# Study of Gaseous Emissions Derived from the Combustion of

## Diesel/Beef Tallow Biodiesel Blends

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## Abstract

Air pollution is one of the main environmental problems of modern society. The road and transportation segment is a key source of polluting gases worldwide. In its research for transportation's emission reduction alternatives, the Brazilian government instituted a wide-spread biodiesel, adding 7% (B7) of biodiesel to the diesel used in the country. Therefore, studies such as this must be carried out to guarantee the environmental sustainability of the new matrix of renewable energies, with the use of biofuels, as well as evaluate the gases emitted to for the environment by the combustion of the same ones. This work was detected CO, CO<sub>2</sub> and NO gas emissions released into the atmosphere from the combustion of blends diesel/beef tallow biodiesel in a bench-scale engine. Using electrochemical sensors, the of these gases concentration were successfully registered for two modes of operation of the engine diesel, low rotation, 3500 rpm, and high rotation, 7000 rpm. The CO levels in this experiment in low rotation varied between values minimum and maximum range of 866.7 to 1333.3 ppm, and in high rotation, ranging of 666 and 1000 ppm respectively. For the CO<sub>2</sub> concentration in low rotation varied between values minimum range of 2.1 to 2.4%, and high rotation, ranging of 2.2 to 2.5%, and for NO concentrations of the samples for the mode low rotation had a variation of 83 to 109.5 ppm, and for high rotation were 81.7 to 98.7 ppm respectively.

#### Keywords

emissions, gas, biodiesel, electrochemical sensors, combustion

## 1. Introduction

Emissions from transportation sector are one important source of air pollution. Reduction of the ozone layer, acid rain, health problems and global warming (Seinfeld & Pandis, 2006; Hansen et al., 2008; Meinshausen et al., 2009; Trenberth et al., 2015; Tian et al., 2016) are all direct consequences of this

sort of impact of this pollution. The IPCC (International Panel on Climate Change, 2013) suggests the increase of renewable energy use, i.e., bio-fuels, in order to mitigate pollutant gas emissions, most notably greenhouse gases.

Brazil's transportation segment is dominantly highway-based, having diesel as its primary fuel for heavy load and mass transit. Diesel (Lloyd & Cackette, 2001; Schramm et al., 2003) is an ecologically compromising combustible, causing a great deal of atmospheric pollution in major Brazilian cities (Silva et al., 2012; André et al., 2012; Torricelli et al., 2013; Fajersztajn et al., 2013; Miraglia et al., 2013). The government, with the intent of minimizing pollutant emissions in the transportation sector, created an incentive program for the use of bio-fuels with a strong focus on biodiesel, seeking the environmental sustainability of its energy matrix. The program started in 2005 with the aim of adding 2% of biodiesel (B2) to the regular diesel formula until 2008 (law nº 11,097/2005) (ANP, 2016), reaching a sum total of 7% by 2014. Following this notion, the heads of the project propose a biodiesel increase of 10% (B10) come 2019 (law nº 13.263/2016) (Anuário, 2016).

According to the ANP (National Petroleum Agency, 2015), biodiesel production amounted to 4 billion m<sup>3</sup> in Brazil, being the second largest producer in the world, only behind the USA. The raw matter involved in biodiesel manufacture, soybean oil corresponds to 77.7%, beef tallow (18.8%), cotton oil (2%) and other greasy materials compound 1.5% of total production (Anuário, 2016), as demonstrated in Figure 1. Beef tallow, which was considered until recently, started being utilized as a bio-fuel feedstock and has been gaining increasing importance as such.

Several studies are realized in this area, but using another detection technique and others types of biodiesel produced by different raw materials, such as soybean oil, palm oil, sunflower (Rocha et al., 2014; Amaral et al., 2016; Bicalho et al., 2016; Cárdenas et al., 2016). The combustion of these blends of biofuels and diesel in engines, allows the identification of the different polluting gases emitted for the environment.

In this context, this article intends to monitor the emission levels for carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>) and nitrogen monoxide (NO) generated by the combustion of diesel/beef tallow biodiesel blends in a standard diesel-based bench-scale car engine, operating in low and high rotation modes. The purpose of this study is to investigate the viability of the utilized fuel, which is still an unknown concoction, in requirement of judicious evaluation in different blends.

This tally is relevant given the damage inflicted upon human health and the environment caused by greenhouse gases.  $CO_2$  is the primal causer of the global greenhouse effect (IPCC, 2013). CO modulates methane in the atmosphere (Brühl & Crutzen, 1999), aside from posing extreme danger to human life (Townsend & Maynard, 2002; Favory et al., 2006; Weaver, 2009). NO, in contact with the atmosphere's oxygen, transforms into NO<sub>2</sub>, a fume that can cause acid rain (McGonigle et al., 2004; Xie et al., 2009). The reaction between NOx (NO + NO<sub>2</sub>) and VOCs (Volatile Organic Composites) in the presence of solar radiation generates tropospheric ozone (Atkinson, 2000; Wolff et al., 1992) a driving constituent of photochemical smog, causing environmental impacts harmful to human health

(Latha & Badarinath, 2004; Sánchez-Ccoyllo et al., 2007).

Gaseous releases derived from the ignition of a bench-scale engine were observed in this study, where blends of animal fat biodiesel in diesel were used in the following proportions: 7% (B7), 15% (B15), 20% (B20), 25% (B25), 35% (B35) and 50% (B50). Electrochemical sensors (Allen & Larry, 2001; Wang, 2002; Maitre et al., 2006) were used to identify and quantify the emitted gas concentrations of the supervised concoctions. The recorded  $CO_2$  levels were given in % and the CO as well as NO quantities, measured in ppm.

#### 2. Materials and Methods

Preparation of the binary blends (BXX) was done by adding an XX amount of beef tallow biodiesel to the regular diesel, taken into account that the standard Brazilian-made diesel contains an obligatory 7% of biodiesel (B7). This procedure was admitted for the following blend compositions of B15, B20, B25, B35 and B50 in order to evaluate the possible emissions of polluting gases. The combustion of these samples was performed on a 7HP, 296cc, and four-stroke, monocylindrical TD70FE Toyama study engine with a horizontal shaft, electronic ignition and direct fuel injection. As this is a simple engine, performing correlations between variables was not possible, such as consumption, rpm (rotations per minute) and others. The motor was kept active for 5 minutes to stabilize it before measurement was started. Vehicles with conventional diesel engines enable only the use of blends with a maximum of 20% of biodiesel in diesel without modifications to the engine, for this reason the experiment was conducted in a bench-scale engine, which allows for blends with up to 50% of biodiesel in diesel (B50). This way, it was possible to simulate a larger number of compounds and analyze the behavior of gaseous emissions in greater percentages of biodiesel. Moreover, the laboratory-scale simulation shows a tendency of pollutant releases, whereas in the reality of everyday pollution is far bigger. With the aid a tachometer (Minipa, model MDT-2238A) the combustion emissions were evaluated in two modes of operation of the engine: low rotation-3500 rpm-and high rotation-7000 rpm.

The electrochemical techniques work as effective tools for detecting various gaseous species, due to some properties inherent to the system, such as elevated fragility, portability, easily handled hardware, miniaturization potential, and low cost (Allen & Larry, 2001). This way, it's possible to make records *in situ* and obtain analytical information on the gas samplings in simple and prompt fashion (Wang, 2002). A typical electrochemical sensor consists of a detection electrode and a reactant electrode, separated by an electrolyte layer. With that, the process consists of the gas passing by the sensor, which, firstly, interacts with the reactant electrode and, later, with the detection electrode (auxiliary electrode), to induce a process of oxidation and reduction. Therefore, applying potential difference to the terminals, which are interconnected to a resistor, will generate an electrical current proportional to the overviewed gas' concentration. The magnitude of this current is controlled by the very amount of fumes oxidized in the electrode.

The sensors are normally made in such a way so that the gas supply is limited by diffusion and the

current produced in the sensor is lineally proportional to the gaseous composition. This direct voltaic stream is one of the advantages of the electrochemical sensors over other sensor technologies, allowing for more precise measurement in low concentrations and easy calibration.

The Optima 7 analyzer (MRU, Air Emissions) was used for detection on the compounds of CO (with a detection limit of 0 to 4000 ppm  $\pm$  20 ppm), NO (with a detection limit of 0 to1000 ppm  $\pm$  5 ppm) and calculate the CO<sub>2</sub> (with a limit of 0 to 20%  $\pm$  0.3%), the collection was made directly at the engine's exhaust pipe, through a probe resistant of temperatures as high as 700 °C (1.292 °F), and the recording was done thrice in real time by the equipment. The measurements of the samples were performed in triplicates; the equipment itself contained filters in order to prevent the water vapor from interfering in the results.

#### 3. Results and Discussion

The Figure 1 presents the raw materials utilized in the production of the Brazilian biodiesel, making evident that 18.8% of the bio-fuel's production consists of animal adipose tissue. Considering that 2010's index was 13%, there has been a noticeable increase of this feedstock in Brazil's biodiesel production. Consequently, this leads to more optimistic projections for sustainability in the bio-fuel industry, considering that beef tallow used to be seen as an undesirable organic reject.

With government's promise of increasing Brazil biodiesel consumption until 2019, which is expected to blend up to 10% (B10) in the national diesel formula, studies on the pollutant emissions of the combustion diesel/beef tallow biodiesel blends are indispensable. For example, emissions of gases harmful to the environment and man, such as carbon monoxide, carbon dioxide and nitric oxide were observed in the ignition of these concoctions, emphasizing the cited argument of systematic experiments validating the safe use of said fuels. In this research is evaluated the emission of these gases derived from the combustion of diesel/beef tallow biodiesel blends for two modes of rotation of the diesel engine, low rotation -3500 rpm—and high rotation -7000 rpm.

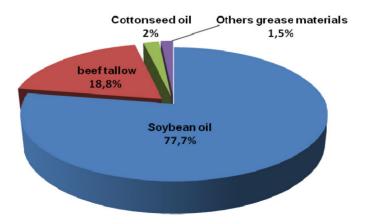


Figure 1. Primary Feedstock Utilized in the Production of Biodiesel (B100) in Brazil in 2015 Source: ANP, 2016.

#### 3.1 Carbon Monoxide Emissions

In the Figure 2 shows the concentrations of the CO gas emitted by the combustion of diesel/beef tallow biodiesel blends in the B7, B15, B20, B35 and B50 proportions by a bench-scale engine. For all blends the CO emission concentrations were lower when the motor was in high rotation mode. In the high rotation mode there is a greater volume of air involved, which causes agitation in the combustion chamber and alters the air/fuel ratio. In general, factors such as the air fuel ratio, the engine speed, the injection timing and the fuel type influence in the CO emissions (Gumus et al., 2012). This reduction in CO emissions can be associated to also higher oxygen content present in the biofuel, which makes it easier to be burnt at higher temperature in the engine, thus increasing the efficiency of the combustion (Buyukkaya, 2010; Rahman et al., 2014).

When the percentage of biodiesel in the blend is increased, it tends to reduce CO emissions in the high rotation scenario, except for the B35 proportion. For the engine's low rotation mode, a behavior pattern was not recorded, for the results were anomalous.

It is noticed that the increase of biodiesel concentration in the blends leads to a reduction of the CO emissions, safe for blend B25 (low rotation), which is environmentally interesting both from the gas emission reduction viewpoint, as well as the point of view of animal fat residues decrease, as it being used as raw material in the biodiesel production. The reduction of carbon monoxide in the atmosphere is a big goal, since this gas is extremely harmful to human health and the environment, namely contaminating breathing air.

In this experiment, the CO concentration of the blends for the low rotation mode (3500 rpm) presented values ranging from minimum to maximum of 866.7 to 1333.3 ppm respectively. Already in high rotation (7000 rpm) reached values between minimum and maximum of 666 to 1000 ppm respectively. In the work developed by Buyukkaya (2010) was evaluated the performance of the emission and combustion of a diesel engine using neat rapeseed oil and its blends of B5, B20 and B70, and standard diesel fuel separately. It was observed that the CO emission decreased with the increase in engine speed. The minimum and maximum carbon monoxide emissions of the blends for 1000 rpm were 830 to 900 ppm, and at 2100 rpm were 300 to 400 ppm respectively.

A study developed by Zhihao et al. (2011) utilized a direct injection diesel engine fuelled with pistacia chinensis bunge seed diesel/biodiesel blends. The results showed that CO emissions too decrease with the increase of the proportions of biodiesel in the blends. At blends used were B0, B10, B20 and B30, and obtained CO concentrations for engine at low rotation speed, 1500 rpm, a ranging from 2000 to 2400 ppm and in high rotation, 2400 rpm and emissions ranging from 800 to 1200 ppm. The results of the CO emissions obtained in this research showed consistency with the values found in the literature of these gaseous emissions, even when performed by different engines, blends diesel/biodiesel and rotational variations.

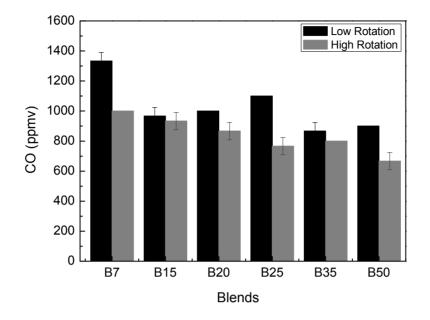


Figure 2. Concentration (ppm) of Emissions CO from the Combustion of Diesel/Biodiesel Blends

It is observed that in Figure 2 the binary blends had lower emissions of CO with respect to the diesel (B7). With this, the higher oxygen content of biodiesel allows more carbon molecules to be burned, promoting a complete combustion. Thus, the carbon monoxide gas emissions are minor when diesel engines burn biodiesel fuel. These results are consistent because during the operation cycle, the catalytic activity is higher, due to the increase of the exhaust temperature, thus reducing CO emissions (Ileri & Koçar, 2009).

### 3.2 Carbon Dioxide Emissions

Figure 3 shows the concentrations of the CO<sub>2</sub> gas emitted by the combustion of diesel and beef tallow biodiesel blends in the proportion of B7, B15, B20, B35 and B50, for a bench-scale diesel engine. For all blends the CO<sub>2</sub> emission concentrations were lower in the engine's low rotation mode, the B50 blend presenting the lowest emission among them. It was observed that, in the high rotation mode, the CO<sub>2</sub> levels did not present significant differences in all the blends. The emission of CO<sub>2</sub> is related to the complete combustion and probably to the temperature of the engine, which tends to increase in the high rotation mode. Carbon dioxide is the most prominent greenhouse gas, and should always be monitored in diesel engine's exhaustions. In this experiment, CO<sub>2</sub> concentrations of the blends were found for low rotation of 3500 rpm values minimum and maximum in the range of 2.1 to 2.4%, and high rotation, 7000 pm, ranging of 2.2 to 2.5% respectively. The research of Rocha et al. (2014) evaluated CO<sub>2</sub> emitted by the exhaust of a diesel engine with binary blends of soybean biodiesel and diesel. The samples were evaluated for low rotation speed, 3000 rpm, with minimum and maximum emission values 1.9 to 2.2% respectively, and in high rotation speed, 9000 rpm, 2.4 to 2.8%, values close to the results obtained in this research, despite being other biodiesel.

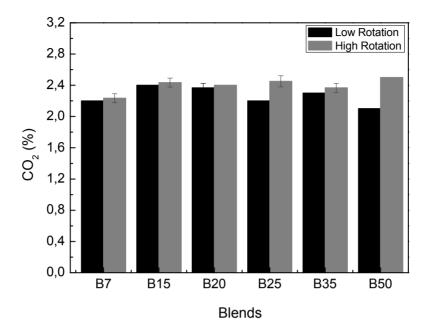


Figure 3. Concentration (ppm) of Emissions CO2 from the Combustion of Diesel/Biodiesel Blends

In diesel engines, the air-fuel ratio significantly affects CO production, because when this rate is kept under control, CO decreases and the  $CO_2$  rate increases (Behçet et al., 2015). The existing maximum level of carbon monoxide causes a reduction in the amount of carbon dioxide in the atmosphere. Thus, when the engine speed increases, the oxygen in the biodiesel contributes significantly to the oxygen-fuel reactions inside the engine.

## 3.3 Nitric Oxide Emissions

Figure 4 shows the concentrations of NO emitted by the combustion of diesel blends and beef tallow biodiesel in the proportion of B7, B15, B20, B35 and B50 for the bench-scale diesel engine. For all blends the NO emission concentrations were lower in the high rotation mode. The B7 blend had the lowest NO emission for both high and low spin rates and the B15 blend had the highest emission also for both operation modes. For blends B20, B35 and B50 there was practically no change in NO emissions in any of the rotation ratios. In general, an increase in NO emission is observed when the proportion of biodiesel in the blend is increased in the low-speed mode. This result is consistent with previous records and may be related to the higher cetane number of the biodiesel, which provides better combustion at higher temperatures.

It should also be noted that the presence of oxygen in the biodiesel molecule can also increase the formation rate of nitrogen oxides  $NO_x$ , in addition to other factors such as compression ratio and fuel chamber geometry, fuel quality, air/fuel ratio, injection temperature and the combustibles' chemical properties. These combined factors make it more complex to assess emissions of this gas for diesel engine combustions.

The reduction of the emission of nitrogen oxides in flames from fuel blends is highly desired, since this gas is extremely damaging, especially due to its role in the generation of acid rain and the formation of tropospheric ozone, which is the main constituent of photochemical smog. NO concentrations minimum and maximum of the blends for low rotation had a variation of 83 to 109.5 ppm respectively, and for high rotation were 81.7 to 98.7 ppm obtained in this experiment.

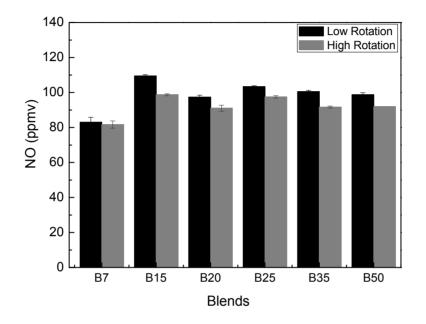


Figure 4. Concentration (ppm) of Emissions NO from the Combustion of Diesel/Biodiesel Blends

The biodiesel is a mixture of monoalkyl esters, where the molecule oxygen is present in its chemical composition, and petroleum diesel is already composed of hydrocarbons (Knothe et al., 2006; Knothe et al., 2005; Demirbas, 2007). With this, the principal source of nitrogen for formation of NO during combustion of petroleum diesel is atmospheric (molecular) nitrogen (Sun et al., 2010). The Figure 4 shows that for diesel (B7) there is lower NO emission, and with increasing concentrations of biodiesel in diesel, an increase in NO emissions occurs.

This result is consistent with the literature and may be related to the number of cetane present in biodiesel (Mofijur et al., 2014), which provides combustion at higher temperatures. Emissions of gas NO do not exhibit definitive trends because the results depends by many factors, among them including engine type, start of injection, ignition delay, fuel composition, radiative heat transfer, and combustion. The NO is also formed when the nitrogen of the fuel reacts with the oxygen present in the air during combustion (Balakrishnan et al., 2016).

#### 4. Conclusion

The electrochemical techniques showed to be selective and sensitive to quantify and identify the CO,  $CO_2$  and NO gases in the study here developed. It was possible to determine concentrations in the range of ppmv for CO and NO and in % for  $CO_2$  from the exhaust of a bench-scale diesel engine that used diesel/beef tallow biodiesel as fuel. Exhaust emission from transportation sector affects the human health. It is the main contributor to degrade the air quality. Biofuel is promising alternative to maintain both human health and environment quality better by reducing harmful emission from biofuel runs diesel engines. The increase in biodiesel use in Brazil, with the projection of 10% of biodiesel in the diesel formula, calls for studies of the emissions of pollutant gases originating from the use of these blends. Brazil is a country with a large territorial dimension, with an eminently road-based transport segment, being therefore a consumer of large volumes of fossil fuels (diesel). Careful studies need to be carried out to ensure the environmental sustainability of the new renewable energy matrix.

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