Application of thermogravimetric analysis for thermal characterization of walnut oil and biodiesel

D Tutunea[1], D Ilie[1], L Racila[1], I Geonea[1], O Otat[1] and L Matei[1]

[1]Vehicles, Transport and Industrial Engineering, Faculty of Mechanics, Craiova, Romania

dragostutunea@yahoo.com

Abstract. The biodiesel is being promoted worldwide as an important alternative to petrodiesel fuel due mainly to availability, low emissions and simple industrial production from renewable sources. Analysis of thermal properties is important showing the distillation and decomposition of the fuel function of temperature providing the temperature range of the combustion processes. In this paper physical and thermal properties of walnut oil were analyzed using Thermogravimetry (TGA/DTG). According to the thermograms the walnut oil presents the highest thermal stability in comparison with diesel fuel and walnut oil biodiesel.

1. Introduction

The rising cost of petroleum derived fuels associated with climate change, global warming and energy security issues have caused the promotion and development of biofuels [1, 2]. Nowadays, biodiesel is considered as a solution for different applications like, transportation sectors, industrial, locomotives and marines [3]. 80% of the world's energy needs is assured by fossil fuels and these fuels are depleting rapidly all over the world causing an energy crises [4]. Beside the maintenance of the carbon cycle, biodiesel can reduce the emission of pollutant emissions which cause the damage of ozone layer and acid rains [5]. Biodiesel can be obtained by vegetable oils and animal fats forming mono-alkyl esters of long chain fatty acids with properties closer to diesel fuel. The key advantages of using biodiesel are: renewability, non-toxicity, thermal stability during handling due to its higher flash point, lubricity and easy biodegradability [6]. The main drawbacks in commercialization of biodiesel is the price of vegetable oil that cost much more than petro-diesel (80% of the total cost of biodiesel production is the raw material used). The solution is the use on non-edible oils [7]. The thermogravimetric analysis (TGA) is a quick and inexpensive technique to measure the properties of a fuel as a function of temperature or time. The thermal decomposition is influenced by chain molecules, the longer is the chain the higher is the boiling point of the fuel. The controlled atmosphere (nitrogen, oxygen, argon, and air etc.) combined with the increases of the temperature determines the weight loose due to the decomposition process. Dantas et al. [8] studied the thermal stability of corn biodiesel obtained by methanol and ethanol routes using a DTA/TG analyzer (SDT 2960, TA Instruments) in a temperature range of 30–600 °C in air and nitrogen and found that: in air atmosphere the corn oil was thermally stable at 225 °C, methanol biodiesel 139°C and ethanol biodiesel 159 °C; in nitrogen atmosphere the corn oil is stable at 336 °C, methanol biodiesel 145°C and ethanol biodiesel 169 °C. Chien et al. [9] investigated soybean biodiesel and found that is thermally stable at 119 °C and has a range of thermal decomposition from 119 to 237 °C. Patil et al. [9] studied the thermal stability of waste cooking biodiesel in a temperature range of 25–600 °C and found two mass loss steps, first between 125–130 °C attributed to the vaporization of biodiesel and second at 232 °C attributed to the non-transesterification of some waste cooking oil. Kok et al. [10] investigated the thermal behavior of canola oil biodiesel and reported a single reaction region from TG/DTG curves of the combustion process using various heating rates (with a peak between 242–260 °C). Santos et al. [11] investigate the thermal stability of palm, sunflower and cotton in a temperature range of 30–600 °C to helium atmosphere with a heating rate of 10 °C min-1. With the exception of palm oil which had two steps of mass loss, the TG curve showed a single mass loss for sunflower and cotton oil biodiesel. Rodrıguez et al. [12] investigated thermal behavior of higuereta and soybean oil biodiesel at various heating rates (5, 10, 20 and 30 °C min-1) in air atmosphere at a temperature range between 25 and 450 °C and found that in biodiesel the mass loss occurs between 185 to 300 °C and in diesel fuel between 50 and 250°C. The objective of this study was to evaluate two different biodiesel samples by thermogravimetry (TG) and derivative thermogravimetry (DTG), and to compare with the thermogravimetric profile of petrodiesel fuel.

2. Material and methods

The walnut nuts were obtained from 2018 harvest in Dolj County. They were used as feedstock for biodiesel production using the methylic route. Diesel fuel was purchased from an OMV station in Craiova on 10 October 2018. The chemicals used for the transesterification reaction were purchased from Laborex Romania. The raw oil was obtained by an extraction process using a press PU-200 and then was filtered to remove impurities. Walnut biodiesel (WME) was obtained by a process called transesterification in order to modify some key properties of oil (viscosity, density) to make him closer to parameters of petrodiesel fuel. An alkaline-catalyzed transesterification was used keeping 6:1 molar ratio of methyl alcohol and walnut vegetable oil, using KOH as catalyst (1%) in a reactor of 30L per batch at a constant temperature of 65°C. After breakage of triglyceride molecules, a mixture of methyl esters appear corresponding to the fatty acids and a co-product called glycerin. After 24 h the glycerin layer was collected remaining only biodiesel. The product was washed with warm distilled water to remove impurities and then heated at 100°C for 2 hours. After the process is finished the physicochemical characterization of the diesel fuel, walnut oil and walnut oil biodiesel was performed according to the international standards. Thermogravimetric curves were obtained in a Diamond TG/DTG Analyzer from PerkinElmer Instruments. The applied heating rates were 5, 10, 15, 20 and 30°C min^{-1}, under air and nitrogen atmospheres, with a flow rate of 50 mL min^{-1} in the temperature range until 700°C, using an alumina crucible and a sample weight 10 mg. The differential thermogravimetric (DTG) curves were calculated by numerical derivation of the TG curves. All thermal conversion data were recorded in a computer coupled to the thermo analytical equipment and evaluated by Pyris software.

3. Results and discussion

The major properties including viscosity, density, flash point, calorific value, cetane number, cloud and pour point were determined using several methods according to ASTM and EN standards (Table 1). Kinematic viscosity is an indicator of the efficiency of the transesterification process and is related to the resistance of fluids to flow. The viscosity of WME is higher than diesel fuel and may cause problems by reducing the quality of the fuel, poor atomization and tubing blockage especially at low temperature. The density of the biodiesel is higher than diesel fuel which will led to the increase in fuel consumption and consequently of NOx emissions. The low calorific value of biodiesel is attributed of the higher oxygen content, however this presence of oxygen promote combustion in diesel engine. The higher flash point of biodiesel has advantages (safe to handle and storage) and disadvantages (low volatility properties). Cold flow properties of biodiesel indicate the biodiesel cannot be use safe in winter conditions.

Table 1. Pysical-chemical properties of fuels

Properties	Units	Method	Diesel	WME (B100)

Kinematic viscosity at 40 °C	mm^2s^{-1}	ASTM D445	3.078	3.88
Cloud Point	°C	ASTM D2500	-18	-6.1
Pour Point	°C	ASTM D97	-32	-10.0
Calorific value	MJ/kg	ASTM D4809	44	41.18
Flash point	°C	ASTM D93	68	170
Density at 40 °C	kg/m^3	EN ISO 3675	816	864
Cetane number	-	ASTM D613	49	54

For the thermal analyses there samples were used diesel fuel, vegetable oil (walnut oil) and walnut biodiesel. The TG and DTG curves indicate the behavior and thermal degradation during the process of pyrolysis or oxidation. From the pyrolysis thermograms (Figure 1) the vaporization process occurs in the case of diesel between 40 and 292 °C, biodiesel between 152 and 393 °C and oil between 320 and 493 °C. The intensity of the mass loss has a peak value at 257 °C (diesel fuel), 305 °C (biodiesel) and 424 °C (walnut oil).

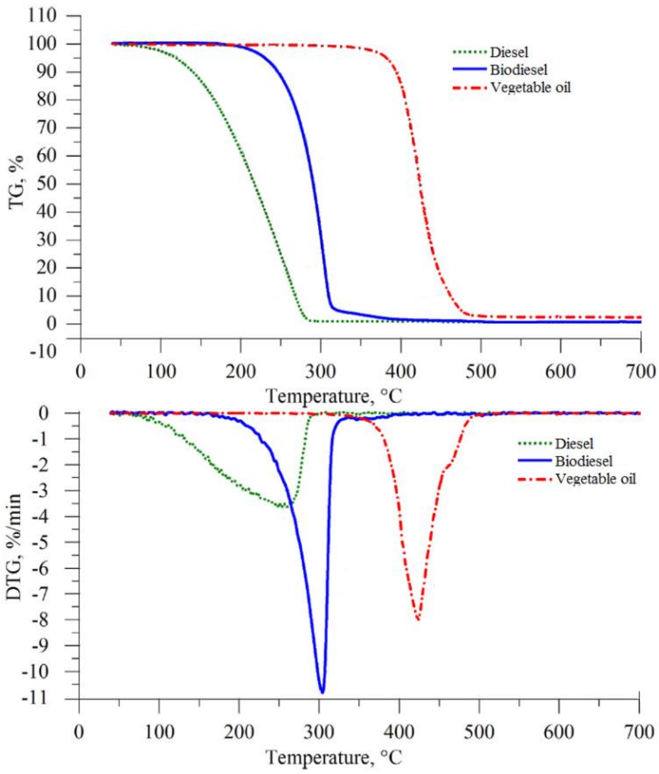

Figure 1. Mass loss and thermal behaviour of fuels during the process of pyrolysis

In the oxidation process the mass exchange processes and heat are more intense with changes in peaks of the DTG curve 252 °C (diesel fuel), 294 °C (biodiesel) and 418 °C (walnut oil) (Figure 2). The combustion temperature for the oil and biodiesel is higher due to the complex structure of methyl esters of fatty acids ((with long chains and oxygen bonds) in comparison with a simple structure of hydrocarbons of petrodiesel fuel. In the case of diesel fuel the combustion reaction starts at a low temperature burning and dissipating the energy to surrounding atmosphere. The walnut oil composed by triglyceride molecules has poor ignition properties since the combustion of fatty acids take place at higher temperatures.

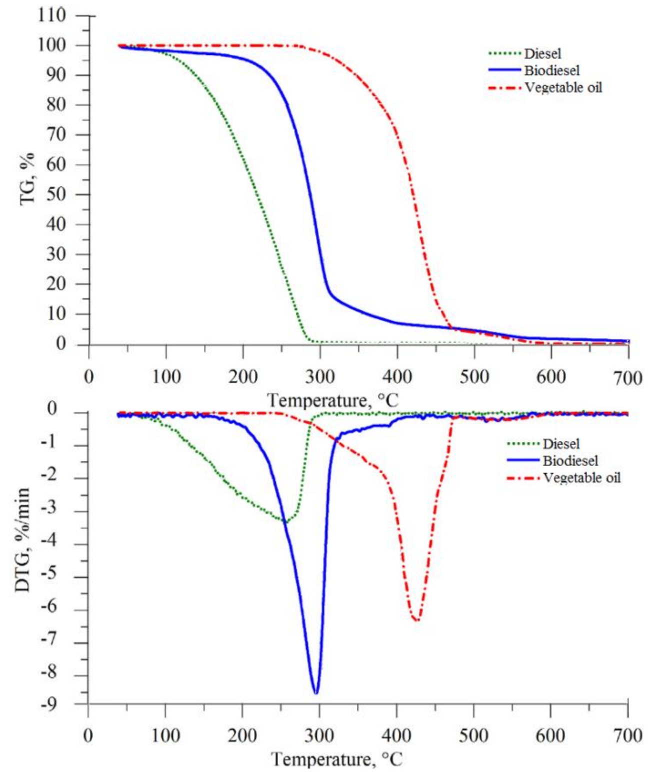

Figure 2. Mass loss and thermal behavior of fuels during the process of combustion

The thermal profile (TG curves) presented in all cases one mass loss step. In the case of diesel fuel the evaporation process take place in a range between 40 and 280 °C. Diesel fuel is thermally stable in nitrogen up to 40 °C. The smoothness of the curve suggests a single step reaction and the same behavior were observed to all heating rates with the exception of a slight displacement of the graph to higher temperatures (Figure 3).

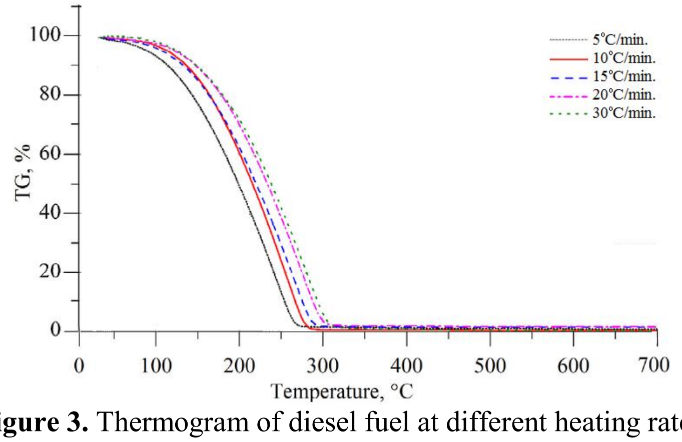

Figure 3. Thermogram of diesel fuel at different heating rates

The walnut oil biodiesel is more thermally stable than diesel starting the vaporization process between 150 and 400 °C. The thermal profile suggests two mass loss steps attributed to volatilization and/ or decomposition of methyl esters. With the increase of heating rate which generate a less uniform heat distribution and a higher temperature gradient, the TG curves shift to higher temperatures (Figure 4).

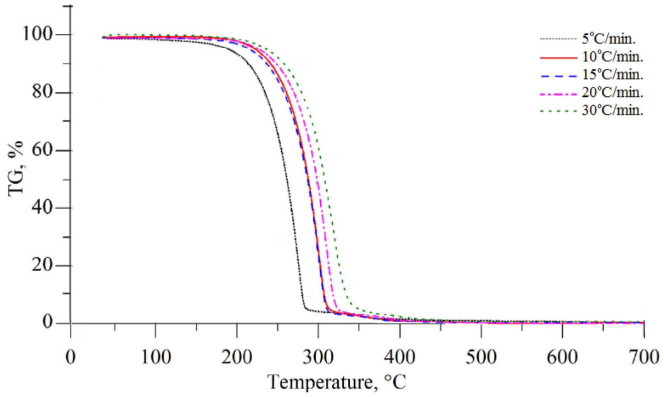

Figure 4. Thermogram of walnut biodiesel fuel at different heating rates

4. Conclusion

Thermogravimetry is an appropriate technique to study the thermal changes during combustion and pyrolysis process. An experiment was performed using a simultaneous TGA-DTG instrument for three samples of diesel fuel, walnut oil and walnut biodiesel. The stability of biodiesel depends on his chemical structure and fatty acid compositions (oils with fatty acids are more stable than the unsaturated). The physicochemical properties of walnut biodiesel are within the EN and ASTM specifications. Biodiesel has a higher viscosity than diesel fuel with problems at low temperature and a low calorific value with an increase in fuel consumption. As the heating rates increases in TG curves was noticed a shift to higher temperatures. The walnut oil was the most thermally stable.

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