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PHYSICAL-CHEMICAL PROPERTIES OF FIRST-GENERATION BIOFUEL AIMING APPLICATION IN DIESEL LOCOMOTIVE

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ABSTRACT

Theoretical framework: A biodiesel fuel is made from long-chain fatty acids derived from vegetable oil or animal fat. Similarities between physical-chemical characteristics of diesel and biodiesel make their mixture feasible. Environmental benefits achieved by using biofuels to drive machines has increased their contribution in energetic matrixes.

Objective: The aim of this research is to produce soybean and sunflower biodiesel in the laboratory using a transesterification reaction and to examine the biodiesel specifications for utilization in compression ignition engines.

Method: The physical-chemical properties of the biodiesel measured in the present work are density, viscosity, cetane index, flash point, pour point, and cloud point.

Results and conclusion: For soybean and sunflower biodiesel, density (867 kg/m³, 860 kg/m³), viscosity (5.29 mm²/s, 5.30 mm²/s), Centane index (53.88, 55.66), flash point (187°C and 135.6°C) are reported respectively. Regarding the pour point, cloud point, were only determined for sunflower biodiesel, respectively, -2°C and 13°C. The results indicate that these properties, density, kinematic viscosity, flash point, as determined from the soybean and sunflower biodiesel are within the limits established by The Brazilian National Agency of Petroleum, Natural Gas and Biofuels, Resolution No. 45 of the ANP of 08/25/2014 – DOU 08/26/2014. These values are, respectively, 850-900 kg/m³, 3-6 mm²/s, at least 100°C.The produced biodiesel presented behavior similar to diesel S10 proving its viability of use.

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Research implications: As a result of such thorough research, we are able to compare many characteristics of soybean and sunflower biodiesel with commercial diesel S10. This research is critical to the performance evaluation of a compression ignition engine and the potential reduction in greenhouse gas emissions associated with conventional diesel.

Keywords: Biofuels, Compression Ignition Engines, Transesterification Reaction.

PROPRIEDADES FÍSICO-QUÍMICAS DO BIOCOMBUSTÍVEL DE PRIMEIRA GERAÇÃO VISANDO SUA APLICAÇÃO EM LOCOMOTIVAS A DIESEL

RESUMO

Estrutura teórica: O biodiesel é um combustível produzido a partir de ácidos graxos de cadeia longa derivados de óleo vegetal ou gordura animal. Similaridades entre as características físico-químicas do diesel e do biodiesel tornam sua mistura viável. Os benefícios ambientais alcançados pelo uso de biocombustíveis para movimentar máquinas aumentaram sua contribuição nas matrizes energéticas.

Objetivo: O objetivo desta pesquisa é produzir biodiesel de soja e girassol em laboratório, utilizando uma reação de transesterificação, e analisar as especificações do biodiesel para sua utilização em motores de ignição por compressão.

Método: As propriedades físico-químicas do biodiesel medidas neste trabalho incluem densidade, viscosidade, índice de cetano, ponto de fulgor, ponto de fluidez e ponto de turvação.

Resultados e conclusão: Para o biodiesel de soja e girassol, as densidades (867 kg/m³, 860 kg/m³), viscosidades (5,29 mm²/s, 5,30 mm²/s) e índices de cetano (53,88, 55,66) são relatados, respectivamente. Quanto aos pontos de fluidez e turvação, eles foram determinados apenas para o biodiesel de girassol, sendo -2°C e 13°C, respectivamente. Os resultados indicam que essas propriedades, densidade, viscosidade cinemática e ponto de fulgor, conforme determinado para o biodiesel de soja e girassol, estão dentro dos limites estabelecidos pela Agência Nacional do Petróleo, Gás Natural e Biocombustíveis do Brasil, Resolução nº 45 da ANP de 25/08/2014 – DOU de 26/08/2014. Esses valores são, respectivamente, 850-900 kg/m³, 3-6 mm²/s e pelo menos 100°C. O biodiesel produzido apresentou comportamento semelhante ao diesel S10, comprovando sua viabilidade de uso.

Implicações da pesquisa: Como resultado dessa pesquisa minuciosa, podemos comparar muitas características do biodiesel de soja e girassol com o diesel comercial S10. Essa pesquisa é fundamental para a avaliação do desempenho de motores de ignição por compressão e a redução potencial das emissões de gases de efeito estufa associadas ao diesel convencional.

Palavras-chave: Biocombustíveis, Motores de Ignição por Compressão, Reação de Transesterificação.

PROPRIEDADES FÍSICAS Y QUÍMICAS DE BIOCOMBUSTIBLES DE PRIMERA GENERACIÓN PARA SU APLICACIÓN EN LOCOMOTIVOS DIESELADOS

RESUMEN

Marco teórico: El biodiésel es un combustible producido a partir de ácidos grasos de cadena larga derivados de aceite vegetal o grasa animal. Las similitudes entre las características fisicoquímicas del gasóleo y el biodiésel hacen viable su mezcla. Los beneficios medioambientales del uso de biocombustibles para alimentar maquinaria han incrementado su contribución al mix energético.

Objetivo: El objetivo de esta investigación es producir biodiésel de soja y girasol en el laboratorio mediante una reacción de transesterificación, y analizar las especificaciones del biodiésel para su uso en motores de encendido por compresión.

Método: Las propiedades físico-químicas del biodiesel medidas en este trabajo incluyen densidad, viscosidad, índice de cetano, punto de inflamación, punto de fluidez y punto de turbidez.

Resultados y conclusión: Para el biodiésel de soja y de girasol, se indican las densidades (867 kg/m³, 860 kg/m³), las viscosidades (5,29 mm²/s, 5,30 mm²/s) y los índices de cetano (53,88, 55,66), respectivamente. En cuanto a los puntos de fluidez y turbidez, sólo se determinaron para el biodiésel de girasol, siendo de -2°C y 13°C, respectivamente. Los resultados indican que estas propiedades, densidad, viscosidad cinemática y punto de inflamación, determinadas para el biodiésel de soja y girasol, están dentro de los límites establecidos por la Agencia Nacional de Petróleo, Gas Natural y Biocombustibles de Brasil, Resolución ANP nº 45 de 25/08/2014 - DOU de 26/08/2014. Estos valores son, respectivamente, 850-900 kg/m³, 3-6 mm²/s y al menos 100°C. El biodiésel producido mostró un comportamiento similar al diésel S10, demostrando su viabilidad de uso.

Repercusiones de la investigación: Como resultado de esta minuciosa investigación, podemos comparar muchas características del biodiésel de soja y girasol con el gasóleo S10 comercial. Esta investigación es fundamental para evaluar el rendimiento de los motores de encendido por compresión y la posible reducción de las emisiones de gases de efecto invernadero asociadas al gasóleo convencional.

Palabras clave: Biocombustibles. Motores de Encendido por Compresión. Reacción de Transesterificación.

1 INTRODUCTION

The majority of the world's energy is generated from oil, coal, and natural gas. These resources are limited and have an expected period of exhaustion. Therefore, the search for alternative energy sources is important (Fantinatti *et al.*, 2023; Sharifi *et al.*, 2023; Silva *et al.*, 2023; Saravanan *et al.*, 2021; Shuchrdt *et al.*, 1998).

The industrial development associated with the increase in both vehicle numbers and global population has increased the world energy demand (Kanna Dasan *et al*., 2023; Venkata Subhash *et al*., 2022). Mineral oil remains as one of the most used sources of energy. According to the Empresa de Pesquisa Energética (EPE) oil supports 39.3% of Brazilian demand of energy. However, mineral oil is a non-renewable energy source and emits high level of pollutant compounds.

The search for renewable fuels from vegetable oils able to reduce or even replace petroleum-based fuels has been carried out worldwide (Brock *et al*., 2020; Xie *et al*., 2022; Grotta *et al*., 2008) to achieve sustainable development (Xu *et al*., 2022; Sakthi Vignesh *et al*., 2020). Brazil is a pioneer country in biodiesel production being ranked as the fourth largest producer, just behind Germany, The United States and France (Pinto *et al*., 2012). The soybean crop is responsible for the majority of the national production of biodiesel. Several other crops are also used such as sunflower, palm oil, castor bean, and coconut, among others (Bergmann *et al*., 2013; Ferrari *et al*., 2022).

The use of vegetable oil as fuel in diesel engines is considered inappropriate, since it presents a series of limitations due to its degradability, high viscosity, incomplete combustion, and low volatility. Such negative characteristics promote fouling formation in the engine fuel injection pumps. The transesterification of vegetable oils is currently one of the most used methods to produce biodiesel. This reaction modifies the vegetable oil physical properties (Farmani *et al*., 2008; Chowdary & Prapulla, 2003). When power and torque are taken into account the engine performance with biodiesel is almost the same than the one with petroleum diesel and it thus does not require change in the engines to work well (Can, 2014; Dias *et al*., 2014; Ramadhas *et al*., 2004).

In addition, the biodiesel is non-toxic, biodegradable, and reduces the emissions of most of the pollutant gases. A problem with biodiesel combustion is the increase of NOx emission (Can, 2014). A study of gas emissions using fish oil biodiesel mixed with mineral diesel as fuel reveled an increase in NOx emissions with an increment of biodiesel percentage in fuel blends. Emissions of NOx also rose with the increment of engine loads (Varuvel *et al*., 2012).

Besides the increase in NOx emissions, other problems can also occur when biodiesel is used in diesel engines, such as low oxidation stability and higher viscosity causing cold flow problems. The stability of biodiesel is determined by its fatty acid chains; feedstock with a higher proportion of saturated fatty acids will be more stable than feedstock with a higher proportion of unsaturated fatty acids. On the other hand, higher contents of saturated fatty acid reduce the temperature properties such as cloud and pour points, thus there is an adjustment between the level of saturation of biodiesel and its cold flow properties (Sharma *et al*., 2008).

However, such problems can be avoided by appending additives in the fuel. Curcumin was used as an antioxidant for soybean biodiesel stored for 180 days. At the end of the experiment, biodiesel presented high efficiency and slow oxidation period, which is important since long fuel storage periods can affect biodiesel stability (de Sousa *et al*., 2014).

Biofuels are classified as first generation, second generation, or third generation. First generation biofuels are those made from edible raw resources. Second generation biofuels are made from inedible agricultural leftovers, whereas third generation biofuels are made from micro and macro algae and microorganisms (Ananthi *et al*., 2021; Awogbemi *et al*., 2021; Mat Aron *et al*., 2020; Chye *et al*., 2018). Researchers (Babu *et al*., 2022; Gangolu *et al*., 2022; Lingam *et al*., 2020; Dhana Raju *et al*., 2019), emphasize that biodiesel is a promising alternative to diesel. This is possible because of biodiesel's many advantages, especially emission levels.

Researchers (Szabados *et al*., 2022; Ahmed & Sarkar, 2018; Bokhari *et al*., 2016) reported the adverse effects of fossil fuels on the environment, thus necessitate the development of sustainable energy, as well as research on biomass waste. The study of waste biomass contributes to the production of second-generation biofuel. These researchers emphasize the importance of alternative fuels for the transportation sector. It is pointed out that biodiesels, being oxygenated fuels, would be a more viable choice to replace commercial diesel (Alruqi *et al*., 2023; Jit Sarma *et al*., 2023; Ashok *et al*., 2022; Sharma & Sharma, 2020).

Finalizing the various contributions of several researchers on the study of first, second, third and fourth generation biomass in the replacement of commercial diesel fuel, we still highlight the research that can contribute to this subject that is in evidence every day. In this context these researchers (Aransiola *et al*., 2023; Karthik *et al*., 2023; Bala & Mondal, 2022; Encinar *et al*., 2002; Jaiswal & Saxena, 2022; Malode *et al*., 2022; Raj Singh *et al*., 2022; Singh *et al*., 2023) deserve to be referenced in this work.

Restrictions due to the use of biodiesel in engines tend to be overcome since investigations in renewable fuel area has been growing because sustainability ideas spread fast in society, which reinforces the necessity of studies with biodiesel and its physical-chemical characterization (Oliva *et al.*, 2023).

This work intends to contribute to the research and analysis of biodiesel properties by producing soybean and sunflower biodiesels in the laboratory using the transesterification process and comparing their physical-chemical properties to petroleum diesel. Thus, making it possible to ascertain the proprieties of this biodiesel are already satisfactory for the use in diesel engines and which proprieties still require improvement. The intention is to use this biodiesel in locomotive engines.

2 OBJECTIVES

The objective of this research is to produce soybean and sunflower biodiesel in the laboratory, using a transesterification reaction, and analyze the biodiesel specifications for its utilization in compression ignition engines.

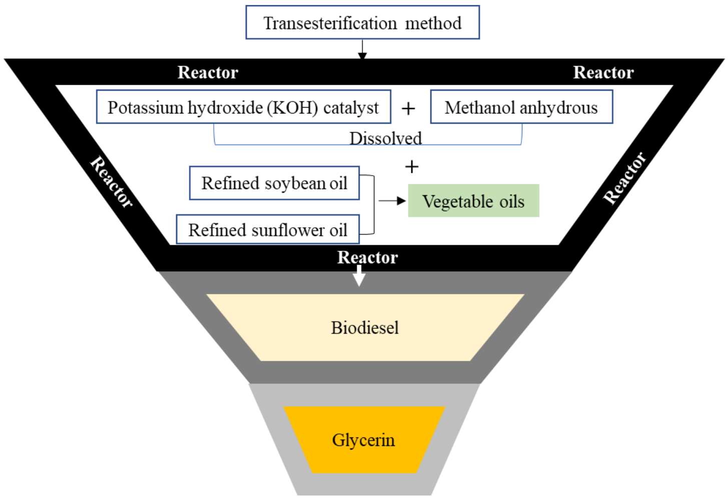
3 METHODOLOGIES

The biodiesel production process carried out at the Biofuels Laboratory of the Federal University of Viçosa/Brazil is represented in Fig. 1.

Samples of S10 diesel and refined soybean and sunflower oils were selected, and the transesterification method was used for the oils in order to obtain correspondent biodiesels. The biodiesel was produced in the laboratory, using potassium hydroxide (KOH) as catalyst and methanol anhydrous as the transesterification agent. In the process, KOH (1% in relation to the oil mass) and methanol anhydrous (6:1 molar ratio) were mixed until dissolution, and then the oil was slowly added. The mixture of oil, methanol and KOH was kept under agitation for about 60 minutes at room temperature. This type of catalyst can be used without addition of heat to the system. After agitation the mixture was maintained under rest to phase splitting. The lower phase was glycerin, and the upper phase was biodiesel. The process was similar for both soybean and sunflower oils.

Figure 1

The schematic of the biodiesel production process



Purified biodiesel was produced after washing it with citric acid solution (0.5% of oil mass), which was prepared by heating at 90ºC, a volume of water similar to the volume of biodiesel to be washed. The acid was added when water reached 90ºC. The acid solution was mixed with biodiesel and the mixture was put to rest for 5 minutes. During this process two phases were formed, the top dense phase (water + methanol) and the upper light phase (biodiesel). After sequent washing steps, the water pH reaches the initial pH of distilled water. Next, the biodiesel was transferred into a flask containing anhydrous sodium sulfate (1 g/100 mL of oil used initially) aiming to dry the sample and preventing contamination by water. The mixture was filtered and distilled. Finally, the biodiesel was filtered under vacuum at 80 °C.

The physical-chemical properties of S10 diesel and biodiesel were determined according to the Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP) methodology. After the biodiesel synthesis, 10 mg of each sample was diluted in 1 mL of hexane (HPLC grade, Sigma-Aldrich, Germany), the mixture was centrifuged at 5000 g (10 minutes at 5 °C), and a volume of 100 µL of sample was withdrawn and transferred to a vial containing 900 µL of hexane. After mixing, the solutions were carried out to the gas chromatography analysis (GC 2010 Shimatzu, Japan) to obtain the fatty acid profile of the sample. The chromatography conditions are: injection of 1 µL of sample, linear heating ramp from 60 °C to 330 °C using a rate of 20 °C·min-1, and high linear velocity for better resolution of peaks. The capillary column used was a SP-2560 (Supelco, Germany) with 100 m length, 0.25 mm diameter, and a film of 0.20 µm of thickness.

4 RESULTS AND DISCUSSION

The conversion rate of neutral soybean and sunflower oils in ethyl esters depends on the way that the transesterification reaction is conducted as well as the process conditions. Thus, the transesterification reaction is influenced by several factors including the type of catalyst (acid or alkali), molar ratio alcohol/vegetable oil, temperature, reagent purity (especially water content), and free fatty acid contents. In this research, alkaline catalysis was adopted due to its better performance, high selectivity, and to avoid problems with corrosion of engine components, which can occur in the presence of traces of acid (Brunetti, 2012).

Refined sunflower and soybean vegetable oils were used for biodiesel synthesis since the refining of oils allows to remove undesirable impurities, odor and reduce the viscosity of the final product.

Figure shows the biodiesel that was produced in the laboratory (Figure (a)) and the purified biodiesel (Figure (b)) after washing it with citric acid solution.

Figure 2

The view of the produced (a) biodiesel top phase and glycerin bottom phase and (b) biodiesel after acid washing

(a) (b)

Table 1

Fatty acid (%) converted to methyl esters in biodiesel

	Biodiesel	
Fatty acid	**Soybean**	**Sunflower**
Unsaturated fatty acid	89.0	86.9
Oleic - C18:1n9c	27.3	40.5
Palmitoleic – C16:1	-	2.6
Linoleic – C18:2n6c	53.3	32.0
Linolenic - 18:3	-	6.1
Other	8.4	5.7
saturated fatty acids	14.2	15.7
Palmitic	11	13.1
Stearic	3.2	2.6

Table 1 presents the composition of fatty acid of the studied biodiesel. Soybean oil has a higher concentration of unsaturated fatty acids than sunflower oil. Oils with high content of unsaturated fatty acids produce a minor cold filter plugging point of biodiesel, because the molecular structure of this type of oil makes the packaging difficult and therefore the freezing. In contrast, high content of saturated fatty acids promotes the increase in cloud point and clogging (de Sousa *et al*., 2014).

Therefore, the soybean biodiesel has the best properties regarding the cold plugging point when compared to sunflower.

4.1 BOILING POINT

An automatic vacuum distiller HDV 632 was used in the distillation test which consists of vaporization of a standard volume of S10 diesel and biodiesel. After that vapor was condensed in a way that it is possible to continually measure the boiling point and the distilled volume. So, the HDV 632 was used to determine the distillation characteristics of the S10 diesel and of both soybean and sunflower biodiesel. Distillations were carried out with pressures of 133.2 Pa for the biodiesel and 1333.2 Pa for diesel.

Table **2** presents the results of boiling points for distillation tests at atmospheric pressure. Atmospheric equivalent temperature (AET) is the boiling temperature which was corrected to the atmospheric pressure. Boiling points are given at 10%, 50% and 90% of recovered volumes of S10 diesel, soybean and sunflower biodiesels.

Table 2

Biodiesel boiling point data

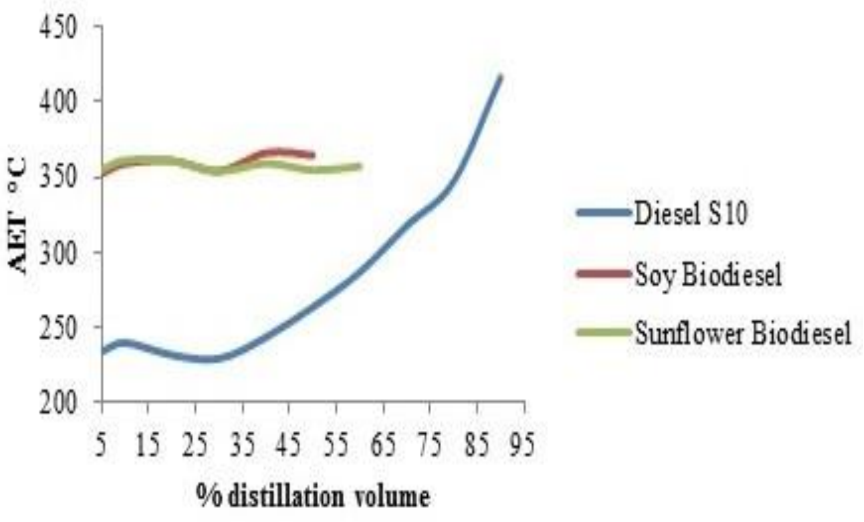
AET	Diesel	Soybean	Sunflower
10%	240.1	359.2	361.5
50%	263.9	364.7	354.8
90%	416.4	-	-

Table **2** reveals that the boiling point of the recovered volume 90% was not obtained for biodiesels. Biodiesels are long chain esters with a high content of non-saturations due to the double bonds in carbon chains. Thus, distillation could occur only up to 50% in this work.

Figure represents the distillation test curve for S10 diesel (recovered volume from 10 to 90%), soybean, and sunflower biodiesel (recovered volume of 10 and 50 %). Distillation temperatures varied from 200 °C to 400 °C for S10 diesel and from 350 °C to 360 °C for biodiesel. A small protuberance in the S10 diesel distillation curve shape can be observed, which is probably caused by the addition of 10% of biodiesel to diesel fuel. For the biodiesel a change in the distillation curve shape is not significantly evidenced.

Figure 3

Distillation test curve



4.2 CETANE INDEX

The distillation process is important due to its influence on the ignition quality of diesel oils. Thus, it is important to calculate the cetane number, because it has a direct influence on the engine start since its works with emissions (Ghiasi *et al*., 2022). Good correlation between the cetane number and the cetane index are described in the literature (Ghiasi *et al*., 2022). However, this work emphasizes the methodology to calculate the cetane index for the S10 diesel, soybean, and sunflower biodiesel.

Calculated cetane index is connected with the ignition quality of the diesel and biodiesels. Actually, the cetane index is a mathematical correlation for the cetane number, allowing it to be estimated through calculation. This correlation reflects the cetane index influences on engine operation (Ghiasi *et al*., 2022).

Thus, distillation results presented in Fig. 3 can be used to calculate the cetane index for diesel and biodiesels. Cetane index calculation is based on the ASTM D-4737 standard, in which four variables obtained in the distillation test at atmospheric pressure are used, as shown in Eq. 1:

$$\mathrm{IC} = -386.26(\mathrm{D}_{15}) + 0.1740(\mathrm{T}_{10}) + 0.1215(\mathrm{T}_{50}) + 0.01850(\mathrm{T}_{90}) + 297.42 \quad (1)$$

Where:

IC is the calculated cetane index;
D_{15} is the fuel density, (g/cm^3) at 15 °C;
T_{10}, T_{50}, and T_{90} are the vapor fraction temperatures when the fuel is distilled by 10%, 50% and 90% of their volumes, respectively, as shown in

Table 3.

Values of vapor temperature for distilled fractions of 10%, 50%, and 90% were determined by ASTM D86 standard method and corrected at atmospheric pressure. The density D_{15} was calculated according to ASTM D1298 standard.

Table 3 presents cetane index calculated by using Eq. 1 for soybean and sunflower biodiesel. The cetane index for both biodiesel samples are similar showing that utilization of these types of biodiesels in association with diesel is technically viable.

In fact, the values shown in

Table 3 are in accordance with the ASTM D-4737 standard range.

Table 3

Calculated cetane index (Eq. 1)

Calculated cetane index (IC)		
Diesel	**Soybean**	**Sunflower**
57.21	46.83	48.74

However, the standard highlights the employment of Eq. 1 for diesel oils with 90% of recovered values in temperatures up to 382°C. One should emphasized that the biodiesels used presented 10 % and 50 % of recovery volumes, respectively. In this context, the difference between the cetane index for S10 diesel and biodiesel is approximately 18.2% in relation to soybean and 14.8% to sunflower, as shown in

Table 3. For the biodiesels, which distilled only up to 50% of the recovered volume, the values of cetane index shown in

Table 3 were not used. Therefore, in this work Eq. 2 was used for cetane index calculation of soybean and sunflower biodiesels, based on ASTM D 976 which uses only two variables.

$$\mathrm{IC} = 454.74 - 1641.416(\mathrm{D}) + 774.74(\mathrm{D}^2) - 0.554(\mathrm{T}_{50}) + 97.803(\log(\mathrm{T}_{50}))^2 \quad (2)$$

Where:

IC is the calculated cetane index;
D is fuel relative density at 15°C according to ASTM D86, and
T_{50} is the temperature of the vapor fraction when the fuels are 50% distilled.

Table 4 presents cetane index calculated using Eq. 2. Such values are similar, which evidences the employment of these biodiesel in association with diesel.

Table 4

Calculated cetane index (Eq. 2)

Calculated cetane index (IC)		
Diesel	**Soybean**	**Sunflower**
57.21(Table 3)	53.88	55.66

In this context, the difference in cetane index between S10 diesel (

Table 3) and biodiesels (Table 4) is approximately of 5.82% and 2.71%, for soybean and sunflower biodiesel respectively. By using data calculated by using Eq. 1 (more general) an error of 14.8% and 18.2 is observed. Cetane index was calculated by using mathematical correlations. This correlation can be used to obtain cetane index, however, a more realistic value is the cetane number measured in the test engine.

It stands out in the work of Bashir et al. (2022) that the IC is an indicator of fuel quality. This happens because biodiesel has different fatty acid methyl esters, called FAME, with variations in molar masses, carbon chain length and molar fractions. Then, according to Encinar *et al*. (2005) and Pinto *et al*. (2005) the composition of biodiesel is mostly determined by the feedstock employed due to the varying types or levels of fatty acid content, with minor variations in the location of the farmed region and harvest time. As the composition of biodiesel changes, so do many qualities of this fuel, such as the *CI*.

It is also necessary to demonstrate that the *CI*, in general, is in the range of 40 to 60, as seen in the current study.

4.3 FLASH POINT

Another relevant property in the study of fuels or biofuels is the flash point (*FP*). In this work, *FP* test was performed in the equipment FP93 5G2 Pensky-Martens, operating according to the ASTM D-93 standard. The results are displayed in Table 5.

Table 5

Experimental data for flash point of the samples

Diesel	**Temperature °C**
S10-Diesel	61.8
Sunflower biodiesel	135.6
Sunflower biodiesel-distilled	142.0
Soybean biodiesel	187.0
Soybean biodiesel-distilled	177.8

For biodiesel the ASTM D-93 standard establishes a minimum expected value of 100 °C, and of 38 °C for diesel. The S10 diesel, soybean and sunflower biodiesel samples exhibited flash point values according to the standard. Table 5 shows values of flash point higher than 130°C for the biodiesels, which means there is no need to analyze the methanol content. The flash point does not influence the engine performance. However, it is important for the safety of handling and the fuel storage.

4.4 DENSITY

Density was measured using a 10 mL pycnometer with sample at 20°C. The results are represented in Table 6. Soybean and sunflower biodiesel presented density according to the standard reference range (ASTM D-1298). The density values of biodiesels are lower than the vegetable oil density used in transesterification and higher than the S10 diesel density. Such behavior indicates that an increase of fuel injection mass in the engine can arise if biodiesel is used instead of diesel, generating more power. However, the increase in injection fuel mass can also lead to higher emissions of particulate matter, also called “black carbon”. Density of the non-distilled soybean and sunflower biodiesel are higher than the distilled fraction of both. Thus, the use of the non-distilled biodiesel will cause higher emission of particulate matter. Values of distilled biodiesel are approximate to the last value of the reference range for the S10 diesel, which is 850 kg/m^3. The ratio between biodiesel and diesel reference interval is 0.7% for sunflower biodiesel, and 1.2% for soybean biodiesel, whereas for the non-distilled fraction is 2.2% for the sunflower biodiesel and 2.5% for the soybean biodiesel. When comparing the non-distilled fraction with the distilled fraction these percentages evidenced an increase of three times for the sunflower biodiesel and two times for the soybean biodiesel.

Table 6

Experimental results for density of the samples

Samples	Obtained value (kg/m³)	Reference value (kg/m³)
Sunflower oil	911	916-922
Sunflower biodiesel	860	850-900
Sunflower biodiesel distilled fraction	856	850-900
Sunflower biodiesel non-distilled fraction	869	850-900
Soybean oil	910	916-922
Soybean biodiesel	867	850-900
Soybean biodiesel distilled fraction	861	850-900
Soybean biodiesel non-distilled fraction	872	850-900
Diesel S10	833	820-850

4.5 KINEMATIC VISCOSITY

Table **7** represents kinematic viscosity values of S10 diesel, soybean, and sunflower biodiesel samples. Viscosity was determined by a reometer, which gives the sample dynamic viscosity, at 40 °C during 300 s for each sample. The kinematic viscosity is the ratio between dynamic viscosity and density of the samples.

Table 7

Kinematic viscosity of the samples

Samples	Dynamic viscosity (mPa.s)	Density at 40 °C (kg/m³)	Kinematic viscosity (mm²/s)	Reference values for kinematic viscosity (mm²/s)
Diesel S10	2.76	833	3.31	2.0-4.5
Soybean oil	31.44	910	34.55	-
Sunflower oil	38.25	911	41.99	-
Soybean biodiesel	4.58	866	5.29	3.0-6.0
Soybean biodiesel distilled fraction	3.86	861	4.48	3.0-6.0
Soybean biodiesel non-distilled fraction	6.47	870	7.44	3.0-6.0
Sunflower biodiesel	4.55	859	5.30	3.0-6.0
Sunflower biodiesel distilled fraction	3.81	855	4.46	3.0-6.0
Sunflower biodiesel non-distilled fraction	5.86	869	6.74	3.0-6.0

In

Table **7** kinematic viscosity values calculated are according to the reference intervals of the Associação Brasileira de Normas Técnicas (ABNT) except for the non-distilled fractions. According to

Table **7**, distilled fraction of both biodiesels shows values of kinematic viscosity lower than the ones in biodiesels without distillation. These values correspond to 15% and 16% for soybean and sunflower biodiesel, respectively. When used in compression ignition engines, high viscosity biodiesels can lead to atomization problems in fuel injection, as well as an increase in particulate matter and smoke emissions. Calculated kinematic viscosity values for the distilled biodiesels approximate to the last reference value of S10 diesel. The high values of kinematic viscosity of soybean and sunflower oils mean the presence of glycerol in these molecules.

4.6 CLOUD POINT AND POUR POINT

Table 8 presents experimental data for samples cloud point (*CP*) and pour point (*PP*). The tests were accomplished in the equipment HCP 852 and the properties were determined automatically according to the ASTM standard. The *CP* and *PP* are physical properties associated to the cold flow characteristics of fuels. At cold temperatures fuels tend to partially solidify or lose their fluidity, compromising the fuel flow.

The CP is the temperature at which liquid begins to cloud, and it is related to engine starting at cold temperatures (Dwivedi & Sharma, 2014). *CP* and *PP* differ depending on the feedstock used in biodiesel synthesis and the type of alcohol employed in the transesterification method. These characteristics are significant in terms of the temperatures at which the fuel will be stored and consumed.

Table 8

Experimental results for the CP and PP of the samples

Sample	Cloud point (°C)	Pour point (°C)
Diesel	8	-1
Sunflower biodiesel	13	-2

As shown in Table 8, the cloud and pour point for the sunflower biodiesel are 13 °C and -2°C, respectively, which means that at temperatures under such values the biodiesel will get cloudy, and its flow can be altered. However, in Brazil temperatures are mild from north to south, and fuel freezing is not a problem, mainly because it is intended to use biodiesel blended in diesel.

5 CONCLUSIONS

This study had conducted experiments on determining the properties of soybean and sunflower biodiesel. These properties are density, viscosity, *IC*, *FP*, *PP* and *CP*. These properties are compared with those of conventional diesel S10. The values of these properties are, respectively, for biodiesel from soybean and sunflower biodiesel, 867 kg/m³, 860 kg/m³, 5.29 mm²/s, 5.30 mm²/s, 53.88, 55.66, 187°C and 135.6°C. Regarding the pour point, cloud point, were only determined for sunflower biodiesel, respectively, -2°C and 13°C.

All results presented are within the limits established by The Brazilian National Agency of Petroleum, Natural Gas and Biofuels -ANP, in accordance with ANP Resolution No. 45 of 08/25/2014 – DOU 08/26/2014.

The similarities in fluid and thermodynamics properties between diesel and biodiesel indicates that these fuels are compatible, especially regarding cetane index in diesel cycle engines. Therefore, the performance and fuel consumption of both fuels are practically equivalent. Moreover, there is no need for any modification or adaptation of the diesel engine so they can run with biodiesel. Due to this equivalence in physical-chemical properties, biodiesel, and diesel are miscible, and they can be blended in any proportion. This condition is advantageous when compared with ethanol, once for biodiesel neither special supply pumps nor different engines are required to work with different fuels or blends. Another matter to consider is the use of a distilled biodiesel, where the physical-chemical properties are even more similar to diesel fuel. However, mathematical correlation of four variables should not be used to determine the cetane index for biodiesels.

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DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationship that could have appeared to influence the work reported in this paper.

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