# Physico-chemical Changes in Biodiesel during the Storage

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*Biodiesel is a natural fuel obtained following the transesterification reaction of the triglycerides of fatty acids from fats in alkaline catalyse.The period of storage represents a main factor in the change of quality of biodiesel. The purpose of this work is to establish the change of the main qualitative indexes of biodiesel obtained from sun-flower oil during the storage (Index of iodine, Index of acidity, Index of refraction, Index of saponification, Cetane number and Disorder point). The obtained values of these parametres lead to the conclusion that after 12 months of storage the biodiesel does not present anymore useful qualities. The chromatographic analysis of the biodiesel tests in the beginning and in the end of the experiment points out their compositional changes.*

*Key words: biodiesel, oxidation, qualitative indexes*

During the storage of Biodiesel oxidation reactions of the esters obtained following the reaction of transesterification of the fatty substances from which is the biofuel obtained are taking place.

These reactions of oxidation are similar to those of oils from which it comes.

The autooxidation of the unsaturated lipids takes place according to a radicalic mechanism in 3 stages[1-8].

The initiation stage in which the unsaturated fatty acid (RH) transforms itself in a free radical under the action of light energy or termic energy:

$$RH + h\nu \longrightarrow R^* + H^*$$

- propagation

$$R^* + O_2 \longrightarrow ROO^*$$
$$ROO^* + RH \longrightarrow ROOH + R^*$$

- interruption

$$R^* + R^* \longrightarrow R - R$$
$$ROO^* + R^* \longrightarrow ROOR$$

The obtained free radical becomes sensible at the attack of atmospheric oxygen and will lead to the forming of a peroxil radical (ROO•) which,in its turn plays a role of initiator and of spreader of subsequent oxidations, so that the oxidative degradation of unsaturated lipids appears as an autocatalitic and irreversible reaction in succession. The final stage of propagation is represented by the forming of hydroperoxides (ROOH) which are very instable molecules, especially at high temperatures in the presence of the metal traces, decomposing in the following way:

-hyroxyl radical (•OH);
-alcoxil radical (RO•);
-peroxil radical (ROO•).

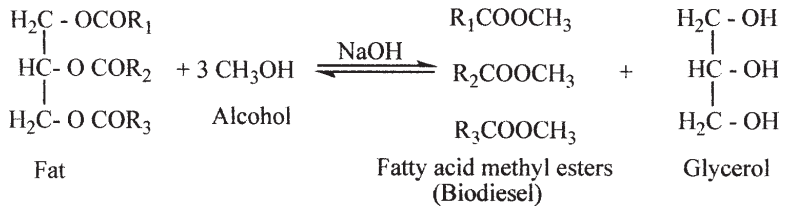
These radicals will be at the origin of other oxidation reactions, as well as of scission, restruction, cyclization, polymerization.

Also, the formed hydroperoxides will form by scission, volatiles (hydrocarbons, aldehydes, cetones, alcohols, acids etc.) giving to the product a bad rancid smell. From hydroperoxides cyclic monomers and polimers can be formed [4-6].

The main factors influencing the oxidation of the unsaturated lipids are:

-the nature of the fatty maters (the saturation degree and the position of the double bounds, respectively the presence of free unsaturated fat acids);
-the contact surface of the product with oxygen;
-the water activity (at a $a_w$ > 0.3 takes place the enzymatic oxidation and the activity of some metals);
-the presence of some enzymes (lipases and lipoxigenases);
-metals Fe and Cu;
-temperature;
-the light and especially the UV radiations and the ionized ones.

From the chemical point of view, biodiesel is a methyl ester of a fatty acid. It is obtained, usually, from the lipids' reaction (triglycerides) with a primary alcohol (the methanol) in the presence of a base (sodium hydroxide) [9-12]:

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The degradation of biodiesel during the storage is given primarly by the direct attack of the oxygen on the unsaturated carbons atoms from the molecules of fatty acids components of oil with forming of compounds which lead to the diminution of its qualities.

**Experimental part**

In order to determine the change of the main qualitative indexes of biodiesel during the storage were used samples of biodiesel obtained from sun-flower oil and stored in dark glass bottles for 12 months. The samples were kept at room temperature.

During the storage the following parametres in biodiesel samples were established [13-25]:

- the iodine value;
- the acidity value;
- the refractive index;
- the saponification index;
- the cetane number;
- the disorder Point;
- the concentration of principal components of biodiesel at the beginning and in the end of the experiment.

*The iodine value*

The iodine value represents the quantity of iodine, expressed into grams, which is added by 100g of lipids. It is a measure of the unsaturated fatty acids grade which enters in the structure of animal and vegetal lipids.

The iodine value was calculated using the Hanus method.

The iodine value was calculated according to the formula:

$$I_I = (V_m - V_p).\, t_r\, f\ 100 / m_p \quad \text{g iodine / 100 g fat}$$

where:

$V_m$ – volume of the solution of sodium thiosulphate 0.1 N used in the titration of sample control, mL;

$V_p$ – volume of the solution of sodium thiosulphate 0.1 N used in the titration of analysed sample, mL.

t-titre of the solution of sodium thiosulphate 0.1 N in relation with the iodine (0.01269 mg/mL);

f-factor of the solution of sodium thiosulphate 0.1 N;

$m_p$ – mass of the analysed sample.

*The acidity value, Ia*

The acidity value, Ia represents the number of miligrams of potassium hydroxide necessary to neutralize the free fatty acids into a gram of oil.

This index modifies itself according to the length and to the conditions of storage of the oil.

The fresh oils have a very small acidity. The acidity value grows with the age and grade of rancidity of the oil and indicates the grade of hydrolises of the fat.

The acidity was established with the formula:

$$\text{Acidity value} = \frac{K \cdot V}{M}$$

where: K – titre of the solution of KOH 0.1 N;

V- volume of the hydroxide used at titration, mL.

M- mass of the biodiesel used at titration, g.

*The refraction Index*

The refraction index, Ir, is determined with a refractometer and is altered together with the growing of oxidation degree of the oil. A bigger degree of oxidation leads to the growing of refraction index.

The establishment of refraction index was done with the aid of Abbe refractometer.

*The establishment of saponification index*

The saponification index ($I_s$) represents the quantity of potassium hydroxide expressed in miligrams, necessary for the saponification of fatty acids from a gram of fat.

The saponification index is calculated with the aid of the formula:

$$I_s = (V_m - V_p)\,.\,t_{KOH} / m_p$$

where:

$t_{KOH}$ – titre of the solution of KOH = 28.055 mg KOH/mL;

$m_p$ - mass of sample submitted to the saponification, g;

$V_m$ – volume of the solution of KOH used in the titration of sample control, mL;

$V_p$ – volume of the solution of KOH used in the titration of analysed sample, mL.

*The cetane index*

ASTM standard D 976 gives the following empirical equation for the cetane index:

$$\text{Cetane Index} = 454.74 - 1641.416\ D + 774.74\ D2 - 0.554\ T50 + 97.803[\log10(T50)]2$$

where:

D = fuel density at 15°C in g/mL.

T50= the temperature corresponding to the 50% point on the distillation curve in Celsius degrees .

*The disorder point*

The disorder point is in relation with the degree of saturation and with the number of carbon atoms from the chain of fatty acids. The disorder point is the temperature at which a fuel becomes disordered because of the forming of wax crystals.

The disorder point was established in a freezing apparatus of Artic type.

The chromatographic analysis, is a method of physico-chemical analysis through which the chemical components existing in a product are separated, identified and quantified.

The Chromatographic analysis was performed on a chromatograph type Focus GC gas chromatograph coupled with DSQ II quadrupole mass spectrometer.

**Results and discussions**

As a result of the anaytical analyses on the biodiesel samples obtained from sun-flower oil were obtained the results presented in the table 1.

The decreas value of the iodine index from 132g Iodine/ 100g biodiesel to 84g Iodine/100g biodiesel points out the presence of polymerization reactions during the storage of biodiesel by obtaining oligomers. The iodine value is an indicator of stability and a measure of total unsaturation of the biodiesel compounds.

The samples with a small value of the iodine index are less sensible at the oxidation reactions during the storage.

The acidity change from the value of 0.11mg KOH/g biodiesel at 1.1mg KOH/g biodiesel is done because of the of free faty acids appeared as a result of the compositional degradations of biodiesel. The high acidity of the biodiesel may produce a corrosion of the component parts of engine, depositions in the supplying system or in the warping of filters. It may be a symptom of the water presence in samples. This index is correlated with the saponification

**Table 1**
VALUES ESTABLISHED IN THE BIODIESEL SAMPLES

| Parameter name | Established value | | Method of establishment |
|---|---|---|---|
| | In the beginning of the experiment | In the end of the experiment | |
| The establishment of iodine value | 132 g Iod/100g biodiesel | 84 g Iod/100g biodiesel | EN 14111 |
| The establishment of acidity value | 0.11 mg HOH/g biodiesel | 1.1 mg KOH/g biodiesel | EN 14112 |
| The establishment of refraction index | 1.4560 | 1.4673 | - |
| The establishment of saponification index | 174 mgKOH/g biodiesel | 210 mgKOH/g biodiesel | AOCS Cd 3-25 |
| The establishment of cetane number | 53 | 36 | EN ISO 5165 |
| The establishment of disorder point | -22°C | -16°C | ASTM D2500-91 |

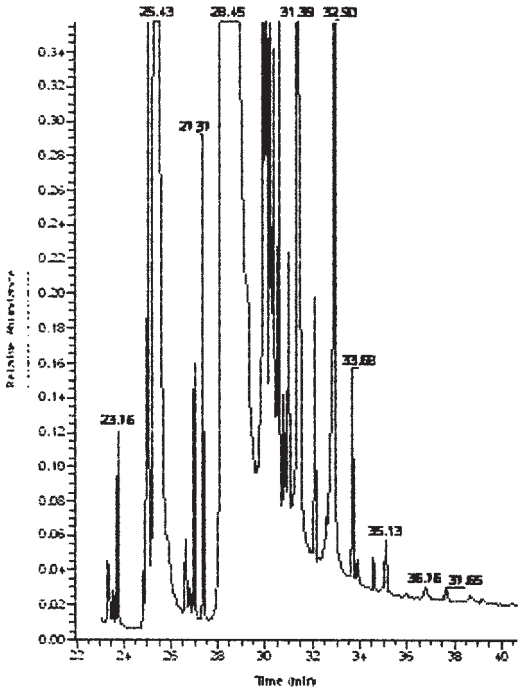


Fig. 1. The chromatographic analysis of the biodiesel sample in the beginning of the experiment

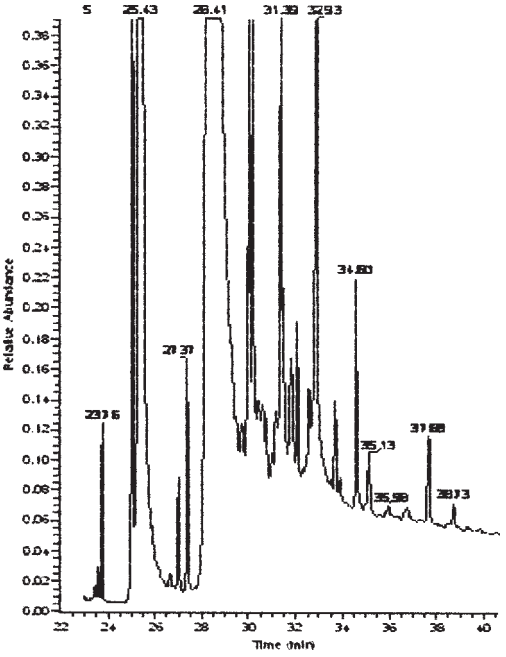


Fig. 2. The chromatographic analysis of the biodiesel sample in the end of the experiment

index which as in the case of the acidity index has high values.

The variation of the refraction index from 1.4560 to 1.4673 which takes place during the storage of the biodiesel samples is due to the accumulation of the oxidation products which establish its growth.

The decrease of the cetane number from the value of 53 to the value of 36 has a direct influence on the starting of engine. This is an indicator of the engine performance and the higher this is, a better start is ensured at reduced temperatures and it also reduces the forming of white smoke.

The small value of the freezing point from -22 to -16°C diminishes the biodiesel performance at reduced temperatures.

The chromatographic analysis of the biodiesel samples at the beginning, figura 1 and in the end, figura 2 of the experiment points out a decrease in the concentration of principal esters of fatty acids (palmitic, palmitoleic, oleic and linoleic) during the storage periods.

## Conclusions

The physical, chemical and biochemical changes which take place during the storage of biodiesel at temperatures of environmental medium lead after a storage period of 12 months to the obtaining of some qualitative parametres which do not recommend anymore the using of the biodiesel.

These compositional changes have an important role not only in the good work of the engines with biodiesel, but also in the integrity of work system of the equipment (forming of depositions and reduction of life period of the pumps and filtres, corrosion of the metalic parts, diminution of the work performances during the cold period etc.).

The results experimentally obtained recomand the using of aditives obtained from natural products (Medicago sativa, Grape seed etc.) with antioxidant activity for the protection of the action components of the oxygen.

The using of natural antioxidants will increase the induction period with direct action on the time of the biodiesel storage.

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