Evaluation of the volatility characteristics of diesel / biodiesel blends using thermal analysis techniques

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ABSTRACT

Since 2008, diesel sold in Brazil receives the mandatory addition of biodiesel (B100). Currently, the blending percentage to B100 in diesel is 10% (B10), but from June / 2019 this value will increase to 11% (B11) and from this date will increase by 1% each year until reaching B15 in 2023. The quality of the diesel sold in Brazil, because the increasing compulsory added B100 content, it has been a cause for concern. Because of its composition and chemical structure B100 is more prone to oxidation than the latter. The purpose of this work was to study the thermal behavior of diesel / biodiesel blends caused by the effect of increasing the B100 content to the mixture using thermal analysis. The blends prepared using soybean biodiesel and S10 diesel, by using the volumetric ratios of 10%, 15%, 20%, 25%, 30%, 35%, 40% and 50%, were analyzed in a simultaneous DSC-TGA mod. SDT-Q600 equipment, from TA Instruments. The experimental conditions used were: dynamic analysis from 25ºC to 600ºC, at a heating rate of 10 $^{o}C.min^{-1}$, in N_2. The results indicate that diesel / biodiesel blends volatilization characteristics depends on the content of biodiesel present in the mixture, which reflects in changes in the respective TG/DTG curves profile. It is also observed that the increase of B100 delays the stages mass losses of the blends to higher temperatures. Consequently, there is a displacement of the volatilization onset temperatures (T_{onset}) to a higher value. . The onset temperature value of diesel is 134 °C, while for the blend B25 and B50 is 140 °C and 164 °C, respectively. The mass loss initial and decomposition endset temperatures (T_{endset}) are not significantly altered by the presence of biodiesel. The values temperatures are, for the B50, 35 °C and 253 °C, that is, 2 °C and 4 °C higher of those of the S10 diesel. The interaction between biodiesel and diesel is not complete, because are observed two peaks in the DTG analysis. This behavior is the result of the difference between their physicochemical properties. The results show that biodiesel modifies the volatilization process of diesel / biodiesel blends, especially for volumetric contents above 20%, which can affect fuel performance.

Keywords: diesel, biodiesel, blends, volatility, Thermal Analysis.

INTRODUCTION

Diesel oil is a light petroleum distillate (distillation range from 170 ^{o}C to 380 ^{o}C at atmospheric pressure), whishes characteristics allow its use in diesel cycle vehicles engines [1]. By the fact that the thermodynamic efficiency of diesel internal combustion engine is higher than that of the gasoline engine, it occupies a prominent position in the vehicular fuel matrix, reflecting its increased demand when compared to other derivatives. In Brazil, it is the most used fuel, mainly in the road sector, representing around 45% of national sales of petroleum derivatives [2].

Internal combustion engines transform thermal energy (heat) into mechanical energy (work). According to the fuel ignition procedure there are Otto (spark-gasoline) or Diesel (auto-ignition - diesel) cycles [3]. In recent years diesel engines have undergone technical improvements as those performed in the engine injection systems, to comply with emissions reduction laws and also to increase their efficiency.

Diesel ignition occurs after its injection at high pressures and atomization inside the combustion chamber. The thermodynamic conditions (pressure and temperature) into the cylinder, allow the auto-ignition of the mixture [4]. Time available for mixing fuel and air, after diesel injection into the combustion chamber, is relatively short, fraction of seconds. The atomization of the liquid should be sufficient to promote its complete evaporation. The effective atomization favors high rates of mixing and evaporation allowing greater energy release, easier ignition and lower pollutants concentration in the exhaust gases. This process depends on the main properties, such as density, volatility, viscosity and surface tension, as well as the mixing efficiency between fuel and the intake air [5]. Volatility is an important factor to be considered in the atomization process, that is, in the mixture air and fuel quality. Fuels with inadequate volatility make difficult the starting of the engine and increase engine warm-up time. At atmospheric pressure as biodiesel vapor pressure is lower than that of diesel, thus its volatility is lower than the latter [6].

Diesel fuel available in Brazil is a blend diesel/biodiesel containing 10% (B10) in volume of biodiesel in compliance with the mandatory minimum percentage established by current Brazilian legislation. Resolution N^{o} 16 / 29.10.2018 of the National Energy Policy Council (CNPE) established a new timetable for the gradual increase of biodiesel content in its blend with petroleum diesel. The biodiesel percentage in the blend will rise one percent per year from June / 2019 to 15% (B15) in March 2023. This increase in the biodiesel content in the blends is conditioned to tests to be performed on the engines [7]. Compulsory increase in the biodiesel content in diesel fuel sold in Brazil has been a matter of concern because of the impacts that may occur due to the use of a fuel that is more susceptible to degradation.

Diesel and biodiesel have compatible characteristics, which allow their use in combustion engines, but have different molecular structures. The former is a mixture of paraffinic, naphthenic and aromatic hydrocarbons with predominantly paraffinic characteristics. Biodiesel is composed of esters of saturated and unsaturated fatty acids which results in significant differences in the physical-chemical properties and in the degradation process when compared to diesel oil.

The objective of this work is to study the effect of the biodiesel content on the volatility behavior of diesel / biodiesel blends using thermal analysis techniques. Sample blends B10, B15, B20, B25, B30, B35, B40, and B50 were prepared with soybean biodiesel and S10 diesel.

MATERIALS AND METHODS

1. Materials

1.1- Diesel S10

The diesel oil S10 (biodiesel free), used in this study, was supplied by the distributor Ipiranga Produtos de Petróleo S. A. free from additives. The analysis data regarding the physico-chemical characteristics of the diesel were provided by Ipiranga according to data from the manufacturer (Refinaria Duque de Caxias - REDUC / Petrobras). All the results met the specifications contained in the ANP resolution no. 50 of 2013, the current resolution for the specification of diesel road marketed in Brazil, contained in the ANP technical regulation nº 4/2013 [8].

1.2- Biodiesel

It was used a commercial soybean biodiesel (B100) containing no antioxidants and supplied by Caramuru Alimentos (Ipameri / GO). The B100 was packed in a plastic bag and stored in a freezer to prevent oxidation. As the biodiesel analysis report was not available, determination of specific mass at 20 ° C, viscosity at 40 ° C and oxidation stability were carried out and the results are shown in Table 1. Only viscosity and specific mass results meet ANP specifications (RANP No. 45-2014) [9].

Table 1: Characteristics of soybean methyl biodiesel

Characterístics	Unit	Method	Limit ANP	Result
Aspect	-	visual	LII	LII
Specific mass @ 20°C	kg/m³	ASTM D4052		876.4
Kinematic viscosity @ 40ºC	cSt (mm²/s)	ASTM D445		4.389
Stability to oxidation @ 110ºC	h	EN 14112	min. 8 h	**5.8**

1.3 - Blends diesel / biodiesel

Diesel / biodiesel blends were prepared using soy methyl biodiesel (B100) and S10 diesel in volumetric ratios of 10%, 15%, 20%, 25%, 30%, 35%, 40%, and 50%. Volumes were measured in a 100 mL graduated cylinder and the blends kept in a closed amber flask and batched at room temperature. The blends were prepared just before being analyzed.

2. Methods

2.1 Thermal analysis

Thermal analyzes of B100 biodiesel, S10 diesel and diesel / biodiesel blends were performed in a the TA Instruments' DSC-TGA model SDT-Q600 simultaneous analyzer. Calibration of the equipment was performed according to the manufacturer's recommended procedures. Open platinum crucibles (110 µL) were used for the sample and reference. About 12 mg (± 0.3 mg) of material were used for the determinations. The experimental conditions employed were: dynamic analysis from ambient temperature up to 600 °C, but in the case of biodiesel, the analyses were up to 800 °C. Heating rate of 10 °C.min^{-1}, nitrogen as purge gas at a flow rate of 50mL.min-1 was used. The results were treated using Universal Analysis software.

EXPERIMENTAL RESULTS

Figures 1 and 2 show the S10 diesel and biodiesel TG / DTG and DSC curves, respectively. The overlay of the TG / DTG curves for both fuels is shown in Figure 3. Figure 4 shows the individual graphs of the TG / DTG curves for the blends, prepared using different volumetric ratios. It is observed that the TG curve of B100, in Figure 1, shows a well defined initial large stage of mass loss, which is attributed to the biodiesel esters volatilization and subsequent decomposition. This can be confirmed by the DTG curve that shows a peak in the range of

112 °C to 268 °C with a respective endothermic DSC peak, as well by the resulting endothermic peak in the range of 185 °C to 283 °C seen on the DSC curve due to the final decomposition stage of the heavier components.

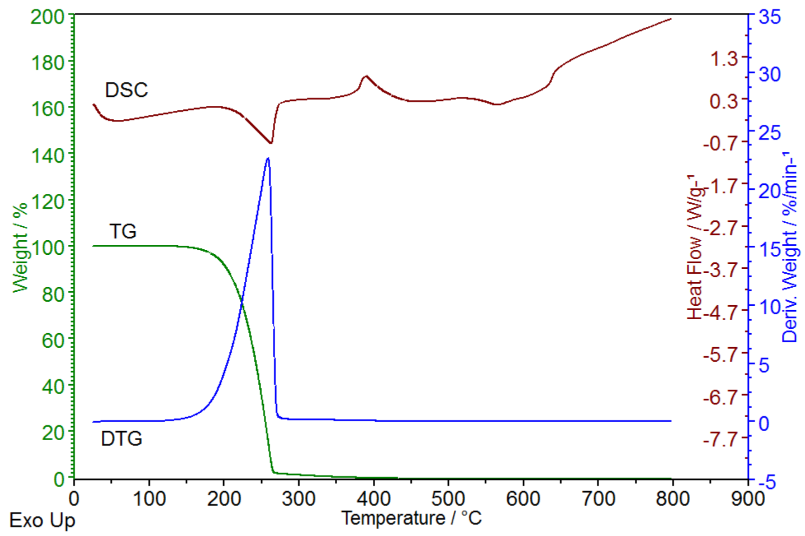

Figure 1: Biodiesel (B100) TG / DTG and DSC curves in N_2.

As shown in Figure 2, the TG curve of the S10 diesel presents a single stage of mass loss, attributed to the volatilization of its components, confirmed by the peak of the DTG curve, which occurs between 35 °C and 256 °C.

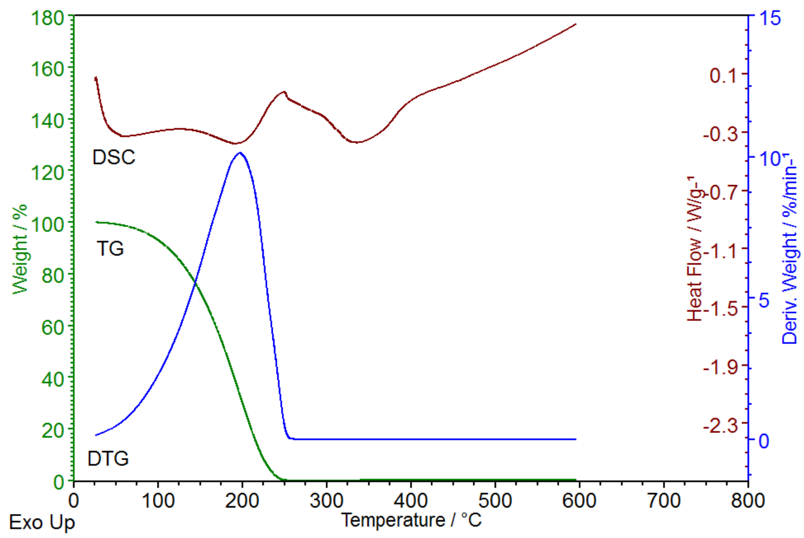

Figure 2: Diesel (B100) TG / DTG and DSC curves in N_2.

Overlapping diesel and biodiesel TG / DTG curves, as shown in Figure 3, it can be observed that diesel is less stable under the conditions of analysis (ambient pressure and gas dragging effect) than biodiesel. Because of its greater volatility when compared to biodiesel, diesel volatilizes first starting to loose mass at 35 °C, while biodiesel begins to volatilize above 100 °C.

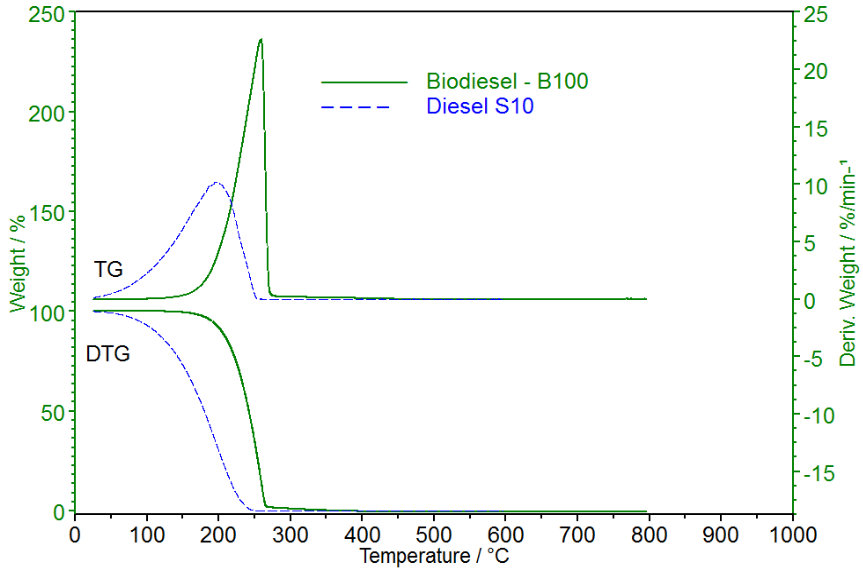

Figure 3: TG / DTG curves of biodiesel B100 and diesel S10.

Biodiesel decomposes almost entirely in a much lower temperature range when compared to diesel, presenting a sharper and higher peak. Diesel has a greater distribution of mass loss, generating a large DTG wide peak, reaching a lower maximum value than biodiesel. At the analysis conditions the biodiesel T_{onset} of volatilization is higher than that of diesel, because its esters have a lower vapor pressure than the components of the diesel light fractions.

Increasing the content of biodiesel, the interactions observed between the two fuels are presented and are a function of their concentration. All blends DTG curves, as shown in Figures 4, exhibit two consecutive and overlapping stages of mass loss. As the biodiesel percentage increases, the second stage of mass loss gradually increases, while the first mass loss decreases. In samples B10 and B15, the second mass loss is subtle, almost like a small shoulder. From sample B20 this second mass loss becomes more evident.

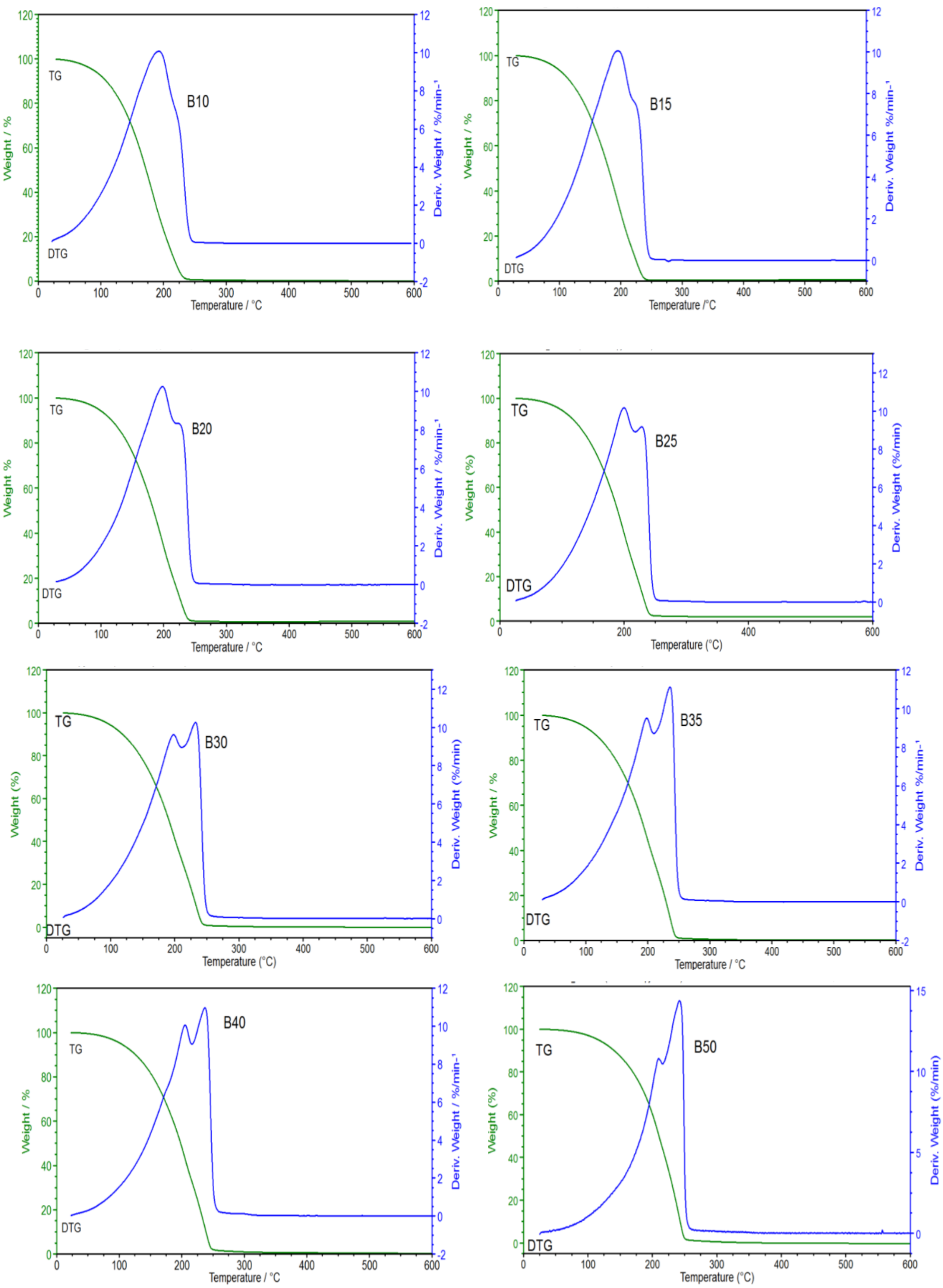

Figure 4: TG / DTG curves of blends B10 to B50.

The overlay of the TG and DTG curves of each blend and those of diesel S10 and B100 are shown in Figures 5 and 6. It is observed a first mass loss DTG peak, probably due to the volatilization and decomposition of light diesel fractions, and a second stage of mass loss related to biodiesel. The blends TG / DTG curves show a partial interaction between the components of the mixture confirmed by the observed displacement of mass loss peaks of diesel and biodiesel. Mixtures with a complete interaction between their constituents present only one stage of mass loss, and not two, as is the case for some diesel and biodiesel blends. In the TG / DTG curves of blends B10 and B15, the onset of volatilization is similar to that of diesel. The change begins to be noticeable in the analysis of the B20 blend and in a more visible way in the B25 blend.

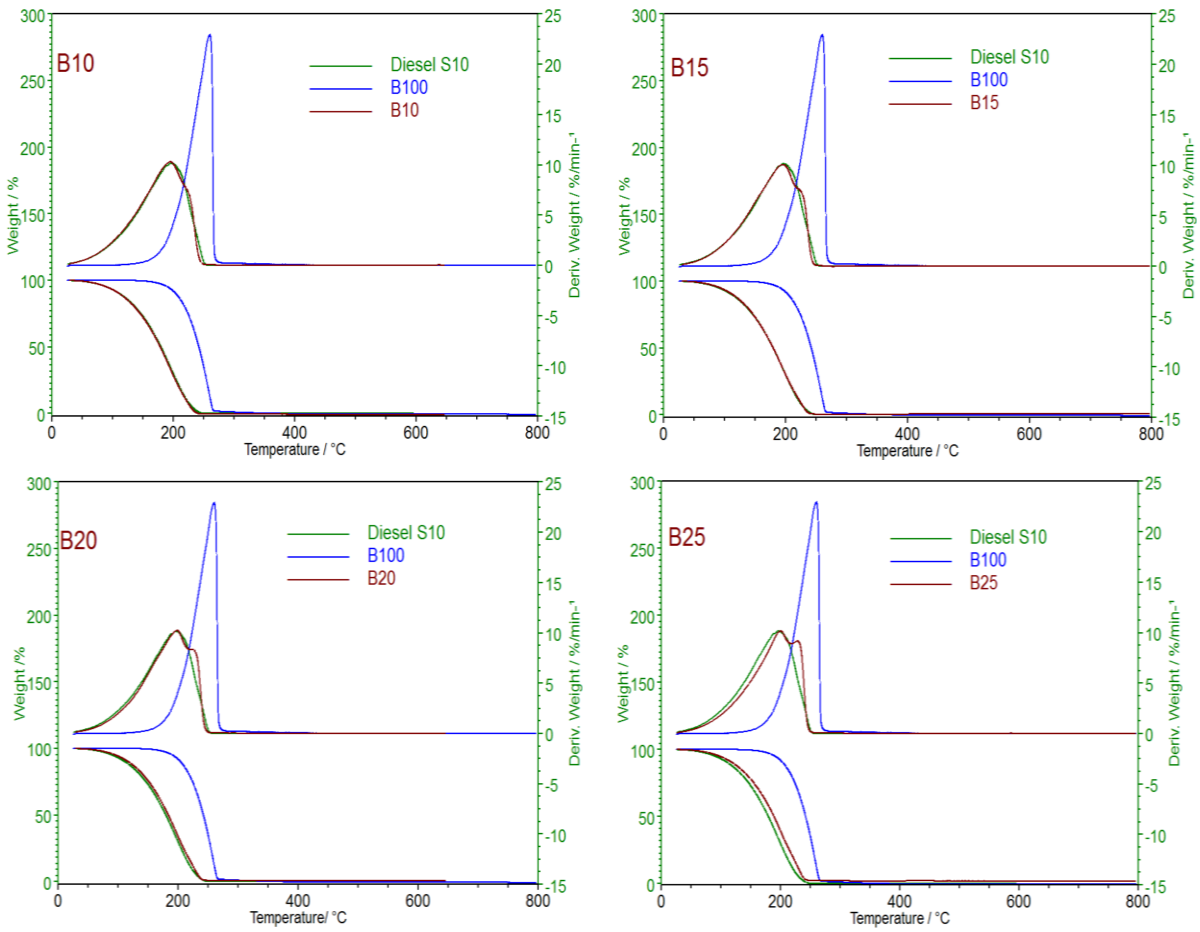

Figure 5: TG / DTG curves of B10, B15, B20, B25, B100 and diesel.

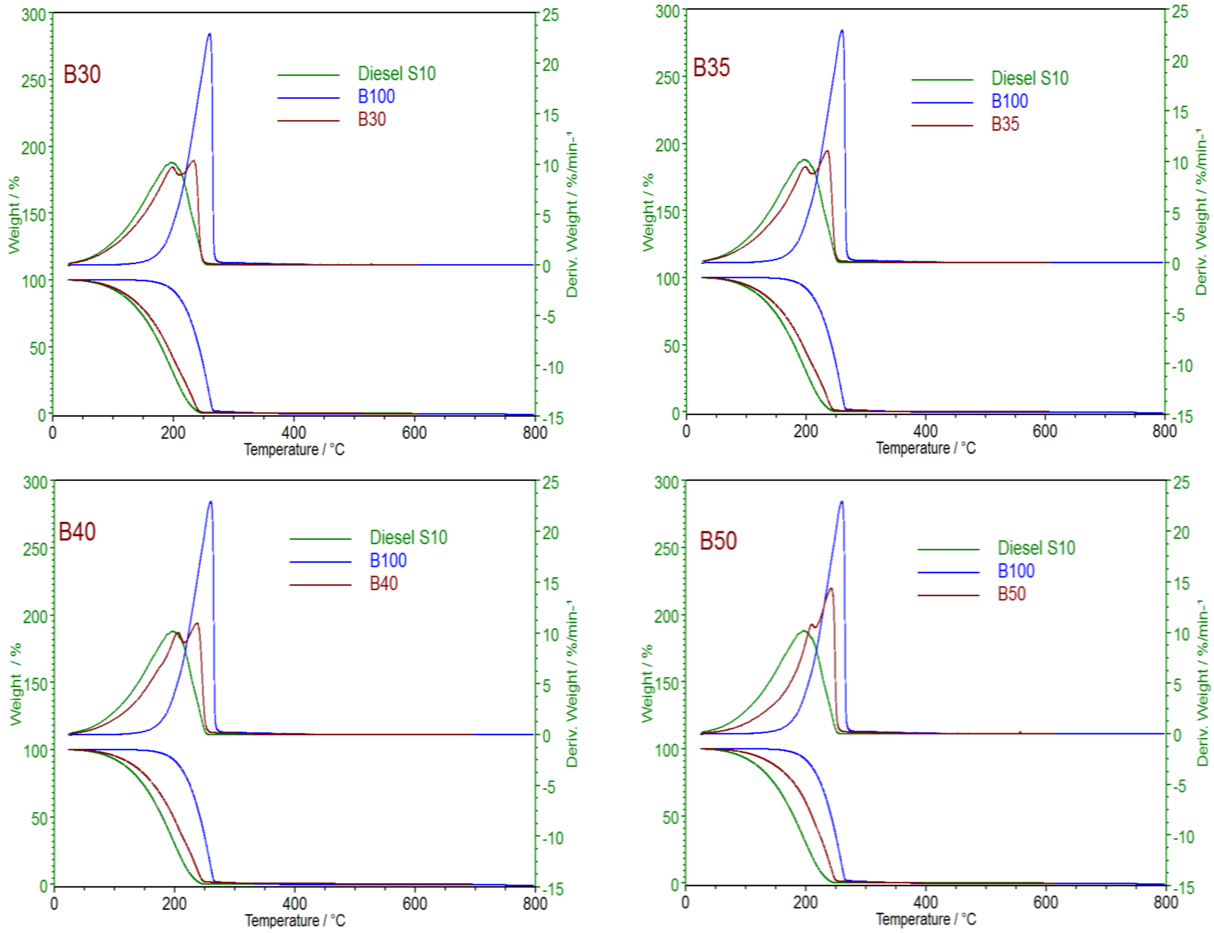

Figure 6: TG / DTG curves of B30, B35, B40, B50, B100 and diesel.

Table 2 shows parameter values obtained from the thermal analyzes of the S10 diesel, biodiesel and blends. The T_{onset} mass loss temperature was obtained from the intersection of two tangent lines to the TG curve. The first, from the beginning temperature of the mass loss variation and the second passing at the point of maximum mass loss rate, obtained from the DTG curve. The T_{endset} mass loss temperature (end extrapolated temperature) was determined from the DTG curve. T_{endset} temperature is obtained by the intersection of the tangent to the descending part of the curve DTG of the last peak with the tangent to this same curve when it touches the baseline.

The temperatures T_{onset}, T_{endset} and the initial mass loss temperature of diesel and biodiesel are quite different which indicates the lower volatility of biodiesel when compared to diesel. There is a difference of about 63 ° C between them at their maximum mass loss rate temperatures.

The initial volatilization temperature of the biodiesel/ diesel blends with increasing B100 content is not significantly affected. There is an increase of 2 ° C in the initial volatilization temperature of the B50 when compared to diesel. On the other hand, T_{onset} raises about 30 ° C when this same comparison is made. The increase in biodiesel content promotes a delay in the stages of mass loss of the mixtures gradually to higher temperature ranges. On the other hand, there is a reduction for T_{endset} for biodiesel contents below 35%.

Table 2 : Parameters obtained from the TG / DTG curves for the blends

SAMPLE	T_{onset}/°C	T_{endset}/°C	Mass loss start/ °C
Diesel S10	134	249	33
B100	222	269	117
B10	132	241	33
B15	133	243	33
B20	137	243	35
B25	140	245	35
B30	141	247	35
B35	143	248	35
B40	149	251	35
B50	164	253	35

The thermal analysis technique allows visualizing the separation of the two fuels according to their respective boiling temperatures, as shown in Figure 7. The DTG curve of each blend has a characteristic profile as a function of the percentage of B100 in the blend. The variation of the maximum DTG temperature of the 1st (diesel) and 2nd (biodiesel) mass loss peaks confirms a physical-chemical interaction between these two components. A shift of the maximum mass loss to higher temperatures is observed as a function of the blend composition.

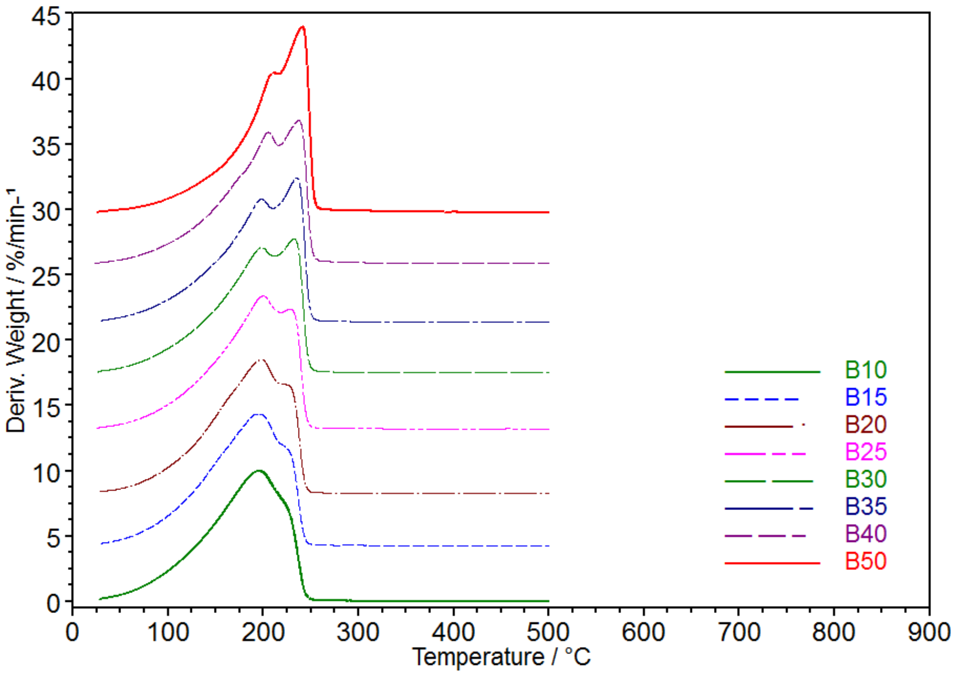

Figure 7: DTG curves for all prepared blends.

CONCLUSION

• Thermal analysis proved to be adequate to evaluate the volatility of diesel, biodiesel and mixtures thereof at respective operation conditions.

• The addition of biodiesel to diesel modifies the vaporization profile of the fuel. The vaporization profile of the blends obtained from the TG / DTG curves is a function of the biodiesel content. It was observed that the increase of the biodiesel content in the mixture increases the onset temperature of the blends.

• The interaction between biodiesel and diesel is not complete and the separation of the components of the diesel / biodiesel mixture (presence of two peaks in the DTG analysis) is due to the individual differences between the physicochemical properties of each constituent. The vaporization biodiesel profile changes according to its content in the mixture, as shown by the respective DTG curves.

• The final T_{endset} and the maximum T_{onset} degradation temperature are affected by increasing the addition of B100. The final degradation temperature does not change significantly when compared to diesel. On the other hand, T_{onset} is gradually delayed for higher temperatures.

• The results show that biodiesel content affects the volatilization process of diesel / biodiesel blends, especially for volumetric contents above 20%, which can affect fuel performance in diesel engines.

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