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EFFECTS OF 2-ETHYLHEXYL NITRATE ON AUTO-IGNITION AND COMBUSTION QUALITIES OF RAPESEED OIL

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ABSTRACT. The main objective of the present work was to investigate the influence of additive 2-ethylhexyl-nitrate (2-EHN) on the characteristics of auto-ignition and combustion of rapeseed oil (used as biofuel in diesel engines). The biofuel for diesel engines must meet several goals: to ensure a safe and fast engine start at any environmental temperature, to allow a safe operation of the engine with a yield as high as possible, to burn completely without producing harmful substances for human health, while maintaining the properties. In this sense, the purpose of the experimental research has been to determine: cetane number, ignition delay, the start of the main combustion, the combustion period of crude and filtered rapeseed oil additived in proportions of 1%, 1.5% and 2% with 2-ethylhexyl-nitrate compared with diesel fuel (witness fuel).

Keywords: *rapeseed oil, 2-ethylhexyl-nitrate, cetane number, ignition delay*

INTRODUCTION

The use of vegetable oils as fuel is not new but dates back in the late 19th century, when Rudolph Diesel, the inventor of the diesel engine [1, 2] at the International Exhibition in Paris in 1900 presented and demonstrated the functionality of a diesel engine, being fed then by peanut oil [3].

Experience demonstrates that reduced combustion and fuel combustion quality, reflected in an increase in ignition delay and a slow or delayed combustion can have significant negative effects on the functioning of compression ignition engines [4].

It is known that diesel engines easy start depends directly on fuel auto-ignition quality and indirectly on fuel's cetane index and viscosity [5]. The high viscosity of vegetable oils as a major cause of poor fuel atomization resulting in operational problems such as engine deposits was recognized early [6, 7].

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The changes made on the refining processes started in the '70s led to an increase of the fuel fractions from a thermal towards a catalytic cracking offered to the heavy oil market. Such fractions have hydrocarbon structures that are not favorable to an efficient use for diesel engines. When these fractions are introduced in the production of fuels, their ability to effectively self-ignite and burn is often irregular [4]. Thus, the direct information on the combustion properties are from this point of view extremely important for insuring a more efficient and fewer of the engine's problems. In addition, even more important is the fact that fuels with good combustion properties reduces the emission of harmful products to the environment. Until now it has been very difficult to determine the properties of combustion heavy fuels. Previously known methods used for determining the quality of these fuels, such as: Calculated Carbon, Aromaticity Index – CCAI and Calculated Ignition Index – CII, have proved to be inappropriate in detecting the fuels' problems. Moreover, such methods cannot detect the effects on the quality of combustion that additives or other contaminants that could be introduced into the fuel might have.

The cetane number (CN) of diesel, specified by ASTM D613 - 10a, is a measure of its ignition delay time. A higher CN, a desirable property in diesel engine, indicates shorter time between the ignition and the initiation of fuel injection into the combustion chamber. The higher CN is correlated with the reduction of nitrogen oxides (NO_x) and unburned hydrocarbons (UHC) exhaust emissions, which is important for alleviating air pollution [8].

Biodiesel from vegetable oil sources have been recorded as having a cetane number range of 46 to 52, and animal-fat based biodiesels cetane numbers range from 56 to 60 [9].

A very important suite of additives is cetane improver used in diesel engines to improve the cetane quality of marketed fuel components by reducing the delay between injection and ignition when fuel is sprayed into the combustion chamber. The chemicals most commonly used as cetane improvers are nitrates and certain peroxides [10].

Additives are abundantly manufactured and mixed with IC engine fuels to meet the proper performance of fuel in engine. Additives act like catalyst so that they aid combustion, control emission, control fuel quality during distribution and storage and reduce refiners operating cost [11].

The aim of this paper is to determine and observe the evolution of characteristics of auto-ignition and combustion of rapeseed oil with additives with 2-ethylhexyl-nitrate in different percent.

RESULTS AND DISCUSSION

The samples that have been used for experiments have been: 100% crude and filtered rapeseed oil (RO), rapeseed oil with additives with 2-ethylhexyl-nitrate (2-EHN) in concentration of 97% in different percent in oil - 1% (RO-EHN-1), 1.5% (RO-EHN-1.5) respectively 2% (RO-EHN-2) and diesel fuel (DF) – witness fuel.

Rapeseed (*Brassica napus*) is widely cultivated throughout the world for the production of animal feed, vegetable oil and biodiesel. Rapeseed oil is one of the preferred oil stocks for biodiesel production, partly because rapeseed produces more oil per unit of land area compared to other oil sources, ranking fourth in the world with respect to production, after soybean, palm and cottonseed [12].

The 2-ethylhexyl-nitrate (2-EHN), the nitric acid ester of 2-ethyl-1-hexanol, is currently added in significant amounts to diesel oil to improve ignition and boost cetane number [13]. Main physico-chemical properties of 2-ethylhexyl-nitrate are [14]: vapor pressure at 20 °C: 27Pa; solubility in water at 20 °C: 12.6 mg l-1; logKo/w: 5.24; liquid density: 0.96.

2-EHN is a large-scale commodity, the worldwide production of which is estimated to be about 100,000 tons per year. It has long been considered as presenting no particular risk to human health. 2-EHN was also nonmutagenic according to the *Ames test*. [15].

The cetane number (or the cetane index) is the numerical value that represents the percentage in volume of cetane (n-hexadecane, $C_{16}H_{34}$) in its mixture to α-methylnaphthalene. In order to approximate the cetane number an arbitrary scale has been chosen according to which cetane ($C_{16}H_{34}$) has the value 100, and α-methylnaphthalene ($C_{10}H_7$-CH_3) has the value 0 (zero). The cetane number shows the tendency to self-ignite of the fuels (e.g.: diesel fuel, etc.) used for diesel engines. The higher a fuel's cetane number is, the easier the fuel ignites.

Cetane number increases with chain length, decreases with number of double bonds and the carbonyl group move toward the center of the chain [16]. The authors have also cited that the cetane number of pure esters of stearic acid was approximately 75, but for esters of linoleic acid with three double bonds, cetane number had dropped to the ~25. Cetane number increased from 47.9 (C12) to 75.6 (C18) for saturated C10 through C18 esters. At and above C12, the cetane numbers were above 60. Knothe has presented that cetane numbers of fatty esters generally increases with: the number of methylene groups (-CH_2) in the chain of fatty compound, number of -CH_2 groups in the ester moiety and with increasing saturation of the fatty compound [17].

An easy startup of a diesel engine depends of the quality to self-ignite of the diesel, as well as on viscosity and the frosting temperature of diesel (especially for external temperatures) [18].

The determination of the cetane number is being done in a special engine at the speed of 900 rot/min, with an injection advance of 13°, at the injection pressure 10.5 MPa, according to ASTM D 613-10a.

The behavior at auto-ignition of the diesel fuels can be calculated with the help of some easy to determine characteristics. Out of these the cetane index can be mentioned.

The density of diesel fuel decreases with the decrease in the content of aromatic hydrocarbons and the increase of the n-paraffins. Using these comparison indexes, it has been established an appreciation criteria of the sensitivity of auto-ignition for diesel, called the Diesel Index (DI). The Diesel index is being established by knowing the value of the diesel's density, expressed in degrees API (*American Petroleum Institute*) and the aniline point according to the standard test ASTM D976-06.

Table 1 presents the main characteristics of the auto-ignition and burning processes of the experimented fuels, and figures 4-9 present the properties of the used fuels in comparison to the witness fuels, diesel fuel and rapeseed oil.

The apparatus used for these experiments was FIA-100 (*fuel ignition analyzer*).

FIA-100 allows the supplier or fuel user to determine the quality of combustion to the compression-ignition engines based on the measured delay in auto-ignition.

FIA-100 device and its operation mode are presented in the *Experimental section.*

Table 1. The results of the main characteristics of the auto-ignition processes of the used fuels

Fuels	Ignition delay, [ms]	Start of main combustion, [ms]	FIA Cetane number	Combustion period, [ms]
DF	8.7	8.7	57.6	11.2
RO-EHN-1	10.71	10.65	48.3	11.5
RO-EHN-1.5	9.21	9.2	55.6	11.5
RO-EHN-2	8.81	8.8	57.2	11.2
RO	9.86	10.7	48.1	12.2

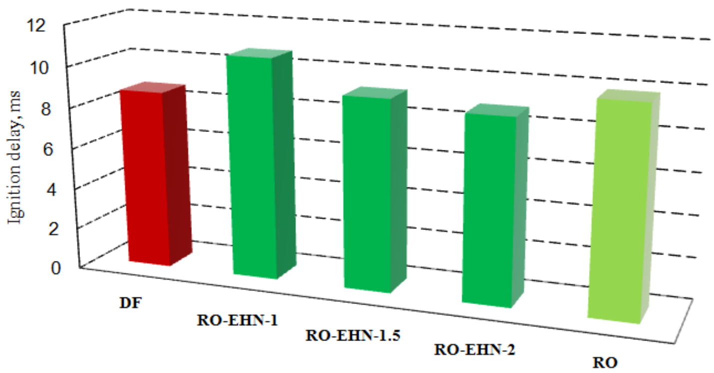

Figure 1. Ignition delay of fuels function to the ethylhexyl-nitrate percent in rapeseed oil

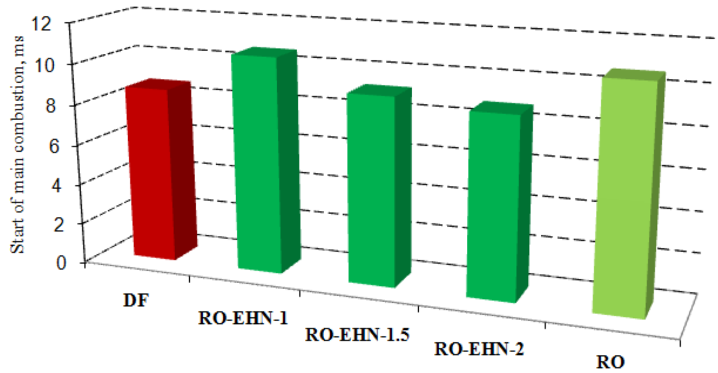

Figure 2. Start of main combustion function to the ethylhexyl-nitrate percent in rapeseed oil

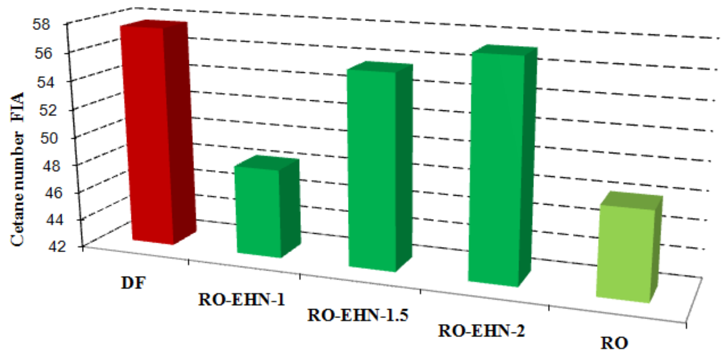

Figure 3. Cetane number of fuels functions to the ethylhexyl-nitrate percent in rapeseed oil

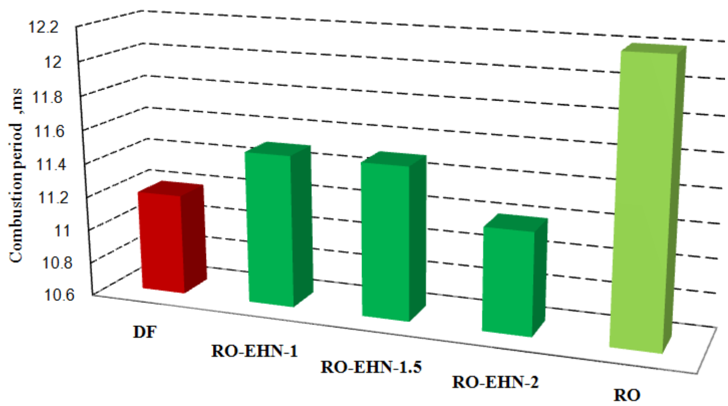

Figure 4. Combustion period function to the ethylhexyl-nitrate percent in rapeseed oil

As a result of the experimental research it can be noticed that rapeseed oil with additives with 2-ethylhexyl-nitrate have values which are really close to the auto-ignition and combustion characteristics of diesel fuel. This additive increases the value of cetanic number with 16.5% in comparison without additives rape oil.

The additive 2-ethylhexyl-nitrate used in a percentage of 2% is the closest to diesel values. Thus, the cetane number is 57.2, being with only 0.69% higher than diesel fuel cetane number. The start of main combustion and the average delay at self-combustion also have values close to diesel's, the differences being with only 1.13% higher than diesel' values.

The period of the main combustion is identical as value with the one for diesel, respectively 11.2 ms. The same happens for rape oil with the additive 2-ethylhexyl-nitrate, in 1.5%, where the cetane number is only 3.4% higher than the value of diesel's cetane number.

CONCLUSIONS

After the experimental results (Figures 1 – 4) it has been noticed that the values of auto-ignition and combustion qualities of rapeseed oil are being improves by additive 2-ethylhexyl-nitrate.

The lowest cetane number belongs to the rapeseed oil (48.1) compared to the cetane number of diesel fuel (57.6). The nearest value for cetane number in comparison to diesel fuel is for RO-EHN-2 (57.2).

For as good combustion of fuel in the combustion chamber, it must burn spontaneously and have a minimum self-ignition delay. According to experimental results, it was found that the nearest value of diesel fuel is for RO-EHN-2 (8.81).

The start of main combustion is closely connected with experienced fuel cetane. When the fuel is injected in the combustion chamber, it does not start to burn immediately. First of all it mixes with the air in the combustion chamber. It is heated until it reaches its self-ignition point, and then begins to burn. All these processes take time. After it starts combustion, the pressure, temperature, turbulences in the combustion chamber and the combustion process accelerates a lot. The diesel fuel- etalon fuel has the value of the start of main combustion 8.7 ms and RO-EHN-2 has value 8.8 ms.

The diesel fuel has the value of the combustion period of 11.2 ms, and rapeseed oil 12.2 ms, with 1 ms more. RO-EHN-2 has the value of combustion period equal to the value of diesel fuel (11.2).

EXPERIMENTAL SECTION

The positioning of FIA 100 and of the computer is presented in figure 5. The fuel's sample injected in the FIA 100’s combustion chamber self-ignites and burns as in a real engine. The auto-ignition and combustion conditions in the FIA 100's combustion chamber have been automatically simulated with an external electric source (230 V CA/50 Hz) and compressed air (at 50 bars).

A sample of the investigated fuel has been injected in this combustion chamber by using a high pressure injection pump, mechanically activated, and an injector. During the injection, the fuel jet self-ignited and burned in the combustion chamber with a constant volume. The testing conditions and the combustion process have been carefully monitored, and the measured data have been registered in a separate electronic unit which includes a microprocessor. The data is immediately presented on the computer's monitor, analyzed, stored and saved in the computer.

Figure 5. The stand with FIA 100: 1 - the apparatus FIA100; 2 - PC unit for data recording.

The instruments for testing the fuel are based on a combustion chamber with constant volume. The basic idea was to stimulate the conditions of the combustion process of a real combustion-ignition engine. The advantage of this technology is the ability to make repeated, highly precision measurements, in a controlled environment.

The combustion chamber is endowed with temperature and pressure sensors that gather the data of the process during the ignition and combustion phases.

Together with an advanced electronic system and a soft for controlling the process the automatic functioning of the instrument has been possible at a high accuracy and repeatability of measurements.

The data obtained by using this instrument have been represented by a number of parameters that can be used for the quantitative as well as the qualitative analyses of the sample.

Sample based on fuel from rapeseed oil was tested on 100 FIA device according to the procedure established for this instrument for heavy fuels (Figure 6). Thus, the investigation took place at an air pressure of 4.5 MPa and its temperature of 500 °C.

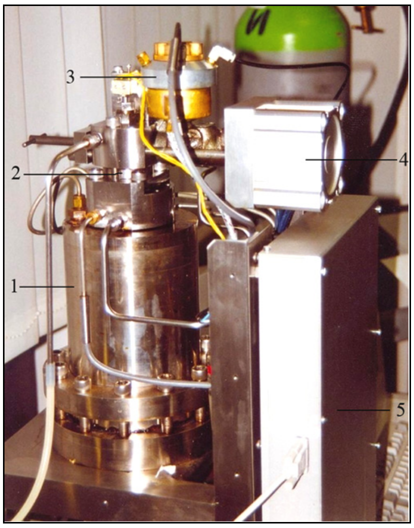

Figure 6. The apparatus FIA 100: 1 - cylinder; 2 - injector; 3 - fuel tank; 4 - high pressure pump; 5 - control electronic unit with microprocessor.

Depending on the viscosity of the sample the fuel was preheated to get an injection viscosity of fuel at about 15 mm^2/s. The kinematic viscosity of crude rapeseed oils is about an order of magnitude greater than that of conventional, petroleum-derived diesel fuel.

During the fuel's combustion, the increase of the pressure is monitored and transmitted towards a computer for analyses and recording. The reported parameters have been calculated for an average of 14 individual combustion cycles.

On FIA 100, the delay in auto-ignition is defined as the time interval, expressed in milliseconds, from the start of the injection when an increase in pressure with 0.02 MPa over the initial chamber pressure has been noticed.

Moreover, the starting phase of the main combustion is determined as being the time (in ms) in which an increase in pressure can be detected, with 0.3 MPa over the initial chamber pressure.

The delay period for auto-ignition is strongly influenced by the physico-chemical properties of the fuel. The physical component mostly depends on viscosity, superficial tension and fractioned composition, and the chemical component on the molecular structure. Thus the delay includes a phase of physical changes, in which the fuel is sprayed, partially vapored and mixed with the air, and another one of chemical changes, when the oxidation reactions take place and the reach of the auto-ignition temperature. The two time periods are simultaneous [10, 19].

The start of the main combustion has been used for establishing the quality of the fuel's auto-ignition tested as "CC FIA" (cetane number). The base for "FIA Cetane Number" is a reference curve for the instrument, which shows the ignition properties for mixtures that are between the reference fuels *U15* and *T22* (standard fuels) determined by *Phillips Petroleum International* [7]. Thus reference curve establishes the relation between the quality of the ignition registered in milliseconds and the cetane number of different mixtures of the basic fuels. In the case of heavy fuels, the auto-ignition properties are between CC=18.7 up to CC=40.

There are usually at least 12 injections/ignitions at each test. Between each injection there is a pause of approximately 5 minutes until the installation reaches the characteristics for starting the injection (chamber pressure, chamber temperature, the fuel's temperature and the cooling water's temperature).

Based on this data, the average delay period for auto-ignition has been established, as well as the starting point of the main combustion, the cetane number – CC FIA and the speed of the released heat.

The determination of the cetane number for Diesel with FIA 100 has been optimized with respect to the comparability to the results obtained on a conventional testing engine. As an evaluation bases the landmarks for the determination of cetane number according to standard DIN 51773 have been used.

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