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THE INFLUENCES OF ULTRASONIC IRRADIATION PROCESS ON BIODIESEL BLENDSOXIDATION STABILITY

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Abstract: *The use of renewable fuels in fueling of IC engines grows rapidly in all over the world, as reaction to attempts to reduce the green house gas emissions. The biodiesel fuels are made from plant or animal feed-stock trough on esterification process; fatty acid methyl ester resulting as we called generic "biodiesel'. There are some major differences between the biodiesel and diesel fuel physico-chemically characteristics, with immediate influence on diesel engine's energetic efficiency, fuel consumption, pollutant emissions, reliability etc. New researches show that it is possible to eliminate those differences (partially or totally) using an external energy conditioning process. Besides of the advantages of this process, a major concern regarding about the biodiesel oxidation stability is occurring. The biodiesel is very sensitive to oxidation and thermal degradation. Oxidation of biodiesel can lead to formation of corrosive acids and gum deposits that reduce diesel engine reliability. The paper presents the experimental results about the influences of ultrasonic irradiation on biodiesel blends oxidation stability. An experimental apparatus was developed and the ultrasonic irradiation process was realized using low-power ultrasonic emitters. To create the cavitation phenomenon in the ultrasonic irradiation of biodiesel blends for the present experiment, we used a small volume of biofuel for conditioning (V_{BD}=300 ml) and an ultrasonic horn that produces 35 W/L,PZT type, at 35 kHz frequency emissions, which was applied continuously. The equipment was manufactured from an ultrasonic bath Sonorex Bandelin RK 11 type. Measurements of physical properties considered in the experiments were carried out after duration of 600 seconds ultrasonic irradiation. The Rancimat Oxidation Stability and the Filter Blocking Tendency methods and procedures were use. The biodiesel blends ultrasonic irradiation has as secondary effect the formation of oxidation products, whose quantity in mixtures rises with increasing volume of methyl ester in blends. If the induction period (IP) value of non-irradiated blends ranged between 25.1 and 8.8 hours (for B25 respectively B100) and for ultrasound irradiation these values are 24.8 and 7.8 hours (for B25Us_irr and B100Us_irr respectively). The biodiesel blends ultrasonic irradiation process has as effect a decrease of the induction period, indicating worsening the storage properties of biodiesel. An increasing of 13.04 % in insoluble polymers and as result, a reducing in long-term storage properties was measured for B100 RME blends. The obtained results show that the external energy conditioning process is feasible only for locally and in real time application in fueling of diesel engines.*

Key words**:** *ultrasonic, irradiation, biodiesel, oxidation stability, storage properties.*

INTRODUCTION

Currently biodiesel blends with diesel fuel became a certainty, the new European regulations imposing the increase of their volumetric participation in mixtures with diesel from 5.75% in present to a rate of at least 10% in 2020 [16].

However, besides the benefits using biodiesel in fueling IC engines regards to reduce emissions related to greenhouse effect, limiting their use in higher percentages of 20% in mixtures, is given by the major differences of physicochemical properties, compared to diesel (Table 1) [1,7].

In comparison with diesel fuel, biodiesel blends have low oxidation stability. Oxidation of biodiesel is due mainly to the presence of molecular oxygen in the component, but also this characteristic helping to improve the combustion process and reduce emissions of

CO, HC and smoke.

Oxidation process (auto-oxidation) of biodiesel occurs by exposure to ambient environment. For low temperatures the oxidation rate is low and for the high temperature oxidation rate increases significantly. Both types of oxidation (low and fast) are present for fueling process of the IC engines with biodiesel.

In the process of oxidation is formed so as to carbonyl aldehyde compounds (formed from hydro peroxides) and polymer compounds with high molecular weight (composed of peroxide radicals), oxidation compounds that lead to increased biodiesel viscosity [2,3,5,11]. Increasing viscosity has immediate effects on the fuel injection process inside the IC engine combustion chamber, in reducing the energy efficiency of combustion and increase pollutant emissions.

Table 1

Physicalproperties of some methylesters [7]

Fuel	Densityat 15° C [kg/m^3]	Higherheatingvalue [MJ/kg]	Kinematic viscosity 40° C[mm/s^2]	Cetanenumber	Cloudpoint [° C]	Flash point [° C]
Diesel fuel	841	42.9	2.7	54.1	–14	64
Rapeseedoilmethylester	882	41.5	4.60	52.7	1	181
Soybeanoilmethylester	865	41.3	4.08	46.4	–1	168
Sunfloweroilmethylester	883	41.3	4.16	49.2	2	178
Olive oilmethylester	881	41.4	4.18	59.8	–2	182

One way to improve the physical parameters of biodiesel (such as viscosity) is to use external energy transfer irradiation with different sources (ultrasound, microwaves, infrared waves, ultraviolet, etc.). Some of these energy sources are able to modify at the micro molecular level the chemical structure of the biodiesel, with immediate influence on its physical properties [8-10]

Ultrasonic irradiation is able to make these changes due to the phenomenon of cavitation, which takes place through the interaction of ultrasound waves with the molecular structure of the biodiesel [4,6,12].

Availability (affinity) of hydroxyl compounds formed in the process of irradiation and combined (being in excess in the mechanism of chemical reactions) leads to the formation of peroxides. Peroxide formations of these groups increases the efficiency of fuel combustion process, with beneficial influences on the further development of thermal processes in the functional cycle of an internal combustion engine, as well as providing changes in the biodiesel's physical properties. The amount of peroxide formed depends directly on the intensity and duration of the ultrasonic irradiation process [6,7].

Moreover, the ultrasonic conditioning process gives rise to conditions where peroxide compounds might form (as oxidation mechanism of FAME), resulting in a negative influence on the storage properties of the biodiesel (especially in the long term)[2].

MATERIAL AND METHODS

Ultrasound propagation in vegetable oil and also in biofuel causes cavitation (under specific conditions). Because of the expansion and contraction of the transfer media are conditions to generate locally bubbles of very high temperature and of pressure (cavitation process). As an immediate result, the physical and chemical properties of the transfer media are modified.

To create the cavitation phenomenon in the ultrasonic irradiation of biodiesel blends for the present experiment, we used a small volume of biofuel for conditioning (V_{BD}=300 ml) and an ultrasonic horn that produces 35 W/L,PZT type, at 35 kHz frequency emissions, which was applied continuously. The equipment was manufactured from an ultrasonic bath Sonorex Bandelin RK 11 type. Measurements of physical properties considered in the experiments were carried out after duration of 600 seconds ultrasonic irradiation.

The biodiesel blends initial characteristics and after irradiation conditioning process are presented in Table 2, respectively Table 3.

To test the ultrasonic irradiation influences on the biodiesel blends oxidative degradation, was done experiments to determinate the oxidation stability and filter blocking tendency (FBT or mg/100mL of insolubles).

Several studies related to the stability of biodiesel have been reported in the literature, and the most common method used was the Rancimat induction period. The Rancimat method is an accelerated oxidation test at a fixed temperature, far above ambient. The obtained results are then extrapolated to the stability under real-world conditions. The induction period (IP) is evaluated according to the EN 14112 [12] for pure biodiesel and the modified prEN 15751 [14] for the biodiesel blends standards. In practice, samples of 3 g of pure biodiesel and 7.5 g of biodiesel blends were analyzed under a constant air flow (10 L/h), that passing through the fuel and bubbled into a vessel contained distilled water. The samples were heated at 110^{o}C. The obtained results regarding the biodiesel blends (B25 and B100) oxidation stability over the ultrasonic irradiation process are presented in Figure 1, using the 873 Biodiesel Rancimat instrument (manufactured by Metrohm).

Table 2

Physico-chemical characteristics of the base tested fuels

Property	Diesel fuel	Rapeseed methyl ester (RME-B100)
Chemical formula	$C_{14}H_{30}$	C_{16}-C_{18}
Molecular weight [g/mol]	198.4	209.6
Density at 20^{o}C [kg/m^3]	831	879
Kinematic viscosity at 40^{o}C [mm^2/s]	2.7	4.9
Boiling point [^{o}C]	278	322
Higher heating value [MJ/kg]	46.94	37.5
Carbon content (%)	87	78.7
Sulphur content (ppm)	233	0.036
Water content [mg/kg]	64	86
Cetane number	54.1	52.7

Table 3

Biodiesel blends'physical characteristics after 600 seconds of irradiation process

Blend	Density (g/cm^3)	Mean heat capacity (J/gK)	Ultrasonic energy density (kJ/L)
B25	0.836	1.958	3519.3
B50	0.853	1.978	3931.3
B75	0.862	1.981	4166.6
B100	0.876	1.993	4521.8

To a better understanding of ultrasonic irradiation influence of biodiesel blends log-term storage stability also the filter block tendency (FBT) methods were applied. The test method to determine the filter block tendency was ASTM D2068 (Procedure A) standard [15]. Was used a 1.6 m glass fiber with 13 mm diameter filter and the filtration procedure was performed at ambient temperature ($25^{o}C$).

RESULTS AND DISCUSSIONS

The biodiesel blends ultrasonic irradiation has as secondary effect the formation of oxidation products, whose quantity in mixtures rises with increasing volume of methyl ester in blends. If the induction period (IP) value of non-irradiated blends ranged between 25.1 and 8.8 hours (for B25 respectively B100) and for ultrasound irradiation these values are 24.8 and 7.8 hours (for B25Us_irr and B100Us_irr respectively). The biodiesel blends ultrasonic irradiation process has as effect a decrease of the induction period, indicating worsening the storage properties of biodiesel.

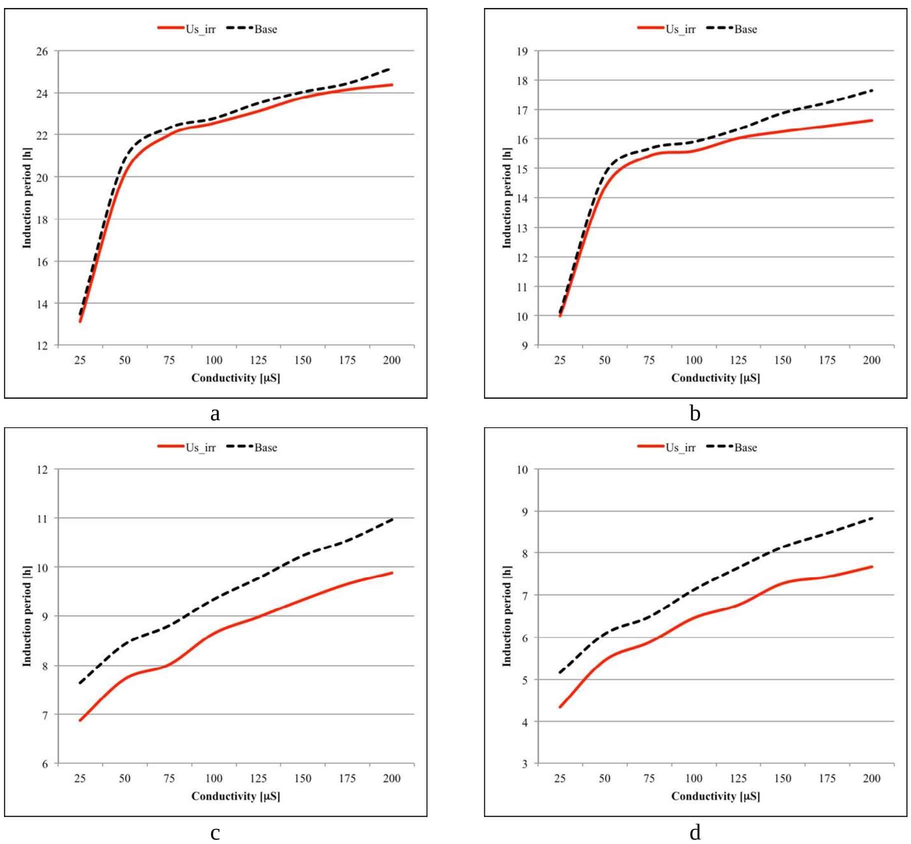

Figure 1. Modification of biodiesel blends induction period as effect of ultrasonic irradiation process (a-B25, b-B50, c-B75, d-B100 RME biodiesel blends)

The reduced induction period were -3.06%, -5.78%, -9.85% and -13.04% lower for ultrasonic irradiated B25, B50, B75 respectively B100 RME biodiesel blends, that indicate the worsening of the long-term storage properties. The results show also that the biodiesel irradiation must be use only in-time process of diesel engines fueling, a longer period of engine non-operation lead to the formation of gum deposits on fueling system components.

The results regarding the filter block tendency of ultrasonic irradiated biodiesel blends are presented in Figure 2.

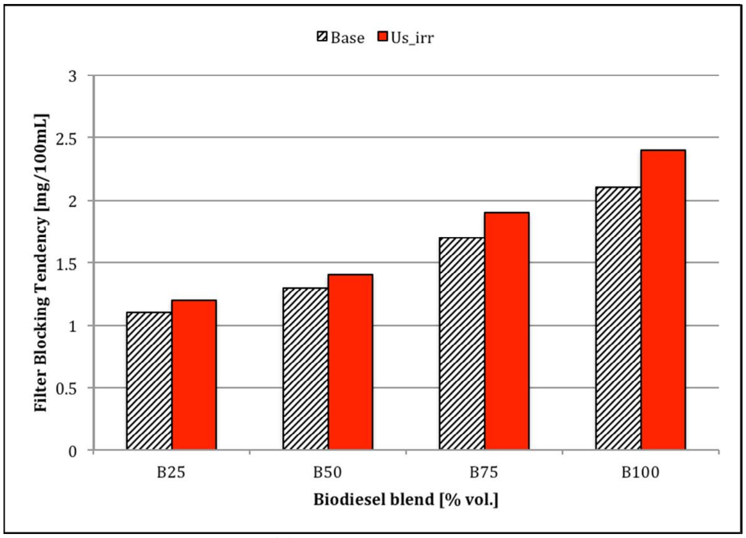

Figure 2 Variation of filter blocking tendency (FBT) parameter

The modification of the induction period for ultrasonic irradiated biodiesel blends are confirmed by experiments performed to determine total insoluble and filter block tendency. In all cases, there is a raising tendency of considered parameter. The maximum value of FBT parameter measured was 2.4 for ultrasonic irradiated pure biodiesel (B100Us_irr) that correspond to an average value of +14.3% bigger than for non-conditioned trough ultrasonic irradiation B100 biodiesel blend.

CONCLUSIONS

The paper presents the effects of ultrasonic irradiation conditioning process on RME biodiesel blends oxidation stability. The oxidation stability property is directly related to the biodiesel long-term storage properties, poor property of biodiesel because of his molecular characteristics (presence of oxygen). The Rancimat Induction and the Filter Blocking Tendency Methods was applied to characterize the ultrasonic conditioned RME biodiesel oxidation stability, in condition of 600 sec irradiation process using a PZT 35 W/L (35 Hz frequency).

Increases in gum polymers products were observed, of which quantity increase with the methyl ester volumetric percentage presence in blends. The gums can lead to blocking the injector nozzle, develop carbonic deposits inside the combustion chamber and affect the proper function of fuel pump. A greater attention must give to the maintenance operations.

Future studies are necessary to determine the optimal intensity of irradiation conditioning process to obtain maximum effect on improving the biodiesel psychical characteristics but with low effect on oxidation stability.

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