Study of the thermal stability of biodiesel and diesel fuel

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Abstract. In this study the physico-chemistry characterization and the thermal behaviour of biodiesel and diesel fuel were carried out. Biodiesel is currently the most suitable fuel as alternative for diesel engines due to the environmental and technical advantages. In Romania the use of blends of biodiesel/diesel as fuels is growing every year mainly to the implementation of Kyoto protocol and to the similar properties to diesel fuel. The tests were realized under atmospheric conditions of pure air flow at various heating rates. The thermogravimetric profile indicates that diesel has three mass losses events and biodiesel of sunflower oil has five mass loss events.

1. Introduction

The demand of energy and the rising costs of the petroleum-derived fuels have triggered the research to develop new type of fuels that can reduce environmental pollution and global warming [1]. The global needs in energy are assured by fossil fuels reducing the reserves of petroleum and increasing the emission of CO₂ [2]. Biodiesel is commonly obtained by the transesterification of triglycerides (TG) in the presence of short-chain alcohol of methanol or ethanol as catalysts to obtain fatty acid methyl esters (FAMEs) [3]. 75% of the total investment is constituted by the vegetable oils or animal fats that are primary resources for biodiesel production [4]. Non-edible oils stand as new promising sources of raw materials (waste cooking oils, crude jatropha oil, algae) for biodiesel production in various countries to satisfy the energy demands [5]. The biodiesel obtained is susceptible to the degradation process when is displayed to heat, light or air due to the chemical composition specific to each feedstock [6]. The thermos-analytical applications have been use with success to the characterization of biodiesel and petroleum derivatives determining the pyrolysis and combustion patterns for the evaluation of thermal properties of heavy petroleum fractions [7, 8]. In generally the kinetics of these processes are monitored by thermogravimetric methods using multiple heating rates to evaluate the complex chemistry of diesel fuel stability [9]. The most important parameters of TG analysis are initial and final decomposition temperature and the maximum temperature of conversion [10]. Dantas et al. [11] investigated the thermal stability of biodiesel of corn and found that the fuel is stable until 225°C. Chand et al. [12] studied the thermal behaviour of the biodiesel of soybean oil and found that the fuel is thermal stable until 150 °C. Li et al. [13] studied the kinetic parameters and thermal degradation of peanut, palm and waste cooking oil biodiesel in a nitrogen atmosphere using various heating rates between 20 – 40 °C min⁻¹ in a temperature range of 25 – 600 °C and found a single mass loss step for all samples. The range of temperatures varies between 155.8–329.8 °C (peanut biodiesel), 164.2–333.5 °C (palm biodiesel) and 142.2–325.5 °C (waste cooking oil biodiesel) with final carbon residues of 4.07%, 3.77% and 3.49%. Santos et al. [8] investigated the thermal stability of palm, cotton and sunflower oil biodiesel and B10 in a helium atmosphere with a heating rate of 10 °C min⁻¹ in a
temperature range of 30 – 600 °C and found that almost all the samples showed a single step mass loss with the exception of palm oil which had two events. The temperature ranges for cotton, sunflower and palm oil were 304–490 °C, 300–495 °C and 325–489 °C and the carbon residue was 97.5%, 98.7% and 88.6%. Silva et al. [14] studied the thermal stability of pequi oil biodiesel obtained by methanol and ethanol in a nitrogen and air atmosphere, with a heating rate of 10, 20 and 40 °C min⁻¹ in a temperature range of 27 – 600 °C and found for all samples a single step mass loss representing the volatilization processes in both used gases. The mass loss starts at around 110 °C. Rodríguez et al. [6] compared the thermal stability of higuereta and soybean oil with diesel fuel using various heating rates between 5, 10, 20 and 30 °C min⁻¹ in a temperature range of 25 – 450 °C and found that in diesel fuel the mass loss is between 50 – 250 °C and in the case of biodiesel varies from 185 to 300 °C. The aim of this study was to investigate biodiesel of sunflower oil determining physical–chemical properties and its thermal stability and compare with diesel fuel.

2. Materials
Sunflower oil was purchased from local shop. Methanol with a purity of 99.5% and NaOH were purchased from S.C. Laborex Romania. Diesel fuel was purchased from a local gas station from Craiova, Romania on November 5th 2017. Euro L Diesel is a diesel fuel from LuKoil Company obtained at Petrotel Ploiesti Refinery.

3. Equipments
In this study, the thermal degradation characteristics of biodiesel blends were studied using a Diamond TG/DTG Analyzer from PerkinElmer Instruments. The physico-chemical tests on biodiesel were performed according to standardized methods ASTM in the laboratory of Fuels at Faculty of Science Craiova. The oil was transformed in biodiesel in a small reactor of 30 L capacity at the Faculty of Mechanics.

4. Methyl ester production
The biodiesel was produced using a ratio of 6:1 of methyl alcohol and sunflower vegetable oil, using NaOH as catalyst (4%), under constant agitation at 60°C. In the first phase, methanol and sodium hydroxide were placed to react under stirring until achieving a complete homogenization of the base catalyst, resulting in sodium methoxide. After 2 hours the transesterification reaction was completed and mixture was withdrawn from the reactor and poured into a separator to remove the glycerine layer. The biodiesel was washed out 5 times to remove impurities and unreacted agents. Finally, biodiesel was dried completely by using silica jell.

5. Results and discussion
Physical–chemical properties. The results for biodiesel samples were tabulated in Table 1. It was seen that the flash point of biodiesel is 168 which helps the transportation of biodiesel but it should be mixed with diesel fuel for better combustion in engine. Biodiesel presents a lower heating value due to the presence of chemically bound oxygen in vegetable oils which lowers their heating values. Kinematic viscosity of biodiesel at 40°C is higher than diesel fuel and suggests a reduced atomization and incomplete combustion in the engine. The biodiesel analyzed has a copper strip corrosion of which indicate that this fuel is not corrosive. The cloud point and pour point of biodiesel is higher than diesel fuel because biodiesel produced from vegetable oils has free fatty acids which cause a higher value of these properties. Methanol used for production was produced from corn and corn has a small quantity of sulphur; hence, biodiesel has a negligible amount of sulphur.

Thermal analysis. The samples were heated at five heating rates of 5, 10, 15, 20 and 25 °C min⁻¹ in a temperature range of 30 – 700 °C. All thermal conversion data were recorded in a computer coupled to the thermo analytical equipment and evaluated by Pyris software.
Table 1. Physical–chemical properties of biodiesel.

| Test               | Method | Unit | Biodiesel | ASTM           |
|--------------------|--------|------|-----------|----------------|
| Flash point        | D93    | °C   | 168       | 130 min.       |
| Kinematic          | D445   | cSt. | 3.6       | 1.9 – 6.0      |
| Viscosity at 40 °C |        |      |           |                |
| Total sulfur       | UOP 357| ppm  | 3.0       | 15             |
| Copper Strip       | D130   |      | 1a        | No. 3 max      |
| Cetane Index       | D976   |      | 49.2      | 47             |
| Cloud point        | D2500  | °C   | -5        | N/A            |
| Pour point         | D97    | °C   | -7        | N/A            |
| Carbon residue     | D189   | Wt%  | 0.002     | 0.050 max      |
| Acid number        | D974   | Mg KO | 0.270    | 0.800          |
| Heating value      | D240   | MJ/kg| 39.59     | N/A            |
| Specific gravity   | D1298  |      | 0.884     | N/A            |

N/A Not Available

Figure 1 shows the TGA (thermogravimetric analysis) and DTG (derivation thermogravimetric) of diesel fuel. The TG curves can be divided in three events; the first represents the evaporation of hydrocarbons with shorter carbon chains, the second represents the devolatilization where the samples loss the 97–98% of the total mass and the third with the carbonization of the sample. The second event takes place between 82.5–273.8 (5 °C min⁻¹, mass loss 98.18%), 95.3–294.5 (10 °C min⁻¹, mass loss 98.11%), 101.4–313.82 (15 °C min⁻¹, mass loss 97.21%), 112.03–317.44 (20 °C min⁻¹, mass loss 96.73%) and 119.03–326.68 (25 °C min⁻¹, mass loss 96.11%).

Figure 2 shows the TGA and DTG for biodiesel samples. The biodiesel has five events, the first is the evaporation, the second associated with the highest mass loss, the third with thermal degradation of the residuals of the different triglyceride components, the forth with the loss of 3–6% of the sample mass and the fifth with the carbonization of the sample. The main mass loss occurs in the second event and takes place between 54.7–300.8 (5°C min⁻¹, mass loss 87.658%), 168.2–319.6 (10 °C
min⁻¹, mass loss 88.69%), 176.9–325.31 (15 °C min⁻¹, mass loss 88.22%) and 185.21–334.63 (20 °C min⁻¹, mass loss 88.11%). Both for diesel and biodiesel samples the higher heating rate create another rate of degradation peak shifting the degradation process to a higher temperature.

Fig. 2. TG and DTG profiles of sunflower oil biodiesel.

6. Conclusion
The thermal behaviours of diesel fuel and biodiesel blends were evaluated using TG and DTG, using thermogravimetric analysis under pure air atmospheric conditions. From the TG curves it was observed that sunflower oil biodiesel has a higher thermal stability than diesel fuel around 130-150 °C. Such temperatures are significant in the storage process. Biodiesel has five events of decomposition whereas the diesel fuel was divided into three events.

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