Role of the Extract Obtained from Seeds of *Vitis Vinifera* on the Oxidative Stability of Biodiesel

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Maintaining the quality of fuel, for biodiesel, in its universal use as alternative fuel depends on the development of resistance to oxidation increased during the storage. Improving the resistance to oxidation of biodiesel can be achieved by using additives (natural or synthetic antioxidants). Using a natural additive obtained from the seed of Vitis vinifera contributes to the increasing of the resistance to oxidation of biodiesel obtained from the sunflower. The biodiesel samples were stored for 12 months in glass bottles dark at the room temperature (the daily average during storage was 22.5°C). The determinations made in the samples of additivated biodiesel (the oxidation stability was determined by the method of Hardorn and Zürcher, the thermal analysis and the peroxide number were determined by the method of Hara-Totani) presented values wihich show us the improve of the performances of the biodiesel additivated with the extract obtained from seeds of Vitis vinifera .

Keywords:Biodiesel, oxidation, Vitis vinifera

The biodiesel is a source of liquid natural fuel yellow, with high boiling point and low vapour pressure (it is less volatile than gasoline).

It is obtained from the transesterification of the vegetable oils or natural fats [1, 2].

From the chemical point of view is a methyl ester of a fatty acid.

It is obtained by the reaction of lipids (triglycerides) with a primary alcohol (methanol) and a base (sodium hydroxide) [3-6].

Following the reaction it is produced the biodiesel and glycerin in a ratio of 10:1.

Depending on the content of the raw material in fatty acids, there are used the following methods for obtaining the biodiesel: the basic catalyst process, when the free fatty acid is higher than 0,5%, the acid catalyst process is combined with the process of alkaline catalyst when the free fatty acid is higher than 1% [4-6].

Using the biodiesel as a fuel for ignition engines or compression combustion for boiler with liquid fuel and others is motivated by the following advantages [7-9]:

- it is obtained from the renewable resources;
- it can be mixed with regular diesel in any proportion;
- it reduces the emissions of sulfur dioxide with 100%, the carbon dioxide with 10-50%, the nitrogen dioxide with 5-10%;
- low toxicity.

Besides all these advantages the biodiesel presents some disadvantages:

- it dissolves easily gaskets made of rubber;
- it cleanes easily the engine deposits, the fuel lines and it brings all these particles in injectors;
- it determines the often change of the fuel filter.

An advantage quite important is given by the relatively low conservation period of this fuel due to the oxidation process of biodiesel under the action of oxygen on the unsaturated carbon atoms.

The oxidative stability of biodiesel refers to its ability to resist to the chemical changes which occur in long times storage. This stability to oxidation is a major factor for biodiesel. The contact with the air (the oxidative stability) and the contact with the water (the hidrolitic stability) are responsible for the damage to storage stability. Generally, the oxidation reaction is accompanied by the increase of acidity and viscosity of the fuel. Often the changes are completed by the intensifying of the colour of biodiesel from yellow to brown and the appearance of a smell of paint.

In the presence of water, the esters can hydrolyse, leading to the increase of its acidity. Therefore, the stability in storage remains a major problem for the storage of biodiesel.

The most important factors which influence the oxidation process are: the nature of the raw materials, the light and especially the UV radiations, the temperature, and the enzymes lipase lipoxigenaze, the transition metals like Fe and Cu, the surface contact of biodiesel with oxygen, the water activity (to a water activity greater than 0.3 is initiated the enzyme oxidation) [10-12].

To prevent or minimize the oxidative degradation of biodiesel,the following measures are required [13-15]:

- use of natural or synthetic antioxydants;
- to reduce of water activity (The water can be present in biodiesel in two forms: as dissolved water and like drops water immersionned in the fuel. Generally the biodiesel is insoluble in water but it absorbs more water than the petroleum diesel. The water from the biodiesel can come from the storage tanks which have water on their bottom from the process of condensation on the tank walls);
- thermal degradation of enzymes;
- avoidance of the machines which contain parts made from the folowing metals: Fe and Cu;
- protection against the light;
- storage of biodiesel at low temperatures.

The additives as antioxidants like butylated hydroxytoluene and tertiary butilhidrochinone were used as factors that can increase the storage stability of the biodiesel [16-21].

In this work was studied the possibility of using a natural antioxidant obtained from seeds of Vitis vinifera[22] which

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can be complementary to the antioxidant capacity of the sunflower oil decreased during the technological process for obtaining the biodiesel.

Experimental Part

Extraction of oil from seeds of Vitis vinifera

The oil was extracted from the seeds of Vitis vinifera with the following characteristics[23]: the appearance - the dry surface without any trace of mold; the color - brown or dark red, various shades, characteristic for the variety of provenance; smell - is specific from the seed of Vitis vinifera, but it is not allowed the smell of mould; seeds altered - less than 5%; impurities (pieces of the bunch, skin) - below 3%; the moisture - 35-40%; density - 1.1-1.3g/cm^3; higroscopicity, mL / 100g - 7-15.

The grinding of seed of Vitis vinifera was realised in a grinder Viacenza – 200 set to obtain particles of Vitis vinifera with the size of 1-1.25 mm.

The determination of granulometric analysis was performed by means of mesh strainer of 2; 1.5; 1.0; 1.25; 0.8; 0.625 and 0.5 mm mounted on a device for sorting, using the method of sorting through refusal. It was used for the determination of small pieces from Vitis vinifera seeds like refusal of fractionation between the tammyes with a side of eye 1.25 mm and 1.0 mm.

The extracting oil from seeds of Vitis vinifera particles was conducted monthly by the Soxhlet device using ether as solvent oil. The extraction time was about 6 h [24].

The calculation of the amount of additive used for biodiesel samples

Calculation of the amount of additive used for biodiesel samples was carried out by the chromatographic analysis of the sunflower oil taking into account the fatty acid concentration (palmitic acid, steraic acid, oleic acid, linoleic acid, linolenic acid).

The chromatographic analysis was performed with a chromatograph Hewlett-Packhard type 6890 equipped with the column HP INNOWAX (polyethylene) 30m x 0.25 mm x 0.17 μm.

Working Conditions:

Column temperature:

$$100^{\circ}C\ (1\ min)\ \xrightarrow{15^{\circ}C/min}\ 160^{\circ}C\ \xrightarrow{5^{\circ}C/min}\ 240^{\circ}C\ (7\ or\ 17\ min)$$

Carrier gas flow: H_2= 2mL/min
Splittess injector, 280°C
The flame ionization detector
Detector temperature: 280 ° C
Air flow: 350 mL / min
H_2 flow: 40 mL / min
N_2 flow: 40 mL/ min

The training of study samples

Were made 2 sets of samples:

- a set consisting of biodiesel obtained from the sunflower seeds;
- a set composed of biodiesel obtained from the sunflower seeds aditivated with the oil extracted from seeds of Vitis vinifera.

The samples were placed in the bottles of dark glass and stored in darkness in the laboratory at ambient temperature for 12 months. Daily it was monitored the temperature and it was resulting a daily average of 22.5°C.

Monthly it was determined the peroxide number in the samples of biodiesel and the biodiesel additivated using the conductometric method Hara-Totani [25, 26].

Quarterly was determined the induction period by the method Hadorn-Zürcher[27].

At the beginning and in the end of the experiment, it was determined the termogravimetric analysis of the samples of biodiesel with a Derivatograf PYRIS Diamond TG / DTA, which combines two systems: a termobalance (TGA) and a differential thermal analysis (DTA).

It was conducted by heating the sample with 10^0 C per minute at the room temperature with a stream of air of 150 mL / min in aluminum crucible.

Results and discussion

Following the calculations performed in the samples of biodiesel and the biodiesel additivated with the oil extracted from seeds of Vitis vinifera were obtained the following results, table 1 and figure 1.

Table 1

INDUCTION PERIOD IN THE SAMPLES OF BIODIESEL AND BIODIESEL ADDITIVATED

Times, months	Induction period, minutes	
	Sample name	
	Biodiesel	Additivated biodiesel
0	510	540
3	440	490
6	395	405
9	210	308
12	110	230

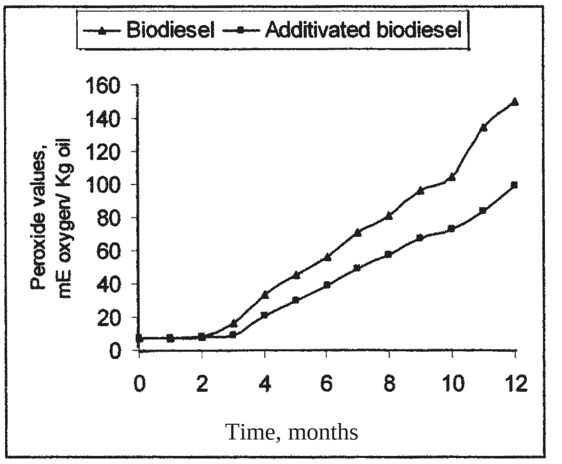

Fig.1. Index of peroxide value in samples of biodiesel and the biodiesel additivated

The index of peroxide values obtained from samples of the biodiesel additivated shows the role played by the antioxidant content in the oil extracted from the seeds of Vitis vinifera.

From 3 months of storage, the samples of the simple biodiesel show a significant increase in the index versus peroxide value in samples with an additive, increase much more slowly. After 9 months of storage, the index of the peroxide value for the biodiesel samples meet a sudden increase in comparison with the samples of the biodiesel additivated which practically continue slowly to grow.

The induction period value for the biodiesel samples shows a significantly decrease from 6 months to over 9 months for evidence of the biodiesel additivated.

The establishing the quantity of the additive was based on the concentration of the fatty acids oil flower Sorel and average composition of Vitis vinifera oil compounds in antioxidant activity.

Chromatographic analysis of, figure 2 oil sunflower follows the following fatty acid concentration:

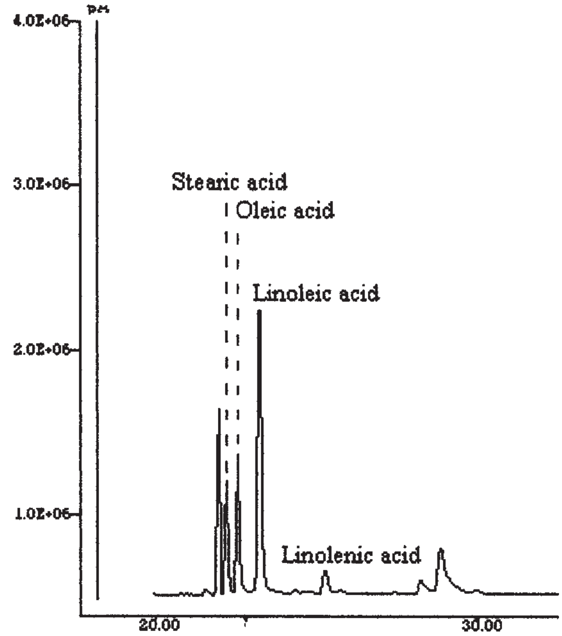

Fig. 2. Chromatographic analysis of sunflower oil

15.3% stearic acid, oleic acid 18.7, 58.9% linoleic acid and linolenic acid 5.5%.

Where as the average concentration of oil seed extracted from Vitis vinifera (128-325 mg / kg oil α-tocopherol; γ-tocopherol 14-31mg / Kg oil; 0.62-1.63 mg / kg δ-tocopherol oil, 100-238 mg / kg oil phenols and vitamin E 800-1200 mg / kg oil)[28-32] used an estimated 0,1% of antioxidant content in 66 g oil extract from seeds of Vitis vinifera. Thermal analysis of samples of biodiesel and biodiesel additive at the end of the experiment led to the following results (3, 4).

TG curve of B20 shows a level of stability up to 32,05° C with three stages of thermal decomposition. The first takes place in the 30.05-257.70° C with a weight loss of approximately 97.518% volatilization of methyl esters of factions and light carbon. The second is easier to 257.70° C to 430°C with a weight loss of about 2% by the decomposition of mono, di and triglycerides and methyl esters of fatty acids with high carbon content. And finally carbonization of the sample is from 430°C to 510°C with a mass loss below 0.4%. The total loss was approximately 99.993%.

On DTA curve there are observed several processes: an endothermic process between 32,05C and 200°C and three exothermic processes at 240, 330 and 325°C. On DTG curve takes place observed speed of mass loss from 220°C.

At a temperature of 510°C takes place carbonization of the sample.

TG curve of B40 shows a level of thermal stability at 14.57°C with three stages of thermal decomposition. The first takes place in the 14.57-280.54°C with a weight loss of approximately 95.792% volatilization of methyl esters of fractions and light carbon.

The second is easier from 280.54°C to 450°C with a weight loss of about 4% by the decomposition of mono, di and triglycerides and methyl esters of fatty acids with high carbon content. And finally carbonization of the sample is from 450 to 510°C with a mass loss below 0.3%. The total loss was approximately 99.996%.

On DTA curve there are observed several processes: an endothermic process between 30 and 200°C and 6 exothermic processes at 260, 340, 400, 420, 440 and 480°C.

On DTG curve is observed speed of mass loss from 240°C. At a temperature of 510°C takes place carbonization of the sample.

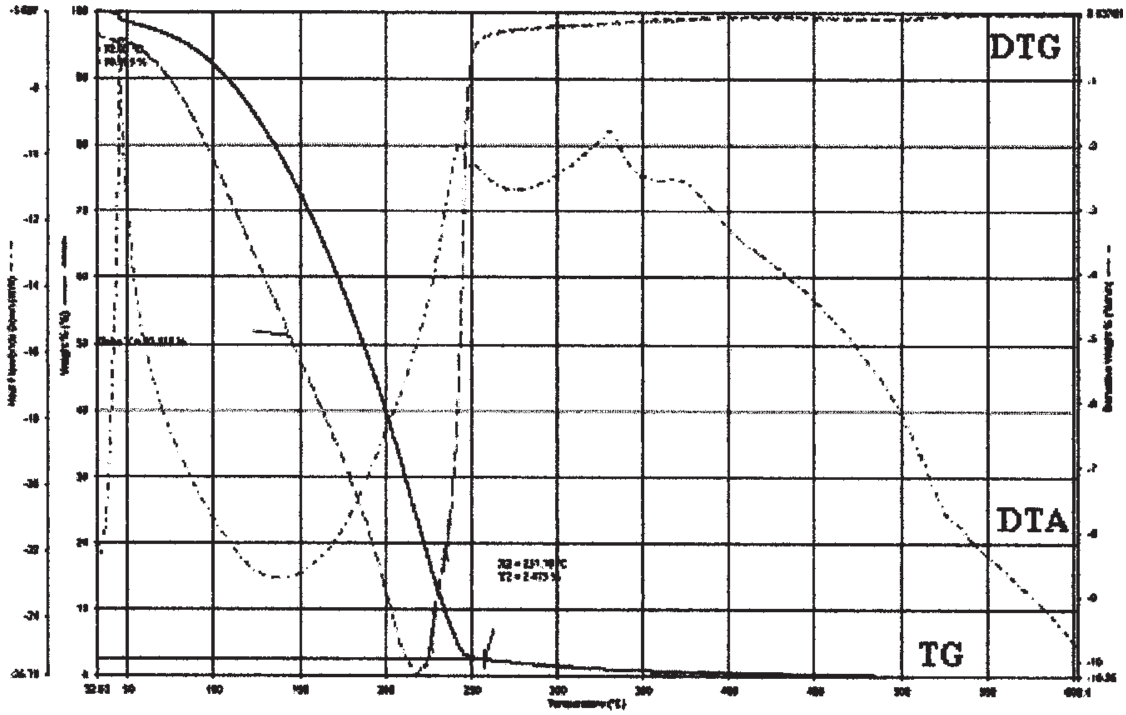

Fig. 3. Thermal analysis to test the biodiesel additive

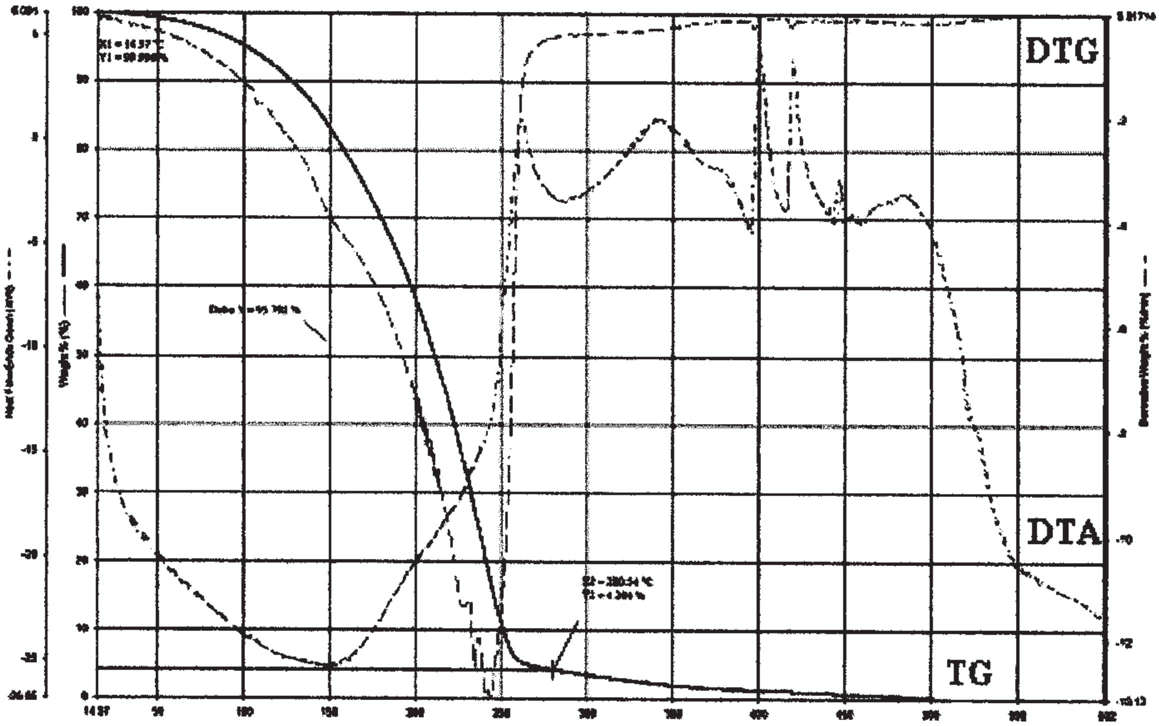

Fig.4. Thermal analysis to test the biodiesel

Conclusions

Following the calculations carried out on samples of biodiesel and biodiesel additive oil extracted from seeds of Vitis vinifera there is a significant change in the ability of fuel to resist chemical changes that occur during storage.

The mixture of α, γ and δ tocopherol in combination with vitamin E and vitamin A in oil extracted from seeds of Vitis vinifera exert strong antioxidant activity on free radicals that are formed in the biodiesel during storage with direct effect on the index and peroxide induction period.

The antioxidant presence in the sample of biodiesel change parameters of the 3 stages of thermal analysis the maximum modification rate of loss of mass and temperature at which it occurs.

Reduced cost of raw materials and antioxidant role of oil obtained from seeds of Vitis vinifera recommended its use in biodiesel.

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