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Detection of Ethylene Emitted by Diesel-biodiesel Engine Using CO_2 Laser Photoacoustic Sensors

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Abstract

The increased use of modern society vehicles is rising the pollutant gas emissions causing several environmental and public health problem in urban centers. Diesel fuel is a major emitter of pollutant gases, especially in Brazil, where the transport is predominantly by land. For this reason, Brazilian government aims to modify the energy matrix with the addition of renewable energy sources, such as biodiesel. In this paper, we studied the emission of ethylene gas from the combustion of binary mixtures, because this gas is directly related to the formation of photochemical smog. The Brazilian government does not have specific regulations for the emission of ethylene yet. Thus, it becomes necessary to monitor and to detect this gas through sensitive and selective methods, such as Photoacoustic Spectroscopy. This method was employed in the analysis of binary mixtures of soybean biodiesel in diesel in the following proportions: B5, B10, B15, B20 and B25, which have been tested for combustion in an engine bench. In all samples, ethylene was found in ppmv concentrations.

Keywords: biodiesel, engine bench, ethylene, phoacoustic spectroscopy

1. Introducation

The gases resulting from vehicles combustion might cause multiple damage to human health and the environment, causing global climate changes, such as the intensification of the greenhouse effect (Michael, Bradley, & Hughes, 1998; IPCC, 2007; Hansen et al., 2008; Nathan et al., 2008; Rosenzweig et al., 2008; Meinshausen et al., 2009; Myles et al., 2009; Solomon, Plattner, Knuttic, & Friedlingstein, 2009; Sthel et al., 2010). Thereby, it is necessary to monitor the emission rates of such polluting gases, with the aim of developing means to reduce them.

Due to the increasing atmospheric pollution and the fact that the fossil fuels are non-renewable sources of energy, it is necessary to make changes in Brazilian energy matrix. In 2005, the Brazilian Biodiesel Program (Law no. 11097) (ANP, 2005) was instituted, establishing the addition of 2% of biodiesel in diesel form with a binary mixture named B2 and in January 2010 was set by addition of 5% biodiesel in diesel (B5), which is currently considered the standard Brazil diesel.

The worldwide usage of biodiesel as fuel has shown promising perspectives (Herrera, 1995). Because of its several common characteristics with diesel fuel, biodiesel can replace it completely or partially in diesel engines, and, in low concentrations, the binary mixtures do not require any changes to the engine. Besides, it improves the lubricity of the fuel, it contributes to the environment, especially in large urban centers (Masjuk & Sapuan, 1995), because emissions of some gases such as carbon monoxide and carbon dioxide are lower and it does not contain sulfur (Canakci, 2007).

Considering the growing fleet of vehicles in Brazil, it is necessary to quantify emissions of pollutant gases, therefore, it is extremely important to develop techniques and methodologies for the detection of these gases. In this work, we will emphasize the ethylene gas emitted from burned fossil fuels, especially diesel engines (Mothe et al., 2010; Teodoro et al., 2010), whose emission does not have specific regulations in Brazil (CONAMA,

1989). Ethylene (C_2H_4) is a major volatile organic compound (VOC) due to the presence of a double bond, which makes it very reactive. One of the reaction products between ethylene and nitrogen oxides, in the presence of radiation, is the tropospheric ozone (Wolf & Korsog, 1992; Seinfeld, 1986). Tropospheric ozone is responsible for photochemical smog, which directly affects the human health and the environment (Seinfeld, 1989; Wolf & Korsog, 1992; Lefohn & Foley, 1993; Atkinson, 2000; Teodoro, 2008).

The Photoacoustic Spectroscopy has some advantages, as multicomponents detection, high sensitivity, high selectivity, excellent temporal resolution and large dynamic range of detection and it does not require sample preparation and buildup (Sigrist, 1994; Harren, Bijnen, Reuss, Voesenek, & Blom, 1990; Meyer & Sigrist, 1990; Bernegger & Sigrist, 1990; Harren et al., 1999; Miklós, Hess, & Bozoki, 2001; Seiter & Sigrist, 1999). This technique is widely used for the detection of several gases in the concentration range of ppbv (Killinger & Mooradian, 1988; Measures, 1988; Sigrist, 1994; Miklos et al. 2001; Schramm et al., 2003; Sthel et al., 2005; Angelmahr, Miklos, & Hess, 2006; Filho et al., 2006; Thomas, 2006; Cristescu, Persijn, Hekkert, & Harren, 2008; Sigrist et al., 2008; Berrou, Raybaut, Godard, & Lefebvre, 2010).

The photoacoustic effect is based on the generation and detection of pressure waves (sound) inside a resonant cell, where the gas samples are inserted. The sample is exposed to the incidence of modulated radiation, absorbing it at determined wavelengths. The resonant absorption of radiation generates a modulated heating in the sample and, therefore, a sound signal is produced and detected by highly sensitive microphones, inside the cell.

In this work we detected ethylene gas emitted from a diesel engine bench powered by soybean biodiesel blends and diesel at ratios B5, B10, B15, B20 and B25.

2. Method

The binary blend of biodiesel soybeans was prepared in laboratory and one liter of the mixture was obtained for each one, varying the quantity of biodiesel added in diesel. The samples were used in the process of combustion of the engine bench (TOYAMA TD70F), with maximum power of 6.7 HP, 296 cc, direct injection system and manual start.

The combustion was carried out with the engine running at low (3000 rpm) and high rotation (9000 rpm). This procedure was adopted in the collection of samples from the diesel-biodiesel blends B5, B10, B15, B20 and B25 (B5 which means a 5% blend of biodiesel in diesel, and so on). The measurements started in B5 because it is the diesel Brazilian standard.

The gases emitted from combustion were collected and stored in a canister, internally coated with teflon and previously evacuated (SUMMA Andersen Instruments), which by pressure difference, aspires the sample gas to inside when it is opened. By means of the vacuum pump of the AVOCS collector (Graseby) (Ambient Volatile Canister Sample) the sample were transferred form the canister to the photoacoustic cell as outlined in Figure 1.

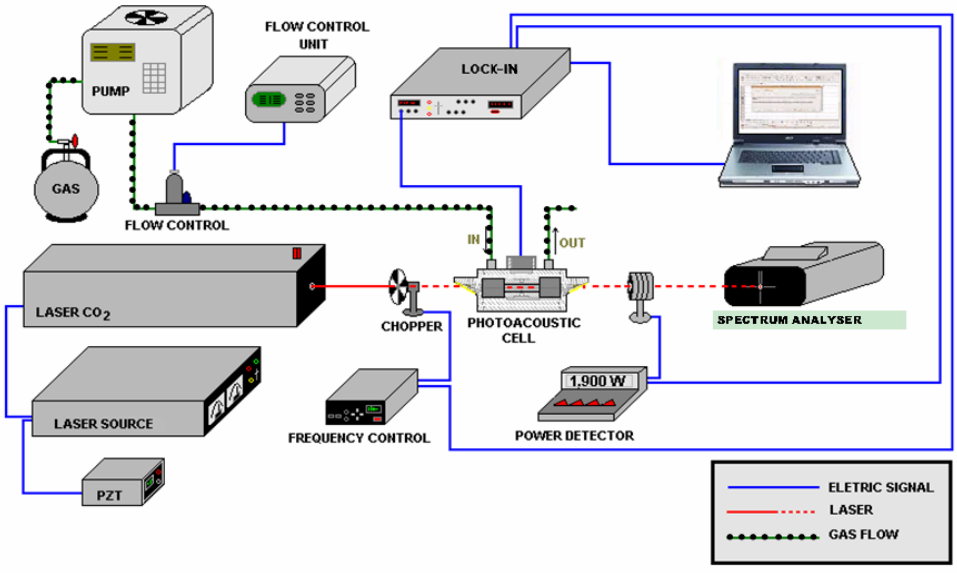

Figure 1. Scheme of the photoacoustic experimental setup

The photoacoustic spectrometer consists on a CO_2 laser (Lasertech Group Inc., - LTG, Model LTG150 626G; 1.9W power) as a source of infrared radiation, a chopper (New Focus, 3605) for mechanical modulation of the beam, a photoacoustic cell developed by the group of Professor M. Sigrist (Swiss Federal Institute of Technology (ETH) – Zurich), flowmeters which control the entry of gaseous samples, a spectrum analyzer, a power meter, a lock-in amplifier (Stanford SR850) and a computer for data acquisition.

The quality factor (Q = 24.7), the coupling constant (C = 40.2 $VcmW^{-1}$) and the resonance frequency (ν = 2.4 kHz) of the photoacoustic cell were experimentally obtained. From these parameters we could determine photoacoustic signal of monocomponent sample by the relationship

$$S(\lambda) = CP(\lambda)Nc\sigma(\lambda), \quad (1)$$

where P is the power emitted by the laser, N is the density of molecules ($\approx 2.5x10^{19}$ moléculas/cm^3 to pressure 1013 hPa and temperature 20°C), c is the mole fraction of gas absorber and σ is the cross-section of the gas absorber.

In multicomponent samples, it is possible to determine the concentration of different gas species and the photoacoustic signal for different wavelengths (λ_i = 1, 2, 3,...), based on the absorption spectrum of each component to be analyzed. For this case we have the relationship

$$S(\lambda_i) = CP(\lambda_i)N\Sigma^{n}_{j=i}c_j\sigma_{ij}. \quad (2)$$

The laser emission lines for each gas are represented by the index i, with i = 1, 2, 3, ..., m, and each gas sample is represented by the index j, with j = 1, 2, 3, ..., n, where n is the number of chemical species in m ≥ n. Thus, it is possible to obtain the concentration according to the generated signal.

2.1. Photoacoustic Cell Calibration and Sensitivity Measurements

To know the cell performance it is required to perform the calibration of the spectrometer in order to determine the limit of detection of the photoacoustic method. Calibration was performed gradually diluting a sample of ethylene in nitrogen gas, initially at a concentration of 1.4 ppmv (certified by White Martins). The reference signal obtained in the initial condition of maximum concentration can be used to adjust the wavelength of the laser to the absorption maximum of the line.

The measurements were carried out in ethylene emission line 10P14 (λ =10.53 μm) of carbon dioxide laser, where the ethylene has its highest absorption. In this same region, there are also considerable absorption intensities from water and carbon dioxide. Therefore, in order to avoid interference of chemical species, chemical filters of potassium hydroxide and calcium chloride, respectively, were used.

3. Results

The calibration of the photoacoustic cell (Figure 2) shows excellent linearity of the photoacoustic signal for dilution of the ethylene in nitrogen. The detection limit of the ethylene achieved (84 ppbv) agrees with the mathematical model shown in Equation 1. Furthermore, we observed a signal/electronic noise considerably low (~ 44), confirming the high performance and stability of the assembly esperimental used in the resonant frequency of approximately 2400 Hz.

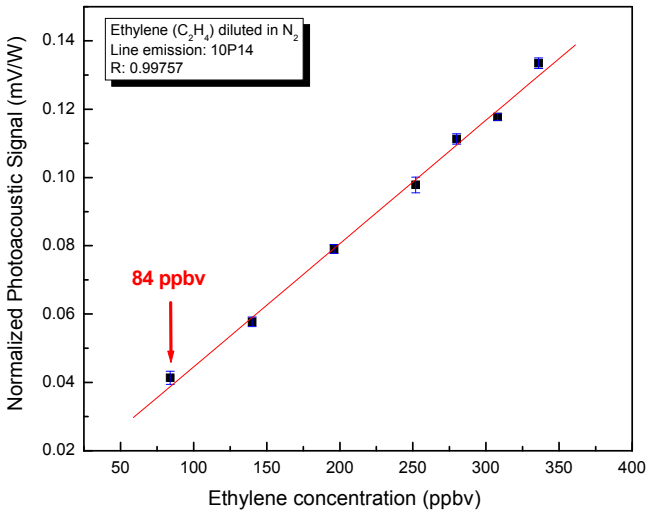

Figure 2. Calibration curve for ethylene

Figure 3 shows the concentrations of ethylene gas, a hydrocarbon from the incomplete combustion of fuel being released when all organic compounds are heated and oxidized from the exhaust of diesel engines. It was verified that in all samples B5, B10, B15, B20 and B25 at both low and high speeds produced the ethylene gas in the concentration range of 67 to 125 ppmv. We also noted that the emission ethylene was higher in the engine at high rotation speed. This is related with the increase of the temperature in the combustion chamber.

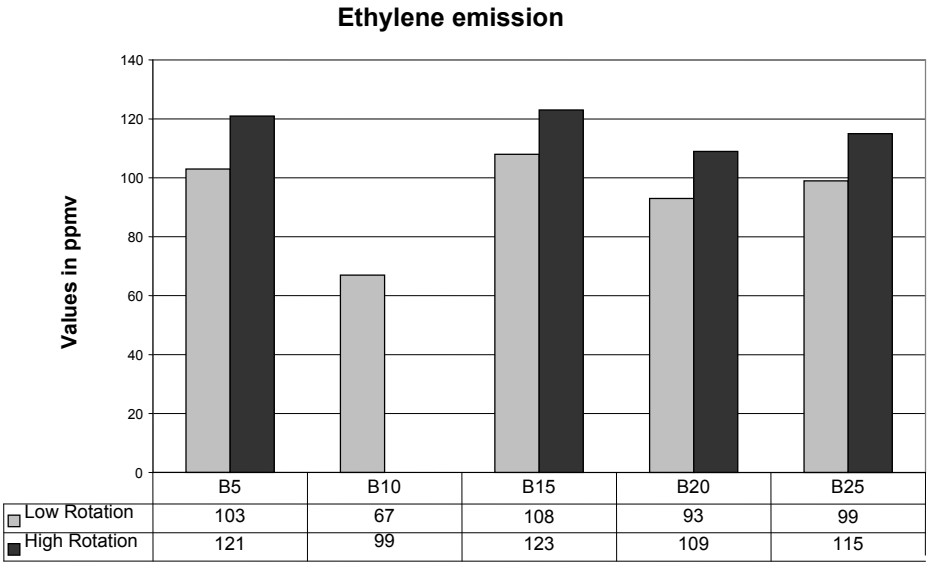

Figure 3. Ethylene gas concentration [ppmv]

The results from Figure 3 indicates that if a diesel mixture of up to 25% of biodiesel (B25) is used, ethylene emission is not significantly reduced. The lower emission of ethylene at both low and high speed was obtained for the sample B10, thus this mixture proved be the better in the environmental point of view.

Brazil is a tropical country with high solar radiation that favors the production of tropospheric ozone. Furthermore, mass transport and loading road is predominantly by land. Therefore, the intense use of diesel fuel plays an important role in the emissions of gaseous pollutants. The combination of these factors contributes to the production of tropospheric ozone, responsible for photochemical smog, which justifies the need of expanding scientific research in order to propose a renewal of the Brazilian transportation and reduce these gases emissions.

4. Conclusions

The Photoacoustic Spectroscopy was sensitive and selective in gas detection from ethylene binary mixtures of diesel-biodiesel. Ethylene concentrations in the range of ppmv could be obtained. Due to the nowadays environmental problems, Brazil has created a program to use biodiesel in its energy matrix related to the transport, which provides the use in the short and long term from 10 to 20% biodiesel in diesel. In this paper, we noticed that the gas samples of a binary mixture B25 showed no significant reduction in the emission ethylene when compared to the emission of the sample B5, which represents the standard diesel in Brazil. Thus, the concentration of biodiesel-diesel had no environmental improvements regarding the emission of ethylene. Further research should be encouraged in order to know the real impacts of the use of binary mixtures nationally and globally, once that diesel is widely used around the world.

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