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# THE USE OF THE OIL EXTRACTED FROM *MEDICAGO SATIVA* AND *VITIS VINIFERA* SEED TO IMPROVE THE OXIDATIVE STABILITY OF THE BIOFUEL OF BIODIESEL TYPE

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## Abstract

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The maintaining of the fuel quality, for biodiesel, in its universal using as alternative fuel depends on the way of achieving its resistance enlargement in oxidation during the storage period.

Through its content in substances with antioxidant properties (á- tocopherol, ã-tocopherol, ä-tocopherol, vitamin E) the additive obtained from the oil extracted from *Medicago sativa* and *Vitis vinifera* seed ensures a good protection of biodiesel during the storage period.

The biodiesel and additivated biodiesel samples were placed in dark bottles and stored at medium room temperature of 23.8°C for 12 months.

The value of the peroxid Index determined monthly through Hara-Totani method was included between 3.2 and 61.2 $mEO_2$/kg biodiesel for the biodiesel samples respectively 3.1 and 43.6 $mEO_2$/kg biodiesel for the additivated biodiesel.

The induction period determined through Rancimat method was included between 8 and 1.5h for the biodiesel samples respectively 9 and 3h for the additivated biodiesel.

*Key words*: biodiesel, oxidation, antioxidants, *Vitis vinifera*, *Medicago sativa*

## Introduction

Biodiesel is a methyl ester obtained from a vegetable oil, having properties of fuel for the diesel engines. The raw material is a pure product of the plant kingdom, obtained from renewable materials, such as vegetable oil, obtained through different processes from cultivated plants, broadly called “oleagenous plants” or “oily plants”, among these, the most important being: soybeans, rapeseed, sunflower, hazelnuts, castor-oil plant, palm, flax for oil, etc. The oil obtained through various processes of the species listed above can be used directly or only after a pre-processing in the supplying of some engine. What is sure is that in nowadays there is a top technology, not only for extraction, but also for manufacture, until we obtain the final shape of biodiesel fuel (according to the standard norm EU 14214). Biodiesel can be also

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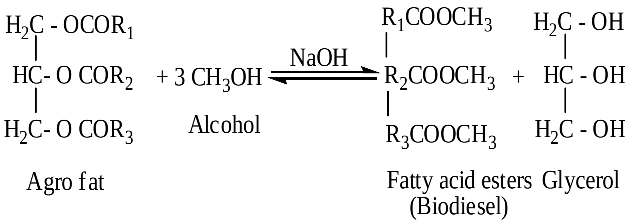
obtained through other raw materials, such as: animal fats and worn out oils, even those used for the preparation of some food products.

Biodiesel is obtained in a chemical technological process of transesterification, whereby the glycerine is extracted from fats or vegetable oils used as raw material. From this chemical process results – methyl esters – biodiesel and glycerine (Assman et al., 1996; Kapilan et al., 2009; Kusdiana,2001; Saka, 2001; Stidham et al., 2000 and Wimer, 1995).




A disadvantage enough important of biodiesel is given by the period enough small of the preserving of this fuel because of the oxygen action on the unsaturated carbon atoms (Divya, 2006; Young et al., 2004 and Sendzikiene et al., 2005).

The chemistry of the biodiesel degradation is the same as that of the oils from which it comes, the main reaction being the oxidation reaction which takes place in three stages:

Initiation

$$X^* + RH \longrightarrow R^* + XH$$

Propagation

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

$$ROO^* + R^*H \longrightarrow ROOH + R^*$$

Termination

$$ROO^* + ROO^* \longrightarrow ROOR + O_2$$

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

$$R^* + R^* \longrightarrow RR$$

Secondary initiation

$$ROOH \longrightarrow RO^* + {}^*OH$$

$$2\,ROOH \longrightarrow RO^* + ROO^* + H_2O$$

Metal-catalysed initiation

$$M^{n+} + ROOH \longrightarrow RO^* + {}^-OH + M^{(n+1)+}$$

$$M^{(n+1)+} + ROOH \longrightarrow ROO^* + H^+ + M^{(n)+}$$

Taking into account that biodiesel belongs to the family of fat acids (oleic acid, linoleic acid and linolenic acid), the chemical changes during the storage will be principle given by the stability of these. In Figures 1, 2 and 3 are given the oxidation mechanisms of these.

Oleic acid produces a mixture of 8-, 9-, 10- and 11-hydroperoxides during autoxidation (Frankel et al., 1977a; Marjukka, 2002 and Hasbleck, 1983). The mechanism involves hydrogen atom abstraction at the 8 and 11 positions of oleic acid to give two allylic radicals. Addition of oxygen to these allylic radicals gives raise to four peroxyl radicals' 11-cis, 9-trans, 8-cis and 10-trans (Figure 1).

For oleic acid, oxidability is much less than for linoleic and linolenic acid because mono-allylic methylene hydrogens are more resistant to abstraction.

The bond dissociation energy of a C-H bond of the bis-allylic methylene is about 75 Kcal/mol whereas that of the mono-allylic methylene is about 88 Kcal/mol (Nef et al., 1978).

From linoleic acid, a mixture of four hydroperoxide isomers is formed during the autoxidation (Marjukka, 2002; Gardner, 1989 and Porter, 1995) (Figure 2).

The formation of these non-conjugated hydroperoxides has been explained by hydrogen abstraction from the mono-allylic carbons of the fatty acid which are more resistant to abstraction than bis-allylic hydrogens (Han, 1977a). Oxygen entrapment at the central carbon of the pentadienyl system would give a non-conjugated hydroperoxides. However, the formation of this hydroperoxide in the absence of good hydrogen atom donors is unlikely because 11-peroxyl radicals rearrange to thermodynamically more stable conjugated diene peroxyl radicals, which then form 9-and 13-hydroperoxides (Porter et al., 1980; 1986; 1995).

The formation of hydroperoxides from linolenic acid may be considered using linoleic acid as a model compound (Chan, 1977b and Frankel et al., 1977c) (Figure 3). A mixture of 9-, 13-, 12- and 16-hydroperoxides are formed about four times than of 12-and 13-hydroperoxides.

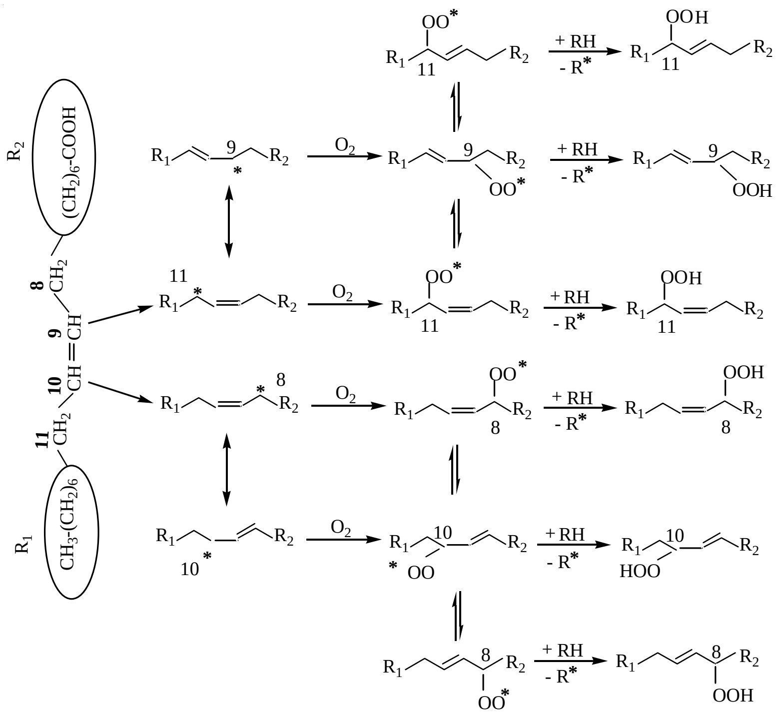



**Fig. 1. The oxidation mechanism of oleic acid**

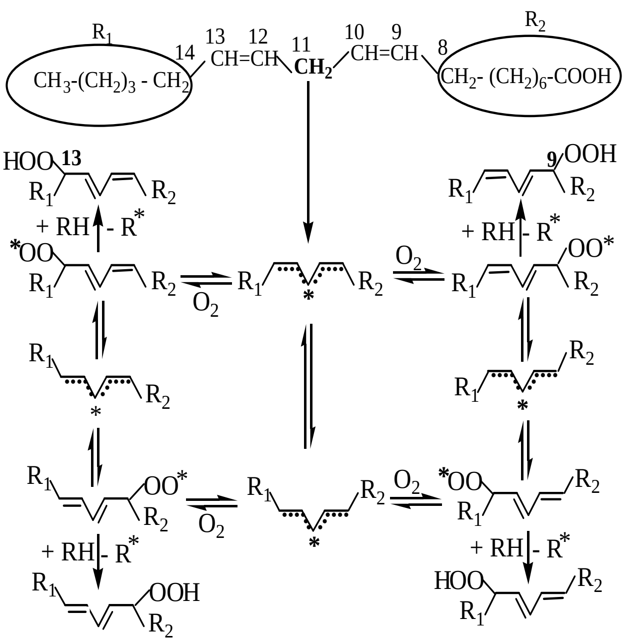



**Fig. 2. The oxidation mechanism of linoleic acid**

This uneven distribution of hydroperoxides is due to 1,3-cyclization. The peroxyl radical of 12- and 13-hydroperoxyl group that permits their facile 1,3-cyclization by intermolecular radical addition to the double bond and the formation of a new radical.

The formation of those structures has been demonstrated by spectroscopic analysis of electronic spin resonance (Basceta et al., 1982; 1983).

These reactions can be slow down by using the antioxidants. The antioxidants used for the unsaturated fats and oils protection, after their way of action, belong to two groups:

- primary antioxidants which intervene in the radicalic mechanism which they interrupt by a transfer of H and which, also, can transform alcoxyl radicals (RO•) and ROH, blocking in this way the formation of aldehides which have a rancid smell and taste. The primary antioxidants are, generally, phenolic compounds.

Tocopherols are the best known and most widely used antioxidants (Frankel, 1996). They can be classified as tocopherols (Toc) and tocotrienols (Toc-3) and within each of these two classes there are four isomers (α-, β-, γ- and δ-) making a total of eight tocopherol isomers 18, 19, 20, 21, 22, 23, 24, 25.

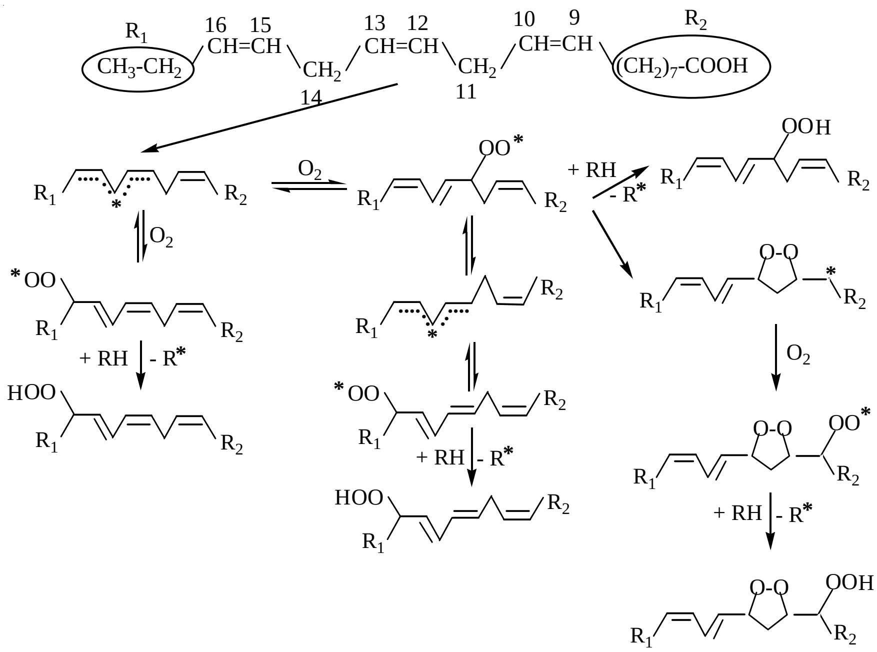
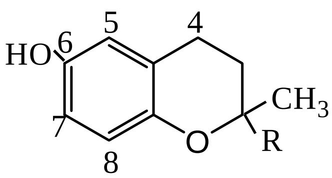



**Fig. 3. The oxidation mechanism of linolenic acid**

They are present, at least in traces, in nearly all food materials. The most important antioxidant of this group is a tocopherol 18, which has lower antioxidant activity in edible oils than other tocopherols.

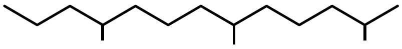
Tocopherols work as antioxidants by donating the hydrogen of the hydroxyl group to the lipid peroxyl radical.

The radical formed from α- tocopherol is established through delocalization of the solitary electron over the aromatic ring structure.




Tocopherols

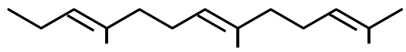
R =



5,7,8- Trimethyl 18 α - Tocopherol
5,8, - Dimethyl 19 β - Tocopherol
7,8- Dimethyl 20 γ - Tocopherol
8 - Methyl 21 δ - Tocopherol

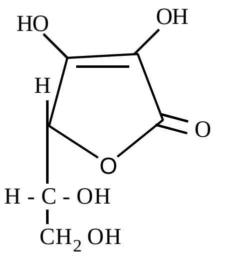
Tocotrienols

R =

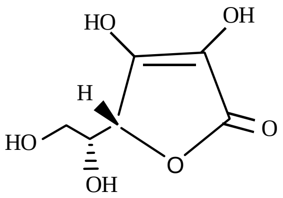


5,7,8- Trimethyl 22 α - Tocopherol
5,8, - Dimethyl 23 β - Tocopherol
7,8- Dimethyl 24 γ - Tocopherol
8 - Methyl 25 δ - Tocopherol

- secondary antioxidants represented by the ascorbic and izoascorbic acids which act as reductives, respectively as traps of oxygen.




Ascorbic acid




Isoascorbic acid

Through its composition (α-tocopherol 128-325mg/kg oil; β-tocopherol 14-31mg/kg oil; γ-tocopherol 0.62-1.63mg/kg oil; phenols 100-238mg/kg oil, vitamin E 0.8-1.2g/kg oil) the extract oil from *Vitis vinifera* alongside of the (violaxanthin, neoxanthin, cryptoxanthin, zeaxanthin, vitamin A and E) extract oil from *Medicago sativa* composition is an efficient antioxidant in the assurance of the biodiesel stability during the storage period (Bita, 2004; Dragoev, 2008; Duke, 1983 and Nilgun, 2007).

## Materials and Methods

***The formation of biodiesel samples***

Two sets of samples were formed:

- a set formed of biodiesel;

- a set formed of additivated biodiesel with 0.5% oil obtained from *Medicago sativa* and 0.5% extract oil from *Vitis vinifera*.

The samples were placed in dark glass bottles and stored in darkness in the laboratory at the environment room temperature. The temperature was daily checked up resulting a daily media of this of 23.8°C. Monthly it was determined the peroxid Index through the potentiometric titration Hara-Totani.

***Determination of the stability in oxidation through Rancimat method***

This method consists in the Biodiesel oxidation in accelerate conditions. The method permits the establishment of the induction period which corresponds with the initiation step of the biodiesel auto-oxidation.

In 1963 Loury demonstrated that through the oxidative decomposition of aldehides (resulted in the biodiesel oxidation) volatile acids are formed which are put into evidence through measuring the solution conductibility in which they are absorbed. To determine the stability in oxidation it was used an instalation which used oxidated Biodiesel samples (10 grames) at a temperature of 110°C (David, 2006 and Sensidoni et al., 1974) (Figure 4).

Through the biodiesel samples it was barboted air with a debit of 8 litres per hour. As a result of the oxidation reactions which take place in a reactor, the formed volatile acids are trained by the air current

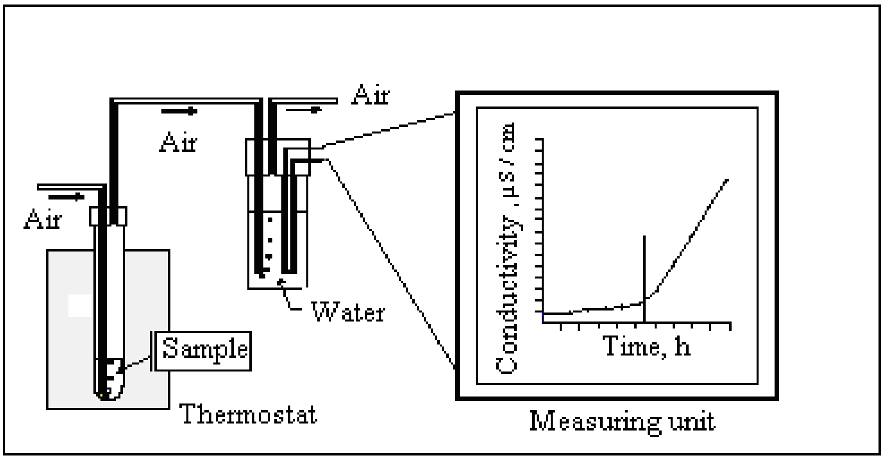



**Fig. 4. Installation for the determination of stability in the Biodiesel oxidation**

and absorbed in the measurement cell where there is bidistilled water. The measurement of the solution conductibility is done with a conductometer of Radelkis type. In the beginning we notice a slow increasing of the solution conductibility, after that it appears a sudden increasing of this as a result of the formation of volatile acids. The induction period is considered the interval until the moment of the suddenly curve‘s change.

## Results and Discussion

After the determination of the peroxid Index in the biodiesel and additivated biodiesel samples were obtained values represented in Figure 5.

The values of the peroxid Index during the storage

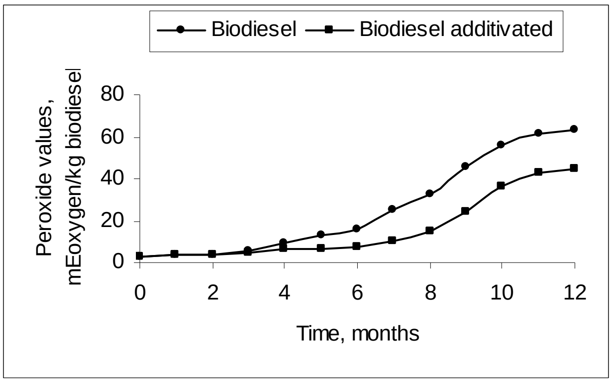



**Fig. 5. The peroxid Index of biodiesel samples**

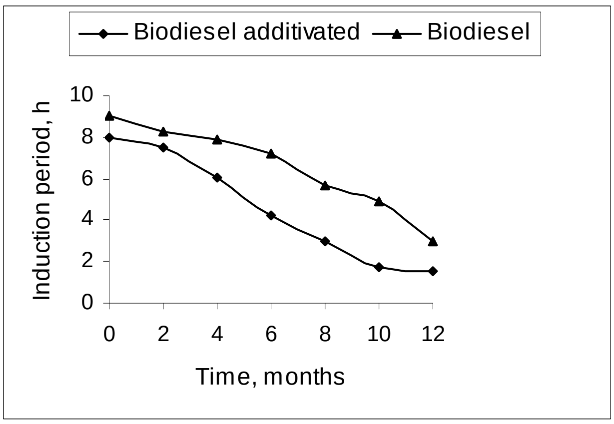



**Fig. 6. The induction period of biodiesel samples**

period as well as its maximum value after 12 months of storage are smaller in the additivated biodiesel samples (45.1mE$O_2$/kg biodiesel) than those unadditivated (63 mE$O_2$/kg biodiesel).

The value of 10mE$O_2$/kg biodiesel of the peroxid Index is considered by some authors being the value which puts into evidence the oxidation development of biodiesel [30] and it is reached in the additivated biodiesel samples after 7 months from the storage comparatively with 4.5 months in the unadditivated biodiesel.

The slowing down of the biodiesel oxidation process as an effect of the antioxidant is put into evidence, too, by the value of the Induction period which is bigger in the additivated biodiesel samples than in the unadditivated biodiesel samples (Figure 6).

## Conclusions

The antioxidant affinity contained in the extract oil from *Medicago sativa* and *Vitis vinifera* for the free formed radicals makes that the value of the Induction period and the necessary time for touching the value of 10 mE$O_2$/kg biodiesel being bigger for the additivated biodiesel samples.

The oxidant presence establishes a reduction of the number of double bounds which oxidates leading in this way to a reduced accumulation of oxidation products. This reduced accumulation of the oxidation products leads to a decrease of the oxidation speed of the additivated biodiesel samples.

The reduced value of the oxidation speed makes that the additivated biodiesel samples present a peroxid Index with reduced values during the whole period of storage comparatively to the unadditivated biodiesel samples.

The experimental dates obtained put into evidence the additive role used in the optimization of biodiesel performances.

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