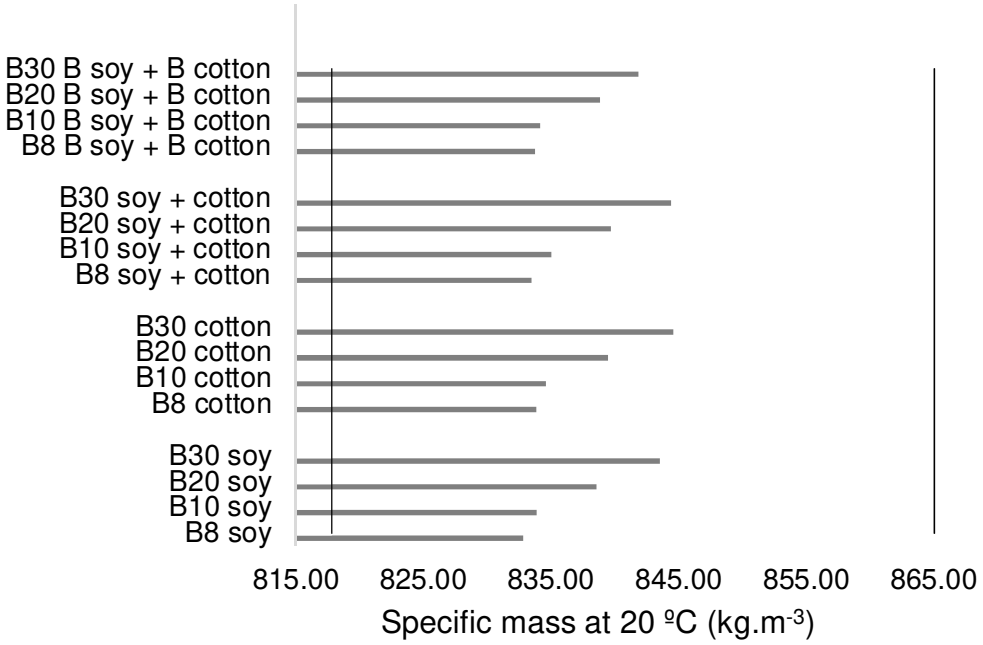

Figure 1. Specific mass at 20 °C of the biofuels produced.

The kinematic viscosity values at 40 °C of the biodiesels analyzed in the different proportions with diesel can be observed in Fig. 2 and it is observed that the values fall within the norms established by ANP Resolution 30/2016 which establishes that these values from BX to B30, produced with diesel S10, must be within the range of 1.9 to 4.1 mm² s^{-1}, represented by the vertical lines (Brasil, 2016).

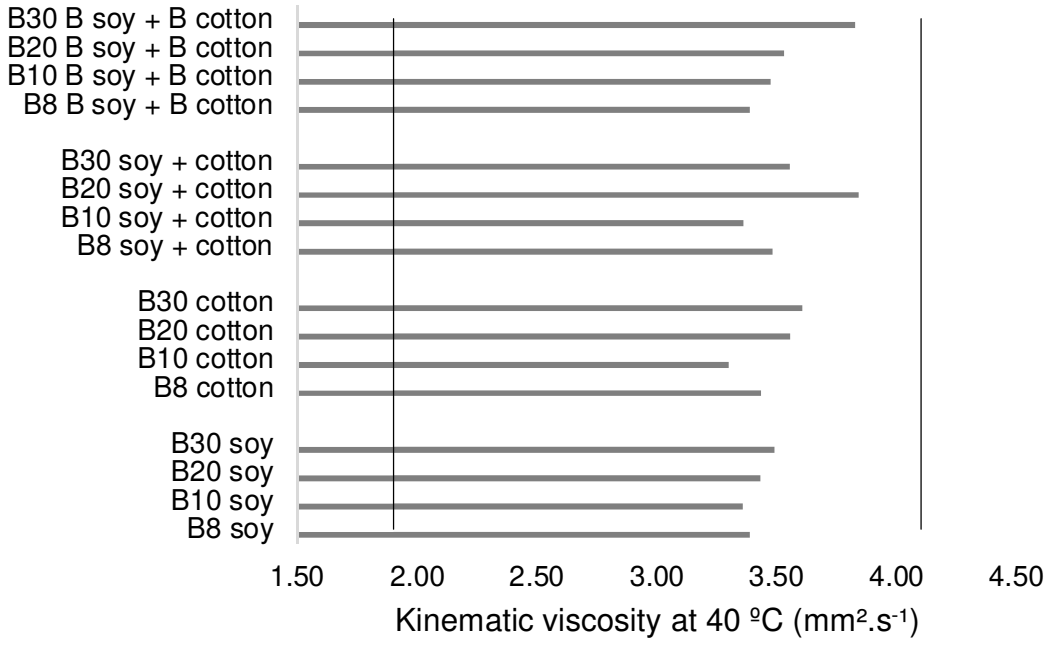

Figure 2. Kinematic viscosity at 40 °C of the biofuels produced.

The graphs obtained through the use of the rheometer in the analyzes at 40 °C, indicating the dynamic viscosity of biodiesel and the line with proportional growth

between the shear stress and the shear rate, characteristic of Newtonian fluids, are shown in Fig. 3 to Fig. 10.

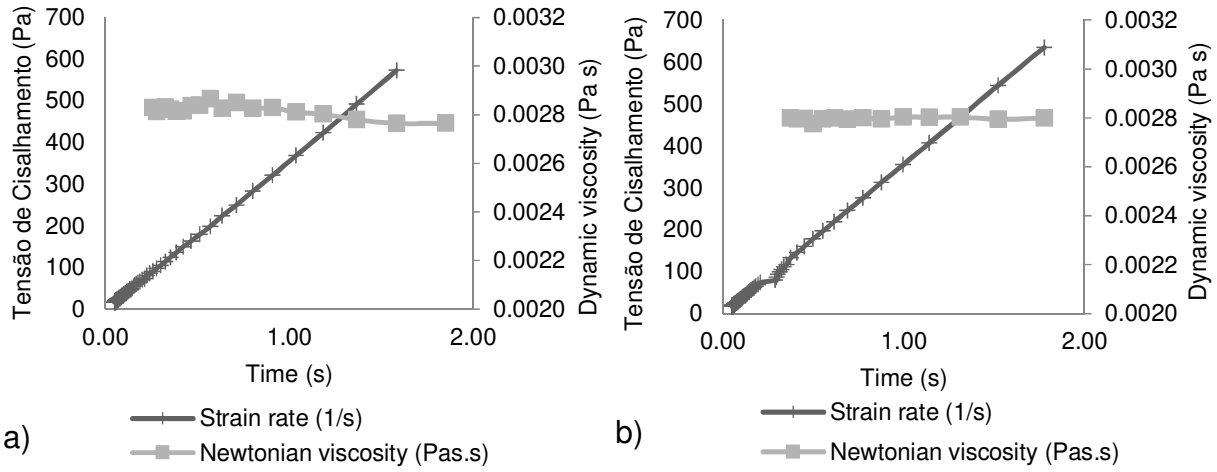

Figure 3. Rheology for B8 Soybean (a) and B10 Soybean (b).

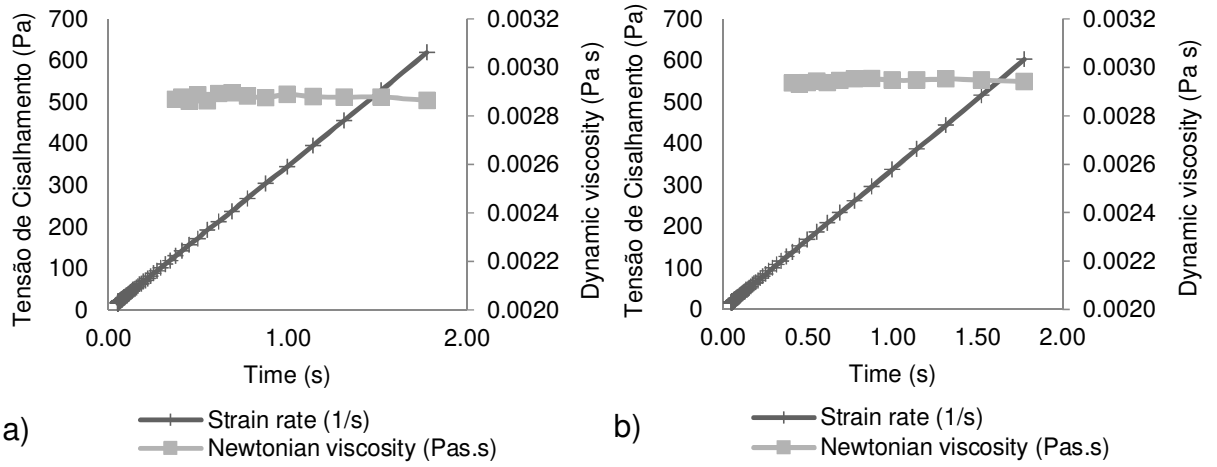

Figure 4. Rheology for B20 Soybean (a) and B30 Soybean (b).

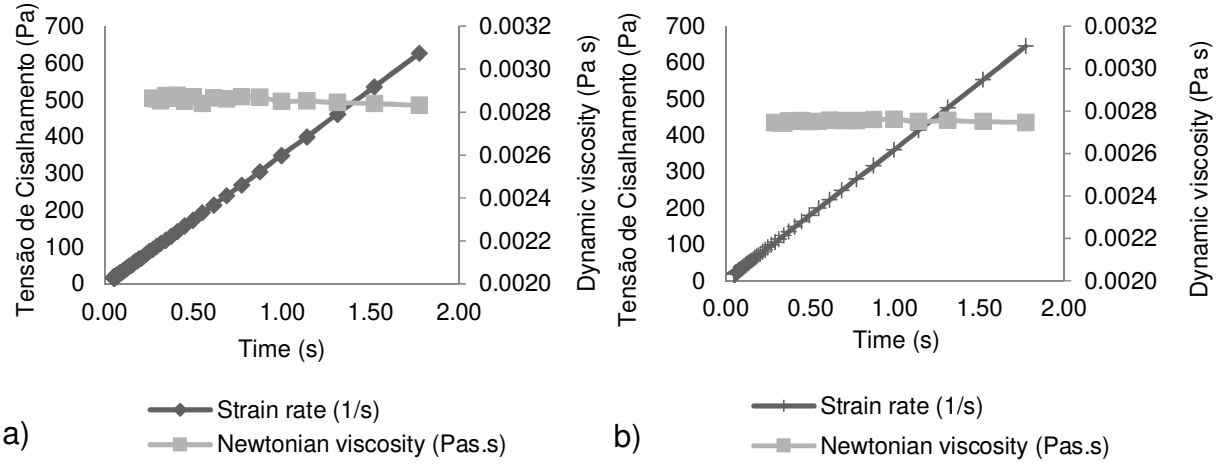

Figure 5. Rheology for B8 Cotton (a) and B10 Cotton (b).

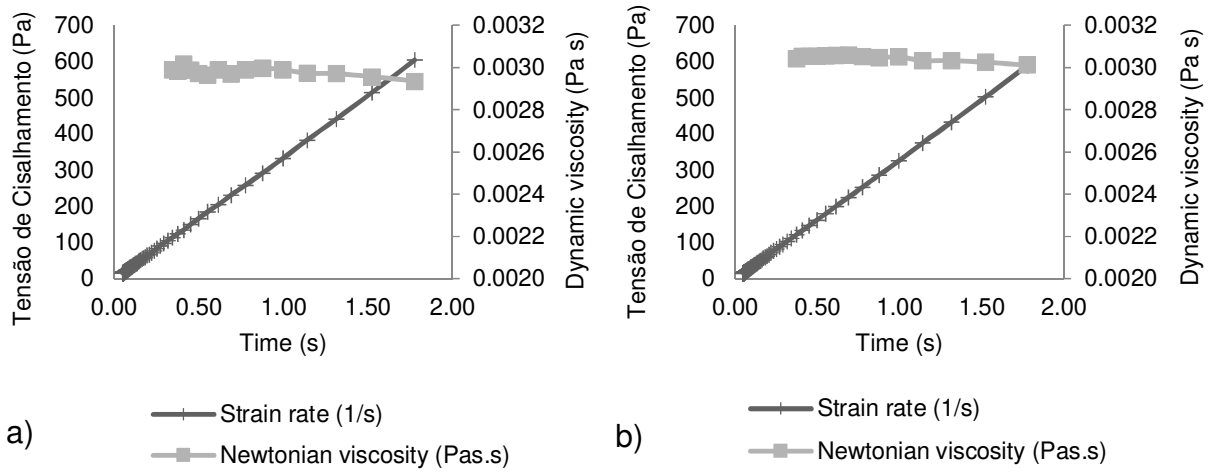

Figure 6. Rheology for B20 Cotton (a) and B30 Cotton (b).

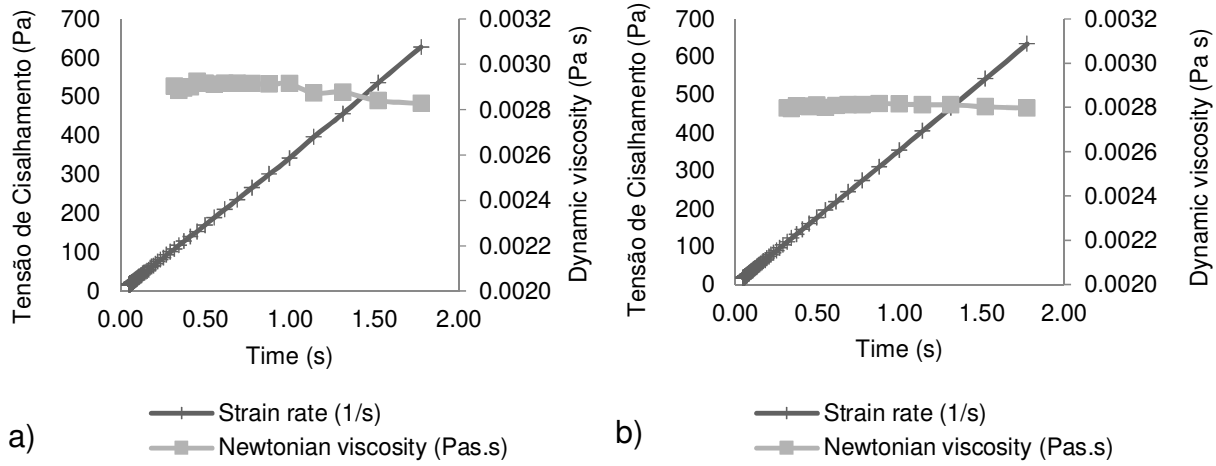

Figure 7. Rheology for B8 Soybean + Cotton (a) and B10 Soybean + Cotton (b).

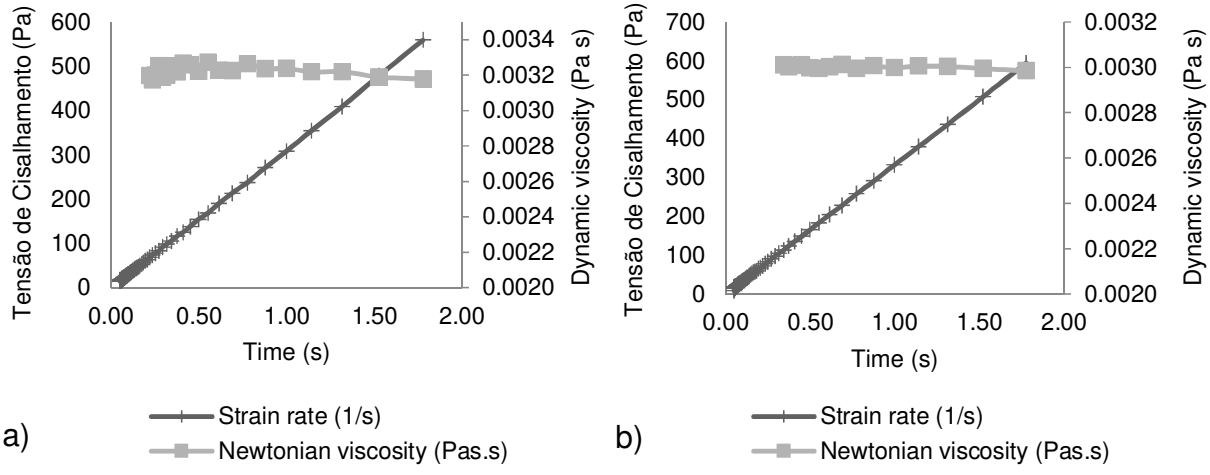

Figure 8. Rheology for B20 Soybean + Cotton (a) and B30 Soybean + Cotton (b).

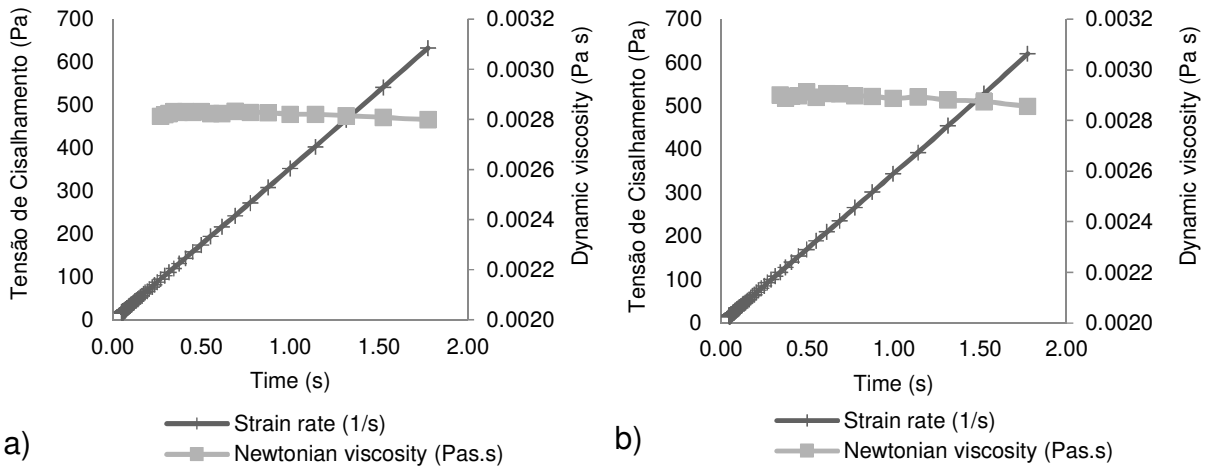

Figure 9. Rheology for B8 B Soybean + B Cotton (a) and B10 B Soybean + B Cotton (b).

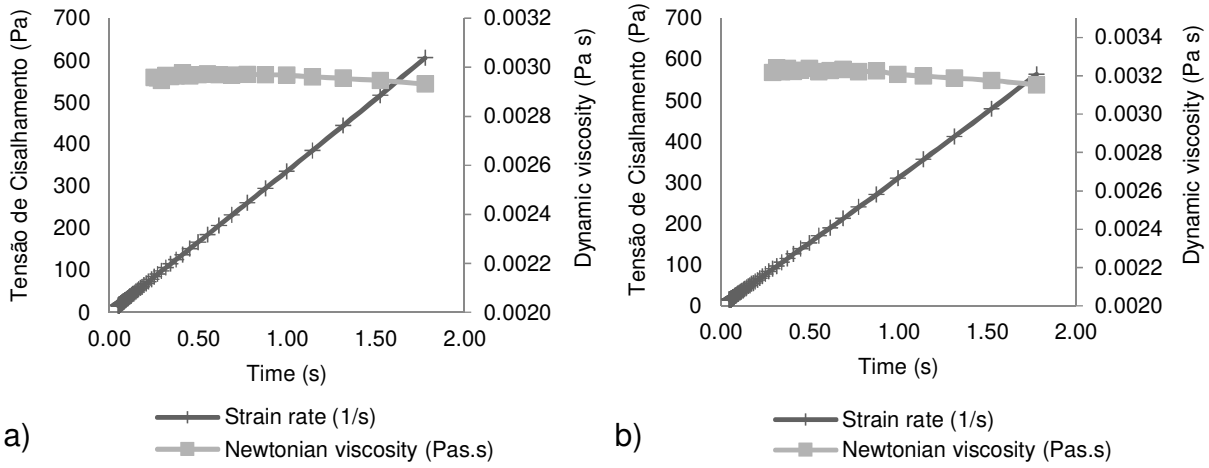

Figure 10. Rheology for B20 B Soybean + B Cotton (a) and B30 B Soybean + B Cotton (b).

From the analysis of the graphs built from the tests on the rheometer, it is possible to identify that all the biodiesels produced and tested in this study behaved like a Newtonian fluid. This behavior can be verified by analyzing that the viscosity found tends to be constant, straight parallel to the abscissa axis, and to be independent of the shear rate at which it is measured. This behavior confirms the results found by Dantas (2006) when analyzing the rheological behavior of biodiesel produced from corn.

The viscosity of the oil from the triglyceride source before undergoing the transesterification process is higher compared to that of biodiesel. After the transesterification stage, there is a sudden decrease in viscosity, promoting the obtaining of biodiesel, whose properties are similar to those found in diesel oil, giving support to this total or partial replacement of this fuel to use in diesel engines and justifying the advantage, if decrease the viscosity of a vegetable oil, present transesterification process (Dunn, 2002; Dorado et al., 2002; Dorado et al., 2003; Lopes et al., 2020; Souza et al., 2020).

It can be noted that the analyzed biodiesels present a Newtonian fluid behavior since the functional relationship between the shear stress and the strain rate is a line whose extension passes through the origin. This behavior found confirms the results found by Cavalcanti (2013) and Cavalcanti (2008) in their study with biodiesels and several BX mixtures. The same behavior was found for Dantas (2006).

According to Cavalcanti (2013), the lines that were constructed from the relationship between the deformation rate and shear stress have angular coefficients that are functions of the temperature and the composition of the components of the mixture, in this case the temperature has an inverse relationship with viscosity. The author also states that the apparent viscosity of the material at a given temperature and the range of strain rate is constant depending only on the temperature and composition of the material, so it can be considered as the dynamic viscosity of the material at that temperature.

CONCLUSIONS

This research investigated the production of biodiesel by the methyl route carrying out the production through mixtures of soybean and cotton, before and after the transesterification process. Therefore, the work was carried out with the objective of optimizing and measuring the production volume, as well as physically characterizing the different proportions of biodiesel mixtures used. The assessment of the values observed in the production of the different types of biodiesel mixtures of soybean and cotton in the different proportions of mixtures indicated efficacy. Thus, they demonstrated its potential for use in internal combustion engines. All biofuels showed specific mass values at 20 °C and kinematic viscosity at 40 °C within the limits established by ANP Resolution 30/2016.

The mixture of soybean and cotton vegetable oils before the transesterification process showed the highest efficiency when compared to the production from only one vegetable oil or from the mixtures of biodiesels.

In general, the results showed an increase in specific mass at 20°C due to the increase in the percentage of Biodiesels, this factor is recommended, since it allows the increase of the biodiesel injected into the combustion chamber, compensating for the lower calorific power presented in biofuels.

The tests with B30 biodiesel showed satisfactory results that support the possibility of continuing to increase the amount of biodiesel in the mixture with diesel for the next years in Brazil, which is higher than the target stipulated throughout the national territory until 2023, the B15 mixture.

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