Quantification and qualification of exhaust gases in agricultural diesel engine operating with biodiesel mixtures

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Quantificação e qualificação dos gases de escape em motor agrícola diesel operando com misturas de biodiesel

Resumo: Motores de ciclo diesel são amplamente utilizados em máquinas agrícolas. O biodiesel oferece a possibilidade de substituição parcial ou total do diesel mineral, reduzindo assim a dependência da agricultura desse recurso não renovável e diminuindo as emissões de poluentes. O objetivo deste estudo foi avaliar as emissões de CO, NOx, SOx, CO2 e O2 de várias misturas de biodiesel (B0 = 0%, B7 = 7%, B10 = 10%, B20 = 20%, B30 = 30% e B100 = 100%) em um motor agrícola monocilíndrico a 1000, 1600 e 2400 rpm. Os gases de escape foram identificados usando um medidor de gás. Os combustíveis com maior porcentagem de biodiesel têm as menores emissões de SOx, com a mistura B30 liberando 65.78, 52.47 e 32.25 partes por milhão a 1000, 1600 e 2000 rpm, respectivamente. As emissões de óxidos nitrosos e de dióxido de carbono diminuem com o aumento da velocidade de rotação do motor. Maiores porcentagens de biodiesel resultam em combustíveis menos poluentes.

Palavras-chave: emissões de gases, trator agrícola, biocombustíveis
Introduction

Since the industrial revolution made the human increasingly dependent on fossil fuels, concentrations of greenhouse gases have risen to critical levels. It is estimated that 75% of these concentrations are the result of burning fuels (Reis et al., 2013).

The search for alternative fuels to supply and/or replace fossil fuels is ongoing. Biodiesels are a potential alternative, as they are renewable, biodegradable, non-toxic, offer reduced sulfur emissions, have superior lubrication, and can significantly reduce greenhouse gas emissions (Vichi & Mansor, 2009).

As modernization and industrialization continue around the world, the demand for energy is ever-increasing. The burning of fossil fuels degrades the environment, especially from the emission of gases that are harmful to human health and to the atmosphere (Hasan & Rahman, 2017).

Biodiesels are advantageous because they have a similar or higher cetane number than diesel. Additionally, they are non-toxic, biodegradable, good lubricants, and require little or no modification to the engine because their properties are similar to those of diesel (Islam et al., 2014). However, biodiesels have some disadvantages, such as their low volumetric energy, high kinematic viscosity, and high NOx emissions (Can et al., 2017).

This study attempts to identify and quantify the exhaust gases from a diesel engine operating at different rotation speeds and with different biodiesel mixtures.

Material and Methods

To obtain different fuel blends, biodiesels with a high degree of homogeneity were produced from soybean oil. Pure mineral diesel was acquired from Distribuidora de Produtos de Petróleo Ipiranga S/A.

The biodiesel production and mixture preparation were carried out at the Agricultural Machinery Laboratory (LABMAQ) in the Departamento de Engenharia Agrícola e Ambiental of the Universidade Federal Fluminense (UFF). The biodiesel was produced by transesterification via the methyl route in proportions of 1 mole of soybean oil to 6 moles of 99.7% p.a. methyl alcohol, in accordance with the procedure described by Tomasevic & Siler-Marinkovic (2003).

The various mixtures produced are denoted as B0 = 0%, B7 = 7%, B10 = 10%, B20 = 20%, B30 = 30% and B100 = 100%. This nomenclature indicates the percentage of biodiesel in pure diesel (petrodiesel), i.e., Bx, where x is the percentage. These mixtures were selected according to the market utilization specifications. The specific mass and kinematic viscosity of biodiesel, the specific mass of each biodiesel was calculated as:

$$\rho = \frac{P_p/(b - P_p)}{1000}$$

where:
- $\rho$ - biodiesel specific mass, kg m$^{-3}$;
- $P_p$ - weight of the pycnometer/biodiesel set, g;
- $b$ - pycnometer weight, g, and,
- $V_p$ - pycnometer volume, mL.

The kinematic viscosity at 40 °C was determined by the capillary viscometer method with the aid of Cannon-Fenske-type viscometers. These viscometers were calibrated by measuring the kinematic viscosity of distilled water at 40 °C and that of a thermostatic bath (N480, New Ethics) with a transparent thermostat (CT52, Schott). This allowed the biodiesel to be stabilized at 40 °C and the biodiesel flow to be visualized in the capillary viscometer.

The determination of the biodiesels kinematic viscosity was initiated by adjusting the thermostatic bath to 40 °C and placing a small amount of fluid, sufficient to fill 2/3 of the lower bulb of the viscometer, in the thermostatic bath. After the biofuel had reached 40 °C, the time taken for it to traverse the two control marks of the viscometer was measured. This procedure was repeated five times for each fuel and the mean for each test was computed. After obtaining the mean time for each biodiesel to flow from the first mark to the second one, the kinematic viscosity was calculated as:

$$\nu = \frac{t}{c}$$

where:
- $\nu$ - biodiesel kinematic viscosity, mm$^2$ s$^{-1}$;
- $t$ - time for biodiesel to flow between the marks of the capillary viscometer, s; and,
- $c$ - capillary viscometer constant, mm$^2$ s$^{-2}$.

The experiments used a micro-tractor with a single-cylinder air-cooled engine of capacity 668 cm$^3$, 4.0 kgf m maximum torque at 2350 rpm and 14.7 hp (10.8 kW) power at 2750 rpm (NBR ISO 1585). Rotation speeds of 1000, 1600 and 2400 rpm were investigated, as these characterize the rotations in the idling speed, operating rotation and maximum speed ranges, according to the manufacturer’s information, operating on a stationary basis. The engine was supplied by an external tank, and the mixtures were tested in increasing order from B0 to B100. Between testing each fuel supply, the tank was completely cleaned by means of washing and
The gas meter consisted of a TESTO® model 350XL gas analyzer with a gas probe coupled to the engine exhaust pipe. This analyzer is capable of verifying the amount of CO, NO, NO₂, SO₂, CO₂, O₂, and H₂ gases released to the environment by combustion. For each fuel, the tractor was running for 16 min. Within this time, three data collections of 2 min each were performed, with 5-min intervals between them. Between tests with different fuels, the engine was allowed to cool to room temperature. The experiments used a completely randomized design with three repetitions for each fuel, whereby the fuel was fixed and the rotation speeds were varied for each test. The variables to be analyzed were programmed in the gas analyzer software, where 120 data points (one per second for 2 min) were recorded for each gas. As there were three repetitions, the analyzer was configured for 360 emission data for each of the analyzed gases.

The SISVAR free software (Ferreira, 2014) was used to perform analyses of variance and Tukey tests at p ≤ 0.05.

**Results and Discussion**

The kinematic viscosity values for the tested fuels ranged from 2.8513-4.0413 mm² s⁻¹ and the specific mass values ranged from 830.28-883.18 kg m⁻³ (Table 1). These are in accordance with ANP Resolution No. 45 (ANP, 2014), which states that biodiesels must have a kinematic viscosity of 3.0-6.0 mm² s⁻¹ at 40 °C and 991.0 kg m⁻³ maximum specific mass at 20 °C. The American Society for Testing and Materials (ASTM) specifies kinematic viscosity values of 1.9–6.0 mm² s⁻¹, but does not suggest any values for the specific mass (Hasan & Rahman, 2017). According to Öztürk (2015), EN 14214 of the European Committee for Standardization specifies that the kinematic viscosity of pure biodiesel should range from 3.5–5.0 mm² s⁻¹; and the specific mass must be 860-900 kg m⁻³. In this study, the pure biodiesel exhibited kinematic viscosity and specific mass values of 4.0413 mm² s⁻¹ and 883.18 kg m⁻³, respectively, which comply with the European standard. Peng (2015) studied the physico-chemical characterization of soybean oil-based biodiesel and reported a value of 4.45 mm² s⁻¹ for the kinematic viscosity.

Note that, for both the kinematic viscosity and the specific mass, the values increased with the percentage of biodiesel; however, the values were close to and within the acceptable values stated above.

Lahane & Subramanian (2015) investigated the specific masses of mixtures from B5 to B100, and obtained results of 823.1-893.6 kg m⁻³. The same authors concluded that the specific mass increased with the biodiesel content in the diesel. The present study confirms these results.

According to Kumar & Sharma (2016), CO is produced by incomplete combustion in the engine cylinder and partially oxidized carbon particles. In this study, the CO emissions at 1000 rpm displayed a different behavior from those at 1600 and 2400 rpm, increasing with the level of biodiesel in the fuel (Table 2).

The CO emissions using B0 increase with the engine rotation speed, whereas those for fuels from B7 to B20 decrease when the engine is operating at 1600 rpm and increase at 2400 rpm. Analyzing mixtures B30 and B100, it is clear that the lowest emissions occur at 1600 rpm and the highest emissions occur at 1000 rpm. While for B100 and B30, the highest emissions occur at the lowest rotation speed, whereas for B0 and B7, the highest emissions occur at the highest rotation speed. These results corroborate the work of Nalgundwar et al. (2016), who claimed that high CO emissions in higher biodiesel mixtures can be justified by the high viscosity and poor air-fuel mixture.

According to Gharehghani et al. (2017), the combustion temperature and amount of available unburnt fuel control the rate of decomposition and oxidation of the fuel and, consequently, the CO formation rate. Accordingly, it can be stated that, at 1000 rpm, the combustion temperature was insufficient to produce a complete burn, thus releasing more CO, when the biodiesel percentage increased or when there was a larger injection of these fuels, resulting in a poorer mixture.

Lahane & Subramanian (2015) concluded that CO emissions decrease in biodiesel mixtures because of the high amount of oxygen. Cleaner and more complete combustion occurs with the help of oxygen by reducing CO emissions.

Perin et al. (2015) identified a 73.2% decrease in CO emissions when utilizing B100 (pure biodiesel) compared with B5. The authors stated that biodiesel contains 10-12% O₂, depending on the raw material.

According to Ganjehkaviri et al. (2016), the rate of NO₄ formation in biodiesel combustion is a controversial issue. The authors believe that the viscosity increase is caused by an increase in the length of the biodiesel molecules which prevents the nitrogen molecules from reacting with oxygen molecules present in biodiesel. This results in a lower formation of NO₄. Moreover, this corroborates the results found in the present study.

The results indicate a slight reduction in NOₓ at 1000 rpm when using the biodiesel mixtures compared with pure diesel.

**Table 1. Characterization of fuel variables**

<table>
<thead>
<tr>
<th>Biodiesel mixture</th>
<th>Kinematic viscosity (mm² s⁻¹)</th>
<th>Specific mass (kg m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B0</td>
<td>2.8513</td>
<td>830.28</td>
</tr>
<tr>
<td>B7</td>
<td>2.9377</td>
<td>834.02</td>
</tr>
<tr>
<td>B10</td>
<td>3.0795</td>
<td>835.59</td>
</tr>
<tr>
<td>B20</td>
<td>3.0866</td>
<td>840.89</td>
</tr>
<tr>
<td>B30</td>
<td>3.1918</td>
<td>846.22</td>
</tr>
<tr>
<td>B100</td>
<td>4.0413</td>
<td>883.18</td>
</tr>
</tbody>
</table>

B0 = 0%, B7 = 7%, B10 = 10%, B20 = 20%, B30 = 30% and B100 = 100%; Values followed by the same letter do not differ according to Tukey test at p ≤ 0.05

**Table 2. Emissions of CO (ppm) for different fuels and rotation speeds**

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Rotation (rpm)</th>
<th>1000</th>
<th>1600</th>
<th>2400</th>
</tr>
</thead>
<tbody>
<tr>
<td>B0</td>
<td></td>
<td>270.19 Ec</td>
<td>300.68 Ab</td>
<td>347.06 Aa</td>
</tr>
<tr>
<td>B7</td>
<td></td>
<td>282.76 Cb</td>
<td>268.13 Cc</td>
<td>319.08 Ba</td>
</tr>
<tr>
<td>B10</td>
<td></td>
<td>269.10 Eb</td>
<td>259.87 Dc</td>
<td>314.46 Ca</td>
</tr>
<tr>
<td>B20</td>
<td></td>
<td>274.29 Db</td>
<td>245.43 Ec</td>
<td>302.22 Ea</td>
</tr>
<tr>
<td>B30</td>
<td></td>
<td>310.37 Ba</td>
<td>276.10 Bc</td>
<td>306.17 Db</td>
</tr>
<tr>
<td>B100</td>
<td></td>
<td>348.57 Aa</td>
<td>257.96 Dc</td>
<td>276.01 Fb</td>
</tr>
</tbody>
</table>

Biodiesel mixture - B0 = 0%, B7 = 7%, B10 = 10%, B20 = 20%, B30 = 30% and B100 = 100%; Means followed by the same capital letter in the column and by the same lowercase letter in the row do not differ at p ≤ 0.05 by Tukey test.
(B0). At 1000 and 1600 rpm, the biodiesel mixtures have lower NO₂ emissions compared to the pure diesel. At 2400 rpm, the NO₂ emissions in pure diesel and biodiesel are equal, being lower in the mixtures. The NO₂ emissions are lower for higher rotation speeds, differing significantly in all engine speed rotations (Table 3).

At 1000 rpm, the highest emissions are given by B0 and the lowest emissions come from B30 and B100. For the other rotation speeds, large variations and oscillations were observed, in line with the results of Ganjehkaviri et al. (2016).

According to Kumar et al. (2016b), it is possible to reduce NO₂ emissions from diesel cycle engines by using a combination of low- cetane-index biofuel mixtures and ignition delay. Kumar et al. (2016a) acknowledged that several studies show differences in biodiesel chemical composition, which is related to the origin source, leading to variations in performance and emission characteristics. Biodiesel obtained from saturated raw materials produce low NO₂ emissions and high resistance to oxidation.

One of the main reasons for the use of biodiesels lies in their ability to lower sulfur emissions (SO₂), which is one of the most dangerous pollutants emitted by fossil fuels. The data obtained in this study demonstrate that lower emissions are obtained with higher percentages of biodiesel added to the fuel.

For all rotation speeds, the lowest SO₂ emissions were obtained for fuels with higher percentages of biodiesel, and B30 emitted the lowest SO₂ concentrations of 65.78, 52.47 and 32.25 ppm at 1000, 1600, and 2000 rpm, respectively (Table 4). Note that emissions of this gas decreased as the engine rotation speed increased.

The SO₂ emissions were not determined in the case of pure biodiesel (B100), as this fuel is derived from vegetable oils, and therefore contains no sulfur. However, the analysis was applied to the other mixtures and the pure diesel, as diesel releases more SO₂ than the biodiesel mixtures because of the lower sulfur content in vegetable-oil-based fuels (Rahim et al., 2016).

As reported by Miranda et al. (2013), sulfur emissions decreased for all mixtures, except for B7 at 1000 rpm rotation. This reduction can be justified by the low or almost null amount of sulfur in biodiesel. Therefore, it is safe to say that the use of biodiesel significantly reduces sulfur emissions.

Carbon dioxide develops when there is a sufficient amount of oxygen present during the formation of CO₂, as a product of combustion. CO₂ emissions are the result of complete fuel combustion. According to Naglundwar et al. (2016), CO₂ emissions become insignificant in the atmosphere when absorbed mainly by plants, trees and plantations.

Observing the CO₂ emissions for the various rotation speeds and fuels, the concentration of this gas is small in all situations, and the lowest emissions occur with the B10 mixture in the three speed rotation (Table 5).

Shahir et al. (2015) stated that oxygenated fuels emit a small amount of CO₂ and water when burned, and that there are no great differences in their mixtures with diesel. These results corroborate those found in the present work. Pereira et al. (2007) found higher CO₂ emissions in soybean biodiesel mixtures, suggesting more complete combustion.

The oxygen (O₂) behavior is important, as it may indicate the efficiency of the fuel burn. The data obtained in this study show that, for all fuels and rotation speeds, O₂ emissions were below the atmospheric 21%, indicating that the oxygen in the fuels was involved in the reaction and also reacted with a little of the oxygen injected into the cylinder, as shown in Table 6. The lower O₂ emission was verified in the pure diesel (B0).

Perin et al. (2015) reported that CO₂ emissions were different from O₂ emissions. As the CO₂ results from combustion, the bonding of atmospheric O₂ to the carbon in the fuel means that the CO₂ emission levels cannot be greater than the 21% of atmospheric O₂. However, Das et al. (2018) proved that there are no major differences in performance (thermal efficiency, specific consumption and exhaust gas

Table 3. Emissions of NO₂ (ppm) for different fuels and rotation speeds

<table>
<thead>
<tr>
<th>Fuel</th>
<th>1000</th>
<th>1600</th>
<th>2400</th>
</tr>
</thead>
<tbody>
<tr>
<td>B0</td>
<td>369.36 Aa</td>
<td>221.60 Ab</td>
<td>136.20 Ac</td>
</tr>
<tr>
<td>B7</td>
<td>294.28 Da</td>
<td>203.87 Cb</td>
<td>125.02 Dc</td>
</tr>
<tr>
<td>B10</td>
<td>320.52 Ba</td>
<td>203.90 Cb</td>
<td>128.94 Cc</td>
</tr>
<tr>
<td>B20</td>
<td>315.42 Ca</td>
<td>213.46 Bb</td>
<td>133.96 Bc</td>
</tr>
<tr>
<td>B30</td>
<td>279.35 Ea</td>
<td>204.78 Cb</td>
<td>125.23 Cc</td>
</tr>
<tr>
<td>B100</td>
<td>259.26 Fa</td>
<td>204.49 Cb</td>
<td>136.60 Ac</td>
</tr>
</tbody>
</table>

Biodiesel mixture - B0 = 0%, B7 = 7%, B10 = 10%, B20 = 20%, B30 = 30% and B100 = 100%; Means followed by the same capital letter in the column and by the same lowercase letter in the row do not differ at p ≤ 0.05 by Tukey test

Table 4. Emissions of SO₂ (ppm) for different fuels and rotation speeds

<table>
<thead>
<tr>
<th>Fuel</th>
<th>1000</th>
<th>1600</th>
<th>2400</th>
</tr>
</thead>
<tbody>
<tr>
<td>B0</td>
<td>77.84 Cc</td>
<td>65.09 Cb</td>
<td>45.61 Da</td>
</tr>
<tr>
<td>B7</td>
<td>93.30 Dc</td>
<td>70.19 Db</td>
<td>44.51 Da</td>
</tr>
<tr>
<td>B10</td>
<td>77.90 Cc</td>
<td>65.63 Cb</td>
<td>34.53 Ba</td>
</tr>
<tr>
<td>B20</td>
<td>74.78 Bc</td>
<td>54.75 Bb</td>
<td>36.14 Ca</td>
</tr>
<tr>
<td>B30</td>
<td>65.78 Ac</td>
<td>52.47 Ab</td>
<td>32.25 Aa</td>
</tr>
</tbody>
</table>

Biodiesel mixture - B0 = 0%, B7 = 7%, B10 = 10%, B20 = 20%, B30 = 30% and B100 = 100%; Means followed by the same capital letter in the column and by the same lowercase letter in the row do not differ at p ≤ 0.05 by Tukey test
temperature) and engine emission characteristics (CO, HC and NO) when using diesel and biodiesel fuels.

Al-Iwayzy & Yusaf (2017) analyzed the exhaust gases from engines powered by mixtures of biodiesel produced from microalgae and compared these emissions with pure diesel emissions. They concluded that there are significant statistical differences in CO, O$_2$, and NO$_x$ exhaust emissions when compared to B100. Using B100, the engine showed a reduction of 28.0, 4.2 and 7.4% in CO, CO$_2$, and NO$_x$ emissions, respectively.

For biodiesel and its mixtures with diesel, variations are more noticeable when the engine is operating at low rotation speeds. This may indicate that biodiesels lead to poor engine efficiency; this may be because the motors are not calibrated to use 100% vegetable fuel.

**Conclusions**

1. The CO emissions when using B0 increased with the engine rotation speed. For the B30 and B100 mixtures, the lowest emissions occurred at 1600 rpm and the highest emissions at 1000 rpm. The highest emissions occurred at the lowest rotation speed, whereas for B0 and B7, the highest emissions occurred at the highest rotation speed.

2. The lowest SO$_2$ emissions were obtained with fuels containing higher biodiesel percentages and operating at higher rotation speeds.

3. Nitrous oxides and carbon dioxide emissions decrease with higher engine rotation speed.

4. Overall, higher percentages of biodiesel in the fuel mixture result in a less polluting fuel.

**Literature Cited**


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