

# DETERMINATION OF THERMAL AND OXIDATION STABILITY OF SUNFLOWER METHANOLIC BIODIESEL AND BLENDS OF BIODIESEL/DIESEL

## DETERMINAÇÃO DA ESTABILIDADE TÉRMICA E À OXIDAÇÃO DO GIRASSOL METANOL BIODIESEL E MISTURAS DE BIODIESEL

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## RESUMO

A utilização de energias renováveis como o biodiesel tem despertado grande interesse industrial e ambiental. Neste trabalho foram avaliadas as propriedades físico-químicas de diesel, biodiesel, e de suas misturas nas proporções: B5 a B70, através de ensaios de ponto de fulgor, massa específica, viscosidade cinemática. Além de estudar a estabilidade térmica e oxidativa por TG/DTA. Como resultado foi observado que com o aumento do teor de biodiesel adicionado ao diesel constatou-se uma melhoria na sua estabilidade térmica e um aumento do resíduo e através do DTA que misturas que contêm biodiesel são mais voláteis que o diesel.

**Palavras-chave:** Biodiesel. Girassol. Termogravimetria.

## ABSTRACT

*The using of renewable energy like biodiesel has attracted great industrial interest and the environment. In this work we evaluate the physicochemical properties of diesel, biodiesel and their mixtures in proportions: B5 to B70, by testing the flash point, density, kinematic viscosity. Also, thermal and oxidative stability by TGA / DTA. It was verified that by increasing the content of biodiesel added to diesel was observed an improvement in thermal stability and an increase of the residue by DTA and the mixtures containing biodiesel which are more volatile than diesel.*

**Key-words:** Biodiesel. Sunflower. Thermogravimetry.

## INTRODUÇÃO

Brazil is a country with a wide variety of oils with potential to be used as feedstock to produce biodiesel [1,2]. Biodiesel consists of saturated and unsaturated long chain fatty acid alkyl esters derived from feedstocks such as vegetable oils, animal fats and used frying oil, obtained through transesterification of vegetable oils or animal fats using short chain alcohols (methanol or ethanol) catalyzed by an acid or a base [3]. Sunflower (*Helianthus annuus* L.), is an important oilseed crop worldwide, yielding approximately 45-50% oil worldwide [4]. Among the vegetable oils, sunflower oil produces high percentages of polyunsaturated fatty acids, mainly linoleic acid (C18:2) [5]. The percentages of linoleic and oleic acid are approximately 90% of total fatty acids present in sunflower oil, therefore, has a greater susceptibility to oxidation in the presence of light and heat. The transformation of sunflower oil by transesterification to produce biodiesel has been studied and the results showed that the biodiesel was an excellent substitute for fossil fuels under optimum conditions [6]. The hydrocarbon chains in biodiesel are generally 16–20 carbons in length and contain oxygen at one end. Biodiesel contains about 10% oxygen by weight. Biodiesel does not contain any sulphur, aromatic hydrocarbons, metals or crude oil residues [7,8]. These properties improve combustion efficiency and emissions. Biodiesel fuel blends reduce particulate material, hydrocarbon, carbon monoxide and sulfuroxide emissions [9]. However, NO<sub>x</sub> emissions are slightly increased depending on biodiesel concentration in the fuel [10,11]. Thermogravimetric analysis (TGA) was used for study of the volatilization and degradation of the samples of diesel, sunflower biodiesel and its mixtures in different proportions.

## 2 MATERIALS AND METHODS

The biodiesel was synthesized using sunflower oil obtained from CAMPESTRE S.A, Brazilian Industry. The sun-

flower biodiesel was obtained by reaction of transesterification, keeping 6:1 molar ratio of methanol to sunflower oil, and KOH as catalyst (1%), under constant stirring at room temperature. After breakage of triglyceride molecules, a mixture of methyl esters was obtained, and glycerin as co-product.

For the preparation of the mixtures of biodiesel and diesel, seven samples with total volume of 250 mL each of them, where prepared with proportions of biodiesel to diesel of 5; 10; 20; 40 and 70%, which were referred as B5; B10; B20; B40 and B70 samples. The samples named as B0 and B100 correspond to mineral diesel and sunflower biodiesel, respectively.

The physical chemical characterization of the sample of biodiesel was performed according to Standards of American Society of Testing and Materials (ASTM), British Standard (BS EN) and Associação Brasileira de Normas Técnicas (ABNT) according to RESOLUTION N°7/2008 [12] of the Brazilian National Agency of Petroleum, Natural Gas, and Biofuels (ANP). Determination of flash point, according to ASTM D 93 [13], was performed in equipment Quimis, open vessel; model Q-292-2. The density analyses were determined automatic densimeter, based on ASTM D 4052 [14]. The kinematic viscosity determined at 40°C by ASTM D 445 [15], were accomplished in an AKV-202 TANAKA viscometer. The thermogravimetry (TG) experiments were carried out using a Thermobalance Shimadzu DTG-60 model, in the temperature range of 30–600 °C, under air atmosphere flowing in a rate of 100 mL min<sup>-1</sup>, using alumina crucible of 70 µL and heating rates 10 °C min<sup>-1</sup>.

## 4 RESULTS

The data of the physical-chemical characterization of the samples is given in the Table 1. It was observed that the sunflower biodiesel was performed in accordance with the specifications of ANP Resolution No7/2008 [12]. For comparison, it was analyzed the pure diesel fuel (B0), sunflower biodiesel (B100) and the mixtures of biodiesel / diesel (B5, B10, B20, B40, B70).

**Table 1** - Physical chemistry properties of Sunflower biodiesel and blend diesel/biodiesel

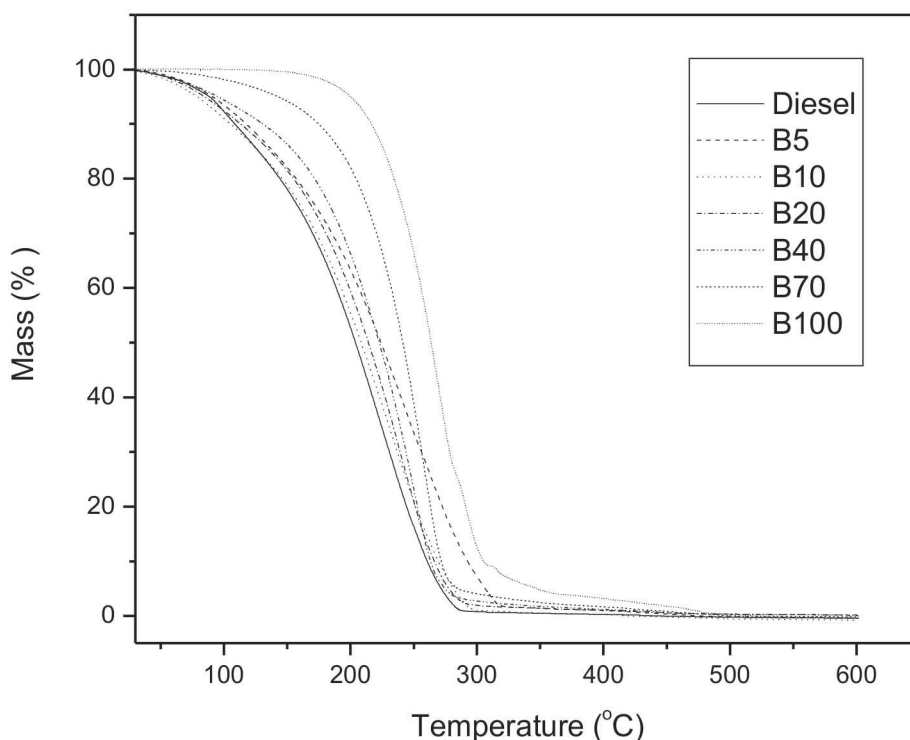
Samples	Parametes		
	Kinematic Viscosity 40°C (mm <sup>2</sup> s <sup>-1</sup> )	Specific Mass 20°C (Kg m <sup>-3</sup> )	Flash Point (°C)
B0	3.768	836.9	44
B5	3.776	839.0	44
B10	3.785	841.2	45
B20	3.859	845.4	47
B40	3.999	854.7	53
B70	4.282	868.1	67
B100	4.703	883.7	160
Method	ASTM D 445	ASTM D 4052	ASTM D 93

The density and kinematic viscosity was increased in all samples due to biodiesel is denser than the diesel, consequently, the density from the addition of percentages of biodiesel increased gradually. This assay was performed according to ASTM D 4052, in which for the diesel fuel and mixtures of the acceptable range is 820-880 kg m<sup>-3</sup> to 20 °C and the B100 is 850-890 kg m<sup>-3</sup> at 20 °C. For the flash point parameter, a gradual increase in temperature with increasing of

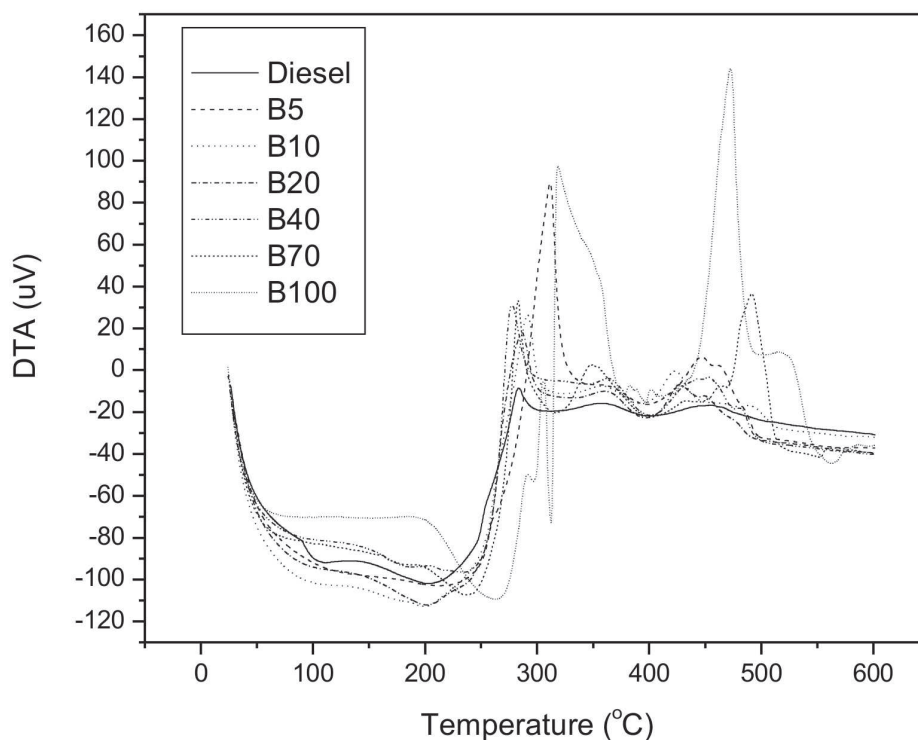
the percentage of biodiesel to diesel was observed, making the mixtures safer for transport and storage.

The **Figures 1** and **2** illustrates the thermal behavior of sunflower biodiesel, mineral diesel and the blends of biodiesel/diesel, in presence of air atmosphere. All curves presented one well defined weight loss, occurred due to the volatilization of the oil in the case of diesel fuel and biodiesel, as presented in the **Table 2**.

**Figure 1** - TG curves of sunflower biodiesel and blends Diesel/Biodiesel



**Figure 2** - DTA curves of sunflower biodiesel and blends Diesel/Biodiesel



**Tabel 2** - Representative TG data of the samples in air atmosphere

Sample	Range Temperature (°C)	Lost Mass (%)	Mass Residual (%)
Diesel (B0)	63-344	99,5	0,5
B5	51-330	98,5	1,5
B10	55-315	99,2	0,8
B20	58-321	98,4	1,6
B40	60-312	97,6	2,4
B70	118-305	96,2	3,8
Biodiesel (B100)	163-352	95,4	4,6

The TG curve of sunflower biodiesel presented one mass loss step between 163-352°C attributed to the triacylglycerides volatilization and combustion processes, which are responsible for approximately 95.4% of mass loss. The blends between B5 and B40 also provides a single step and decomposition starting temperature between 50-60 °C and their percentage of weight loss was about 97%. The increasing of the percentage of biodiesel to diesel increased the temperature for thermodecomposition and the amount of final residue. This is due to presence of high molecular weight methyl esters present in the mixtures, thereby requiring more energy to decompose. Combining TG with DTA, was verified the exothermic and endothermic transitions of the processes. The endothermic transitions are assigned to the volatilization of the components present in the samples, while the exothermic are due to the combustion of waste. It was observed a displacement of the peak temperature occurring in the first transition (endothermic) on DTA. This is because the samples containing biodiesel are more volatile than diesel, proving once again that biodiesel offers greater

security in terms of storage, handling and use as fuel.

## 5 CONCLUSION

Sunflower biodiesel, obtained by the transesterification route, showed appropriate characteristics for use in diesel engine. By adding higher concentrations of biodiesel in diesel was observed an increase in the kinematic viscosity, specific gravity and flash point. However, all blends studied can be used as fuel in accordance with ANP. From TG curves was observed an increase in thermal stability and an increase in the oxidative residue content with the gradual addition of biodiesel diesel. It was found that mixtures containing biodiesel are more volatile than diesel, as observed in DTA curves.

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