THE ROLE OF WATER ON THE BIODIESEL STABILITY AND ITS EFFECT ON GASEOUS EMISSIONS

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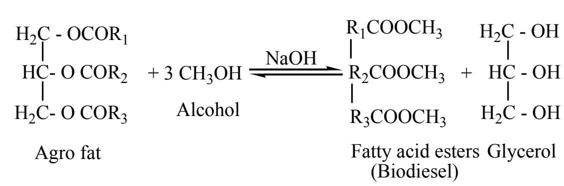
Abstract
The storage stability is the fuel ability to resist to the chemical changes that occur during long storage periods. The contact with air (oxidative stability) and the water contact (the hydrolytic stability) are responsible for a change in storage stability. Oxidation is generally accompanied by an increase of acidity and viscosity values with a direct effect on the gaseous emissions.
The gaseous emissions (CO, CO_2, hydrocarbons, O_2) discharged by burning of samples in a monocycle diesel fuel R Y50 were determined using a device COSTECH ECS 4010-CHNS-O. They had lower values for biodiesel samples containing 500 ppm water / kg biodiesel.
Acidity determined for samples stored for 12 months at an average temperature of 22.5°C which water content were about 500 ppm respectively 2000 ppm shown an increase from 0.55 mg KOH/g to 1.02 mg KOH/g fuel.
The oxidation stability of the samples determined by the method Hadorn-Zurcher was about 6,5h for the biodiesel samples containing 500 ppm and 4.3h for the biodiesel samples containing 2000 ppm water.
The chromatographic analysis reveals significant compositional changes in the samples of biodiesel whose water content were about 2000 ppm/kg biodiesel compared to samples containing 500 ppm/kg biodiesel.

Key-words: storage stability, oxidation, biodiesel, gaseous emissions.

1. 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 "oil plants" or "oily plants", among these, the most important being: soybeans, rapeseed, sunflower, hazelnut, 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 engines [1, 2].
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 [3-6].



The technology for obtaining the biodiesel includes the following main stages: the response, the recovery of unreacted methanol, the glycerol phase separation, the purification of biodiesel, the biodiesel drying and filtration.
For the reaction is proposed an amount of catalyst, sodium hydroxide, of 0.3% calculated weight at the total mass of the reactants, over the necessary amount for the neutralization of the oil acidity.

Working at a temperature of 60°C, a complete reaction time is about two hours [4-6].
Biodiesel is a finished product which must carry out strict standards in force.
After the production process intervene a series of factors which affect the quality of biodiesel. Water and sediments are two very important factors for the quality of biodiesel. Water may be present in two forms, as dissolved water or water in drops immersed in the fuel mass. Biodiesel is generally insoluble in water, but absorbs more water than petrodiesel (ASTM D6751 specifies a limit of dissolved water of 500 ppm/kg Biodiesel) [7,8].
The present water in biodiesel, contributes to the microbial increase in fuel, to the acidity increase and to the modification of stability in oxidation [9,11].

2. EXPERIMENTAL PART

To achieve the experimental part two sets of samples were used:
- biodiesel samples with a content of water below 500ppm/kg biodiesel;
- biodiesel samples with a content of water of 2000ppm / kg biodiesel.

The samples were placed in dark glass bottles and stored for 12 months at room temperature. Daily the temperature was measured resulting an average of 22.5 °C.
To determine the influence of water the acidity index was established, the induction period of samples at the beginning and in the end of the experiment and the chromatographic analysis.

Determination of the acidity Index
The principle of method is to neutralize free fatty acids with a basic solution.
The experiment consisted of weighting 10 g biodiesel at analytical balance in a conical vial and its dissolution in 40 mL mixture of ethyl alcohol - benzene 1:2. The mixture is titrated with 0.1 N KOH solution in the presence of phenolphthalein and the acidity was calculated using the formula:
Index of acidity = KV/M
where:
K – the titre solution of 0.1 N KOH;
V – the volume of hydroxide used in titration, mL;
M – the mass of biodiesel used in titration, g.

Determination of the induction period
The susceptibility of biodiesel to oxidation was studied using the Rancimat method.
This method measures the induction period (5g) of biodiesel at 110 °C at an air flow of (8 L h^{-1}), fig.1 [12-17].

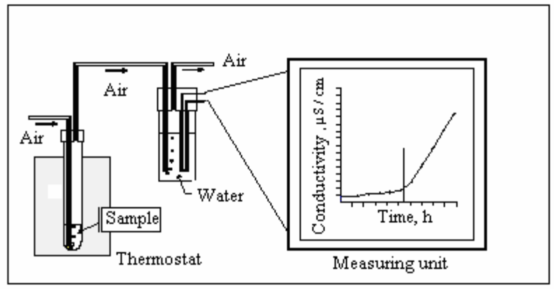


Figure 1. Principle of Rancimat method

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

GC-MS analysis of biodiesel samples for identification of fatty acid
1 µL of biodiesel extract was analyzed on Focus GC gas chromatograph coupled with DSQ II quadrupole mass spectrometer. Column used for analysis was a capillary column, Thermo TR-WaxMS with 0.25 µm in thickness, 0.25 mm ID and 30 m length. The column oven temperature was programmed to 270 °C through the following steps: 40 °C to 100 °C at a rate of 5 °C·min^{-1}, held at 100 °C for 5 minutes, 100 °C to 200 °C at the rate of 10 °C·min^{-1}, held at 200 °C for 7 minutes and the last steps was 200 ° to 270 °C at the rate of 8 °C·min^{-1}. The column was maintained at 270 °C for 13 minutes. During the analysis process the injector temperature was set at 200 °C. The interface temperature between GC and MS was kept at 260 °C and the ion source was set at 220 °C and 70 eV ionization energy of impact ionization was used to fragment the elements from capillary column. Mass spectra were recorded in SIM mode for fatty acid identification, (Figure 3).

by burning samples of Biodiesel in a monocycle diesel engine was made by Y50 using the COSTECH ECS 4010-CHNS-O device.

3. RESULTS AND DISCUSSION

To establish the behavior of the two types of the biodiesel samples, were compared the results obtained from samples containing 500 ppm water/kg biodiesel and water containing 2000ppm water/kg biodiesel.
The value of the acidity after 12 months of storage is 0.55 mgKOH/g of the biodiesel in the water samples containing 500 ppm/kg biodiesel and 1.02 mgKOH/g of the biodiesel for the water samples containing 2000 ppm/kg biodiesel, fig.2.

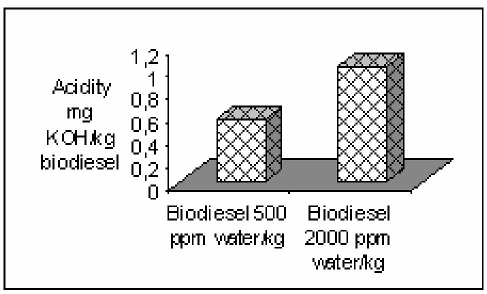


Fig. 2. The acidity values for Biodiesel

The Induction period is higher in the samples with a low water biodiesel from biodiesel samples with a high water content, Fig.3.

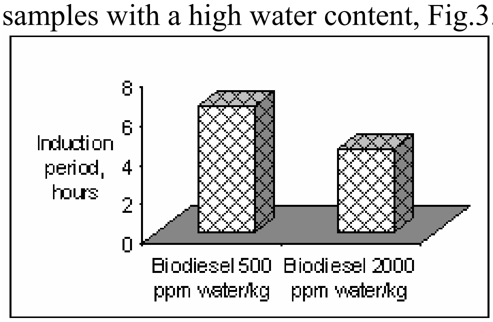


Fig.3. The induction period for Biodiesel

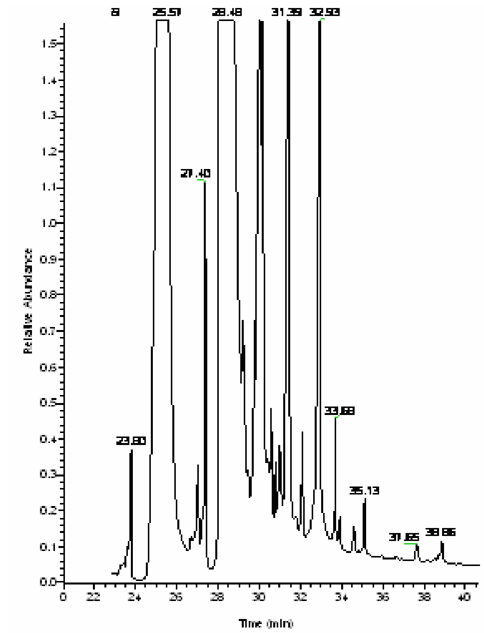


Fig.4. The chromatogram of biodiesel samples with a content of 500 ppm water/kg

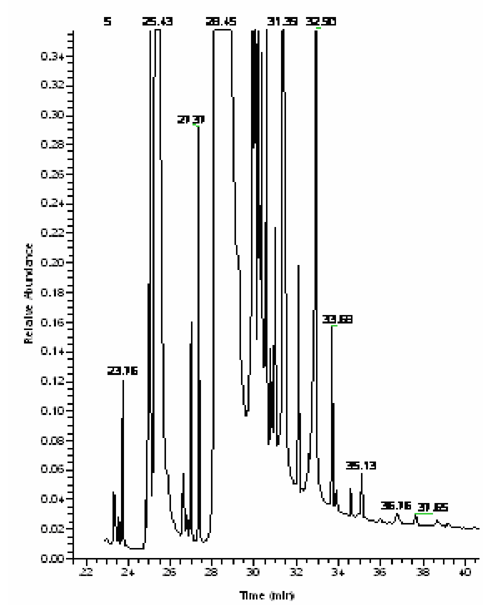


Fig.5. The chromatogram of biodiesel samples with a content of 2000 ppm water/kg

The concentration of the major components of the biodiesel during the storage is showing a significant reduction in the biodiesel samples containing 2000 ppm water/kg biodiesel Fig.4, Fig.5. The measurement of the gaseous emissions made by COSTECH ECS 4010-CHNS-O device have revealed changes of the concentrations of CO, CO_2, HC, O_2 in the biodiesel samples containing 2000 ppm water/kg biodiesel, table 1 and Table 2.

Table 1. Experimental Data obtained for samples of Biodiesel 500 ppm water / kg.

No	Fuel type	Time [min.]	Rpm	CO [%]	CO_2 [%]	HC [%]	O_2 [%]	Oil temp. [^{0}C]	Ambient temp. [^{0}C]
1	B100	5	1200	0.078	2.22	61	17.42	79	25
2	B100	10	1400	0.076	2.05	60	17.64	80	25
3	B100	15	1600	0.075	1.93	59	17.76	80	25
4	B100	20	1800	0.070	1.90	59	17.80	81	25
5	B100	25	2000	0.066	1.90	58	17.97	82	25
6	B100	30	2200	0.064	1.87	57	18.00	83	25
7	B100	35	2400	0.061	1.84	55	17.97	83	25
8	B100	40	2600	0.058	1.84	53	17.96	84	25
9	B100	45	2800	0.060	1.90	52	17.86	85	25
10	B100	50	3000	0.060	1.93	50	17.85	85	25

Table 2. Experimental Data obtained for samples of Biodiesel 2000 ppm water / kg

No	Fuel type	Time [min.]	Rpm	CO [%]	CO_2 [%]	HC [%]	O_2 [%]	Oil temp. [^{0}C]	Ambient temp. [^{0}C]
1	B100	5	1200	0.075	2.15	61	17.45	80	25
2	B100	10	1400	0.075	2.03	61	17.68	80	25
3	B100	15	1600	0.072	1.91	60	17.80	81	25
4	B100	20	1800	0.068	1.89	60	17.82	81	25
5	B100	25	2000	0.065	1.89	56	18.03	82	25
6	B100	30	2200	0.064	1.87	55	17.99	83	25
7	B100	35	2400	0.059	1.84	55	17.98	83	25
8	B100	40	2600	0.059	1.86	54	17.98	84	25
9	B100	45	2800	0.060	1.92	53	17.90	84	25
10	B100	50	3000	0.061	1.95	52	17.87	85	25

From the obtained results, we see that water is a very important factor for the quality of biodiesel. Water may be present in two forms, as dissolved water or water in drops immersed in the fuel mass. Biodiesel is generally insoluble in water but it absorbs more water than petrodiesel. For biodiesel, this water includes also an amount of immersed water coming from the storage tanks which have water on their bottom submerged from condensation. The suspended water is a problem for the fuel injection equipment because it contributes to the corrosion of the bundle pieces from injectors. Water can also enhance the microbial fuel.

4. CONCLUSIONS

The contact with the air (the oxidative stability) and the contact with the water (the hydrolytic stability) are responsible for the storage stability of biodiesel.
The presence of the peroxides in a higher amounts in the biodiesel samples with an increased water content, contributes to the formation of new compounds of oxidation, followed by the reduction of the number of double bonds in the unsaturated fatty acids with a consequence in the increasing of acidity,

of the induction period, the composition change of biodiesel and of gaseous emissions. There is a hydrolysis of esters with direct action on the acidity increase and on the stability of biodiesel.

Often, the changes are completed by the intensification of biodiesel colour from yellow to brown and by the appearance of a paint smell.

5. REFERENCES

[1]. Dunn OR, Food and Industrial Oils Research, USDA Agricultural Research National Service Center for Agricultural Utilization Research, 1815 N. University St. Peoria, IL 61604-3999, United States;

[2]. Setting national fuel quality standards. Paper 6. Proposed by Environment Australia, March 2003;

[3]. Bajpai, D., Tyagi VK, Journal of oil Science, Biodiesel: Source, Production, Composition, Properties and Its Benefits, Vol 58, No.10, 487-502, 2006.

[4]. Grecu R.D., Bita M.G., Tutunaru D., Popescu A., Bica M., Role of the extract obtained from seeds of Vitis vinifera on the oxidative stability of biodiesel International UAB-B ENA Conference, 6-7 May, 2009.

[5]. Fangrui MA, Milford A. and Hanna, Biosour Technol., Biodiesel: Source, Production, Composition, Properties and Its Benefits Vol.70, 487-502,1999.

[6]. Srivastava A.and R. Prasad, Triglycerides-based diesel fuels, Renew. Sustain energy. Rev., Vol 4, 111-133; 2002.

[7]. ASTM D 6751;

[8]. ASTM D 975;

[9]. Bondioli P Gasparoli A., Lanzani A., Fedeli E, Veronese S., Storage stability of biodiesel. A.Am. Oil.chem. Soc.72, 699-702, 1995.

[10]. Go Plesis LM, JBM de Villiers, Van der Walt, Stability studies on methyl and ethyl esters of sunflower seed, J.Am. Oil. Chem. Soc.62, 748-752, 1985.

[11]. Canakci M, Mony A., van Gerpen J.H. , Accelerated oxidation processes in biodieselTrans. Asae 42, 1565-1572, 1999.

[12]. Hardorn, H. and K. Zürcher, Sandard AOCS Methods, Dtsch ebensmittelrdsch.70, pp. 57, 1979.

[13]. Mihaela Gabriela Bita, Valeria Ghivercea, The oxidative stability of raw corn oil in the mixture with grape seed oil, Annals of University of Craiova, Series Chemistry, Volume XXXVI, p.69-71, 2007;

[14]. Akoh, CC, "Oxidative Stability of Fat Substitutes and Vegetable Oils by the Oxidative Stability Index Method," Journal of the American Oil Chemists' Society, V.71, No. 2, February. pp 211-216, 1994.

[15]. Ali, Y. and MA Hanna, "Alternative Diesel Fuels from Vegetable Oils," Bioresource Technology, V. 50, pp 153-163, 1994.

[16]. Hill, S.E. and E.G. Perkins, "Determination of Oxidation Stability of soybean Oil with the Oxidative Stability Instrument: Operation Parameter Effects," Journal of the American Oil Chemists' Society, V.72, No. 6, pp 741-743, 1995.

[17]. Bondioli, P., A. Gasparoli, A. Lanzani, E. Fedeli, S. Veronese, and M. Hall, "Storage Stability of Biodiesel," Journal of the American Oil Chemists' Society, V.72, No. 6, pp 699-702, 1995.