ATTEMPTS TO REDUCE BIODIESEL BLENDS NO\textsubscript{x} POLLUTANT EMISSIONS BY ULTRASONIC CONDITIONING

Florin Mariasiu

Dept of Automotive Engineering and Transports, Technical University of Cluj-Napoca, Romania

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Abstract. The conditions imposed by the renewable energy Directive 2009/28/EC make it mandatory for EU member countries to ensure that by 2020 fossil fuels used in the transport sector contain a 10% component of biofuel. The 10% limit is based on results of experiments conducted by engine manufacturers and researchers in the biofuels domain, which show that this percentage can be used in IC engines without major technical changes to equipment and engine systems. Taking into account that increasing the percentage of biodiesel in blends results in significant reductions of CO\textsubscript{2} emissions, an immediate way to surpass the 10% limit is to carry out external and/or internal processes that will act on the physico-chemical properties of those biofuels. This paper presents data and results from experiments examining the process of ultrasonic irradiation of rapeseed oil methyl ester type biodiesel. The results show the effects of the irradiation process on biodiesel physical parameters such as density, kinematic viscosity, speed of sound through the medium, and isentropic bulk modulus. The values of these parameters directly influence the operation, performance and pollutant emissions of diesel engines. Primary results obtained demonstrate the possibilities of using what we call here the B25 blend with low-cost procedures and without major technical intervention in the equipment used to construct diesel engines. Two parameters important for the injection process (kinematic viscosity and density) show equal values for B25Us\textsubscript{irr} ultrasonically irradiated for 350 seconds and diesel fuel ultrasonically irradiated for 420 seconds. The range of the achieved NO\textsubscript{x} pollutant emission reduction was between 18.2% for the ultrasonically irradiated blend B25Us\textsubscript{irr} (no load) and 1.4% for the ultrasonically irradiated blend B100Us\textsubscript{irr} (100% load), when compared with untreated basic biodiesel.

Keywords: biodiesel, diesel engine, ultrasonics, irradiation, nitrous oxide, pollution control.

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Introduction

It is widely accepted that biodiesel is one of the current solutions in an attempt to limit the effect of Internal Combustion (IC) engines greenhouse emissions.

The pollution caused by nitric oxides emissions is capable to forming a variety of cytotoxic species, which contribute to lung pathology and disease, with implication in pathogenesis of acute respiratory distress syndrome (Sunil et al. 2009).

Nabi and Hustad (2010) and Zhu et al. (2010) showed that in case of biodiesel use for fueling diesel engine, emissions of NO\textsubscript{x} increase by 2+4% (for B20 blend) as much 12+20% (for B100). The biodiesel NO\textsubscript{x} specific increase effect is related to the differences in physico-chemically characteristics (viscosity, density, bulk modulus of compressibility, bond structure, and cetane number), fuel injection timing and spray characteristics, and engine operation condition, with major influences on the combustion process (Mazzoleni et al. 2007; Knothe 2008).

The differences between the physical properties of methyl ester based biodiesel and diesels are major and some are presented in Table 1. These differences lead to difficulties in using biodiesel in high blends (>30%) with diesel fuel in existing compression ignition engines (Kegl et al. 2008; Park et al. 2009; Payri et al. 2011).

One way to improve the physical parameters of biodiesel (to reduce the pollutant emissions) 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 (Stavarache et al. 2006; Dzida, Prusakiewicz 2008;
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The biodiesel chosen for experimentation was Rapeseed Methyl Ester (RME), mainly used in Europe. The samples of vegetable oil-based biofuels blended with diesel fuel used as the subject for the experiments had the following composition:

- fuel sample control – diesel (diesel fuel);
- fuel 1 – B25 (75% diesel fuel + 25% rapeseed oil methylester);
- fuel 2 – B50 (50% diesel fuel + 50% rapeseed oil methylester);
- fuel 3 – B75 (25% diesel fuel + 75% rapeseed oil methylester);
- fuel 4 – B100 (100% rapeseed oil methylester).

The BXXUs_irr abbreviation was used for the ultrasonic irradiated biodiesel blends (where XX represents the volumetric percentage of methyl ester in the blends with the diesel fuel). The initial properties of the biodiesel were determined in laboratory conditions and are presented in Table 2. The variants of the physical parameters on which the experiments were focused, were the density (determined by Anton Paar 5000 apparatus), the speed of sound passing through the medium (Opel measuring device) and the viscosity (Haake viscometer).

The isentropic bulk modulus of the biofuels conditioned by irradiation with ultrasound was determined by using the Newton–Laplace formula (Tat, Van Gerpen 2003b; Dzida, Prusakiewicz 2008):

$$\beta = \rho \cdot u^2,$$

where: $\beta$ is the isentropic bulk modulus [Pa]; $u$ is the speed of sound [m/s]; $\rho$ is density of the sample [kg/m$^3$].

Determination of the isentropic bulk modulus value is significant in measuring the effect of ultrasonic irradiation on the process of ignition and combustion of conditioned biofuels. This is because the isentropic bulk modulus value influences the injection time. Furthermore, Tat and Van Gerpen (2003a), Szybist et al. (2005, 2007) and Bakeas et al. (2011) noted that a higher value of isentropic bulk modulus corresponded to higher NOx values. The experiments conducted by Boehman et al. (2004), Torres-Jimenez et al. (2011) confirm totally or partially this hypothesis.

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).

### Table 1. Physical properties of some methylesters (Mariasiu et al. 2009)

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Density at 15 °C [kg/m$^3$]</th>
<th>Kinematic viscosity at 40 °C [mm/s$^2$]</th>
<th>Cetane number</th>
<th>Cloud point [°C]</th>
<th>Flash point [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel fuel</td>
<td>841</td>
<td>2.7</td>
<td>54.1</td>
<td>–14</td>
<td>64</td>
</tr>
<tr>
<td>Rapeseed oil methyl ester</td>
<td>882</td>
<td>4.60</td>
<td>52.7</td>
<td>1</td>
<td>181</td>
</tr>
<tr>
<td>Soybean oil methyl ester</td>
<td>865</td>
<td>4.08</td>
<td>46.4</td>
<td>–1</td>
<td>168</td>
</tr>
<tr>
<td>Sunflower oil methyl ester</td>
<td>883</td>
<td>4.16</td>
<td>49.2</td>
<td>2</td>
<td>178</td>
</tr>
<tr>
<td>Olive oil methyl ester</td>
<td>881</td>
<td>4.18</td>
<td>59.8</td>
<td>–2</td>
<td>182</td>
</tr>
</tbody>
</table>

Lee et al. (2011). 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 (Kang et al. 2001; Stavarache et al. 2006; Wu et al. 2007).

The models proposed by Kang et al. (2001) and Mason and Lorimer (1989, 2002), explain the kinetics of chemical transformations whereby the action of external energy influences the cavitation process at the molecular level. The models describe how the process of ultrasonic irradiation conditioning and characteristics such as high local pressure and temperature, substances undergo chemical reactions in two main directions:

- pyrolysis-type chemical reactions – the transformation mechanism is decisive in the development of a chemical high-intensity thermal effect (local temperature can reach 5000 K) at the molecular level;
- a multiphase chemical reaction in the formation of radicals.

Availability (affinity) of hydroxyl compounds formed in the process of irradiation and combined (being in excess in the mechanism of chemical reactions) lead 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 (Mariasiu et al. 2009; Lee et al. 2011).

### 1. Material and Methods

#### 1.1. Laboratory Experiments

The aim of the research was to provide a primary image of the processes taking place during the ultrasonic irradiation of biodiesel. Was used experimental methods and methodologies employed (and validated) by other researchers. For the sound of speed measurement we used the proposed methodology of Dzida and Prusakiewicz (2008), and for determining the intensity of the ultrasonic waves we took into account the experiments carried out by Wu et al. (2007) and Gogate and Kabadi (2009). Also taken into account were the related observations made by other researchers (Tat, Van Gerpen 2003a; Payri et al. 2011).
As an immediate result, the physical and chemical properties of the transfer media are modified (Stavarache et al. 2006).

Gogate and Kabadi (2009) show that the effectiveness (efficiency) of the ultrasonic horn in creating a cavitation effect depends on the magnitude of energy and operating frequency supplied by the equipment. It was observed that the cavitation intensity decreases exponentially until it vanishes completely at a distance of as low as 20÷50 mm from the ultrasonic horn. To create the cavitation phenomenon in the ultrasonic irradiation of biofuels 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 emission, which was applied continuously. Measurements of physical properties considered in the experiments were carried out after a duration of ultrasonic irradiation of 0, 100, 200, 300, 400, 500 and 600 seconds and were compared with the values of the same physical properties of diesel fuel that was not irradiated (sample control). The energy density transferred to the biofuel volume was analyzed by the method proposed and used by Ramírez-Del-Solar et al. (1990) and Lee et al. (2011).

The ultrasonic power was calculated from:

\[ P_{us} = \frac{E_{us}}{t}, \]  
(2)

where: \( P_{us} \) is ultrasonic power [W]; \( E_{us} \) is ultrasonic energy [J]; \( t \) is time [seconds].

The \( P_{us} \) is constant (from the installation construction) and therefore the energy density can be calculated using (Lee et al. 2011):

\[ U_{us} = P_{us} \frac{t}{V_{BD}}, \]  
(3)

where: \( V_{BD} \) is the volume of irradiated biofuel (biodiesel) [ml].

For the experimental conditions described above, the values of the transferred ultrasonic energy density in biodiesel blends are presented in Table 3.

<table>
<thead>
<tr>
<th>Blend</th>
<th>Density [g/cm³]</th>
<th>Mean heat capacity [J/gK]</th>
<th>Ultrasonic energy density [kJ/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>B25</td>
<td>0.836</td>
<td>1.958</td>
<td>3519.3</td>
</tr>
<tr>
<td>B50</td>
<td>0.853</td>
<td>1.978</td>
<td>3931.3</td>
</tr>
<tr>
<td>B75</td>
<td>0.862</td>
<td>1.981</td>
<td>4166.6</td>
</tr>
<tr>
<td>B100</td>
<td>0.876</td>
<td>1.993</td>
<td>4521.8</td>
</tr>
</tbody>
</table>

Moreover, the ultrasonic conditioning process gives rise to conditions where peroxide compounds might form (as oxidation mechanism of Fatty Acid Methyl Ester – FAME), resulting in a beneficial influence on fuel combustion, but this may also have negative influence on the storage properties of the biodiesel (especially in the long term).

1.2. Test Bed Experiments

To determine the influence of the instantaneous ultrasonic irradiation process on biodiesel with regard to NOx emission, we used an experimental test bed equipped, developed and adjusted in accordance with the methodology of the research in the field (Szybist et al. 2007; Kegl et al. 2008).

The experiments were carried out to determine the differences between the emission of NOx, for irradiated and non-irradiated biodiesel (compared with the same values for diesel fuel) using an engine experimental test bed, presented in Fig. 1.

The constructive details of vessel use to ultrasonic conditioning the biodiesel blends (patent pending) are presented in Fig. 2. The engine was run at constant speed of 2400 min⁻¹, and a Weinlich M 8000 dynamometer was also use to load the engine. The loads at 25, 50, 75 and 100% correspond to 0.10, 0.20, 0.31 respectively 0.41 MPa of Brake Mean Effective Pressure (BMEP).

The structural parameters and functional characteristics of the Yanmar diesel engine L 100 AE used in the experiments are presented in Table 4.

The experimental test was performed examining the full range of engine load. The NOx emissions were measured with a Testo 330 XL exhaust gas analyzer (with NOx measurement cell). The calibration procedure for...
the gas analyzer was done before each test (in accordance with the manufacturer’s recommendations in order to achieve measurements errors of less than 2%). The experimental tests were performed 10 times, and the results of those repetitions were averaged to reduce the level of uncertainty.

Table 4. Technical characteristics of the test engine

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>4-stroke, air cooled, vertical single cylinder</td>
</tr>
<tr>
<td>Bore × Stroke</td>
<td>86×70 mm</td>
</tr>
<tr>
<td>Displacement</td>
<td>406 cm³</td>
</tr>
<tr>
<td>Combustion type</td>
<td>direct injection</td>
</tr>
<tr>
<td>Continuous rating output</td>
<td>6.6 kW at 3600 min⁻¹</td>
</tr>
<tr>
<td>Fuel injection pressure</td>
<td>19.6 MPa</td>
</tr>
<tr>
<td>Fuel injection timing</td>
<td>17±0.5° BTDC</td>
</tr>
</tbody>
</table>

2. Results and Discussion

The biodiesel parameters considered for determining the influence of the ultrasonic irradiation process were: speed of sound through the medium, density, isentropic bulk modulus and kinematic viscosity. The results obtained from the experiments are presented in Figs 3–6 (laboratory tests) and Figs 7–10 (engine test bed experiments).

As the duration of treatment increased, the overall trend for the speed of sound variation among the ultrasonic irradiated blends was downward (Fig. 3). After 600 seconds of irradiation, all values (except for B100Us_irr) were equal or smaller than the value for the diesel fuel speed of sound.

The induced thermal effect caused by the ultrasound interaction with the conditioned volume of blends was measured, to determine the magnitude of the induced temperature on biodiesel blends physical parameters characteristics.
The variation is linear with the time; a slope of 2.15 °C/min, 2.21 °C/min, 2.36 °C/min and 2.44 °C/min was measured for the B25, B50, B75 and respectively for B100 blend. The maximum temperature was achieved for B100 blend (42.4 °C after 600 seconds of ultrasonic conditioning; initial biodiesel blend temperature was 18 °C), but according to the experiments effectuated by Bari et al. (2002), a temperature of the fuel less than 60 °C, did not have a significant effect on the fuel consumption and effective power.

For a period of approximately 420 seconds of ultrasonic irradiation conditioning, the density of biodiesel B25Us_irr density fell below that of the diesel fuel (Fig. 4). For the other blends (B50, B75 and B100) the density decreased by an average value of 2.49 %, but the final values were higher than those of the diesel fuel. The effect of density decreasing is beneficial regarding the fuel injection process, with immediate consequences for the pollutant emission levels (Park et al. 2009).

In general, the trend of the isentropic bulk modulus variation was decreasing, with a minimum value of 4.71% (B100Us_irr) and a maximum of 9.68% (B25Us_irr) (Fig. 5). Isentropic bulk modulus values dropped below those of the diesel fuel mixture for B25Us_irr (after 100 seconds) and B50Us_irr (after 350 seconds) blends. Szybist et al. (2005, 2007) and Bakeas et al. (2011) show that higher bulk modulus causes advanced injection timing, one of the reasons for increased NOx pollutant emissions. From the point of view of the presented experiments, the decreasing tendency of the isentropic bulk modulus for all the blends shows possibilities for reduced NOx emissions from biodiesel-fueled engines. The variation of isentropic bulk modulus has direct effect on biodiesel's ignition timing (that are more appropriate in conditions of ultrasonic irradiation to diesel fuel one). Further, from this reason, the peak combustion temperature in the NOx formation interval is decrease, because the premixed combustion intensity is reduced (Wang et al. 2007).

Only B25Us_irr blend's kinematic viscosity shows lower values than those of diesel fuel in the process of ultrasonic irradiation (after 350 seconds). The difference between the kinematic viscosity of the B25Us_irr blend subjected to the full irradiation time of 600 seconds and that of the diesel fuel after 600 seconds was 28.25% (Fig. 6). Ultrasonic irradiation was also beneficial for the other considered blends (B50, B75 and B100): kinematic viscosity was reduced by an average of 19.74%. Viscosity is considered a more important biodiesel parameter that density, owing to its direct influence on the operation of fuel injection engines’ equipment (Mariasiu et al. 2009). Szybist et al. (2005) highlight the beneficial effect of a fuel with lower viscosity on injection process parameters. Furthermore, the effect is related to reduced NOx emissions.

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The results obtained in experiments to test the fueling of a DI diesel engine with ultrasonically irradiated biodiesel confirm the interpretation of previous assumptions about biodiesel's physical parameter changes under the effects of ultrasonic irradiation. The generally decreasing tendency of the treated biodiesels’ density,
Using the ultrasonically irradiated biodiesel, reductions in NO\textsubscript{x} emissions of greater than 10% were obtained for low and medium load engine regimes. For B25\text{Us}_irr these load regimes are 0% and 75% (−18.2% and −11.9%); for B50\text{Us}_irr they are between 0% and 50% (−14.3% and −11.1%); and for B75\text{Us}_irr, they are for 0% engine load regime only (−10.7%).

To be able to judge the real effect of biodiesel blends ultrasonic irradiation process on NO\textsubscript{x} pollutant emission level, were analyzed also the engine's Break Specific Fuel Consumption (BSFC) and the brake power variations. The results are presented in Figs 11 and 12, considering the relative variation of measurements before and after ultrasonic conditioning of biodiesel blends.

From above presented results it can said that the effect of ultrasonic irradiation conduct to a generally (but smaller as values) decreasing tendency of BSFC. The major reduction in BSFC was achieve for the B100\text{Us}_irr blend equal to 2.95% (at 0% engine load). In the case of effective brake power a increasing tendency was measured with major influence on B75\text{Us}_irr and B100\text{Us}_irr blends (4.28% at 0% engine load, respectively 4.43% at 75% engine load).

Based on the presented results, it can say that the reduction of NO\textsubscript{x} pollutant emission is major caused by the effect of ultrasonic biodiesel blends conditioning on the isentropic bulk modulus parameters change. The decreasing in BSFC correlated with a small increasing of engine's effective power, are the immediate effect of a more appropriate ignition timing (that are influenced by the value of isentropic bulk modulus) of ultrasonic biodiesel conditioned, to that of diesel fuel.

However, the NO\textsubscript{x} pollutant emission values, using the ultrasonic irradiated biodiesel to fuel a DI diesel engine, remain higher than that using diesel fuel.

**Conclusions**

The ultrasonic irradiation process leads to important variations in the physical parameters of biodiesels. In terms of density and viscosity (important parameters for the injection process) the obtained results show equal values for the B25 blend and diesel fuel for an ultrasonic irradiation period of 420 seconds and 350 seconds respectively. The variations of ultrasonically irradiated biodiesel physical characteristics show potential in NO\textsubscript{x} pollutant emission reduction: potential confirmed through experimental bench research on the performance of a direct injection diesel engine.

The major reduction in NO\textsubscript{x} pollutant emissions was observed for the B25\text{Us}_irr blend conditioned by ultrasonic irradiation (18.2% for no engine load to 8% for 100% engine load) when compared to basic untreated biodiesel. However, there were still NO\textsubscript{x} emissions values greater than those measured from the diesel fuel and the biodiesel's conditioning process by ultrasonic irradiation worse storage properties for long periods (by increasing oxidative products in blends).

The results obtained can be improved through future research of the ultrasonic irradiation process on different types of methyl esters (soy, palm oil, sunflower, etc.) and with different values of transmitted ultrasonic density in fuel (taking into consideration the use of low-power and also low-cost ultrasonic horns).

Through the ultrasonic irradiation process it is feasible to incorporate biodiesel fuels into blends (with diesel fuel) for use in compression ignition engines without having to make major or important changes and adjustments to the fuel injection systems of these engines.
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References


