Evaluation of Gaseous Emission in the Use of Biofuels in Brazil

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1. Introduction

In the seventies, the human society was faced with an important issue: the environmental problems. Is it possible to continue the exploitation of natural resources indefinitely? What to do with industrial waste and toxic gases emitted by industries and vehicles that use predominantly fossil fuels as energy source? Since the beginning of environmental awareness to the present day, many events have occurred, mobilizing international public opinion. In 1992, the International Convention on Climate Change has occurred and in 1997, the Kyoto Protocol aimed at reducing emission of greenhouse gases.

The Intergovernmental Panel on Climate Change (IPCC) report [1, 2] concluded that the use of fossil fuels, intensified after the Industrial Revolution, is closely related with the increasing of the average temperature of the earth, due to increased emissions of greenhouse gases (GHGs).

A possible alternative to minimize this problem is the use of renewable energy in large scale in order to reduce greenhouse gas emissions [3]. The IPCC report suggests that, in the transport sector, biofuels can play an important role in reducing emissions of greenhouse gases, depending on their production pathway.

It is projected that biofuels used as additives / substitutes for petrol and diesel will increase its participation to 3% of the total energy demand for transport in 2030. This value can increase to about 5-10%, depending on future oil and carbon prices, improvements in vehicle efficiency and the success of technology in the use of cellulosic biomass [4, 5].

Policies aimed at solving issues such as traffic congestion, air quality and energy security are closely associated with emission reductions in the transportation sector.

Currently, the transport matrix in Brazil is predominantly by road, with intensive use of fossil fuel sources (diesel and gasoline). Thus, the government created two programs that encourage the use of biofuels in the transport sector: the Biodiesel National Program and the Ethanol National Program. Currently, all diesel fuel sold in Brazil has 5% of biodiesel (B5), whereas the gasoline used in the vehicles has 20% of ethanol. Recently, with the increased use of flex-fuel vehicles, which may be fueled with gasoline and ethanol in varying percentages, the use of biofuels becomes more prominent.

Brazil has a great ability to produce bioenergy, once it is a tropical country (insolation), with extensive arable lands, regular rainfall, water resources and rich biodiversity, enabling the success of ethanol and biodiesel programs.

The use of biofuels has generated controversy in the scientific, technical and policy areas around the world [6-8], particularly in regard to emissions of carbon dioxide, oil prices, fuel and food security, destruction of forests, soil erosion, impacts on water resources, energy balance and energy security.

In relation to the greenhouse effect, not only the carbon dioxide emissions from burning fuels must be considered, but the hole production chain. It is necessary to consider the use of nitrogen fertilizers, the land use and nitrous oxide emissions [9-11]. In the case of ethanol, we must consider the emissions generated by agricultural machines, sugarcane transportation, ethanol transportation to consumption centers, generation of carbon dioxide during the fermentation of ethanol and the energy source that powers the ethanol industry. Similar concern should be considered in the production cycle of biodiesel, produced predominantly from soybean in Brazil. All these criteria need to be evaluated in the sustainability studies of biofuels production chain.

This chapter presents some environmental aspects of Brazilian studies biofuels (biodiesel and ethanol) evaluating pollutant emissions from gasoline and ethanol vehicles exhaust and also from bench engines powered by biodiesel and diesel. Furthermore, we evaluated the emissions of greenhouse gases in sugarcane soils.

For this study, we used techniques that ensure high selectivity to identify the gaseous species in a mixture of gases, high sensitivity for detecting low concentrations of gases, good temporal resolution and the possibility of online measurements. The photoacoustic technique has all the characteristics to be used in these measurements.

Photoacoustic spectroscopy is used for the detection of several gases in the concentration range of parts per billion by volume (ppbv) and sub-ppbv [12-21]. This methodology is based on the generation and detection of pressure waves (sound) inside a resonant cell, where the gas samples are placed. These samples are exposed to the incidence of modulated radiation, absorbing it at determined wavelengths. The resonant absorption of radiation generates a modulated heating in the sample. Therefore, a pressure wave or a sound signal is produced and detected by highly sensitive microphones, inside the cell. These microphones convert the sound signal into an electric signal, which is filtered and detected by a lock-in amplifier. We will use this technique to detect the gas ethylene (C_2H_4) in parts per million by volume (ppmv) and ppbv concentrations.

As a complementary technique, electrochemical sensors [22, 23] and infrared analyzer, URAS [24] were used. By combining these two techniques, gases such as CO, NO, NO_2, CO_2, N_2O, could be detected in ppmv and ppbv concentrations.

2. Ethanol in Brazil

2.1. Historical aspects

In Brazil, the first sugar production centers were established in the mid-sixteenth century, with seedlings of cane sugar from the Madeira Island. In the same century, the first mills were built in northeastern of Brazil, which soon became a major producer of spices. The climate was a factor in the success of the sugarcane planting. [25]. During the colonial period, Brazilian sugar production has changed a few times, keeping intact some characteristic features: grown on monoculture plantations and using compulsory labor for its development.

The first ethanol powered vehicle in Brazil was produced by Peugeot and brought by the family of Alberto Santos Dumont. This idea fascinated the Brazilian President, Rodrigues Alves. In 1919, a decree of the Pernambuco government officiated ethanol as a "National Fuel". [26]

By 1930, Eduardo Sabino de Queiroz published some articles on the use of ethanol as a fuel in vehicles. In this period, the President Getulio Vargas became interested in such articles, and in February 1930, he promulgated the Decree No. 19117, which established the addition of 5% alcohol in each liter of imported gasoline in Brazil. At September 1931, another decree was intended to support research on the ethanol fueled engine, charging a tax per liter of imported gasoline, to finance research. [26]. Despite the incentives given to ethanol in the 30´s, due to external pressures and disaffection of subsequent governments, ethanol lost its strategic importance in the Brazilian energy matrix.

After the first oil shock in 1973, the sudden rise in the price of the oil barrel has created a major crisis in Brazil. To reduce oil imports (90% of the gasoline consumed was imported) and to offer an alternative market for sugar, ethanol again figured as a strategic option. The National Alcohol Program (Proalcohol) was thus created, through Decree 76.593/75. [27]

In the first phase of the program, the Brazilian government established a mandatory blend of 22% of ethanol in gasoline, low-interest loans and guarantees for construction of new units for ethanol production. These actions produced an increase in more than 500% of ethanol production between 1975 and 1979. [28]

The second phase started in the second oil shock in 1979, when the Brazilian government encouraged the manufacture of vehicles that run exclusively on hydrous ethanol. To encourage the purchase of such vehicles, various tax incentives were offered, ethanol price was fixed below gasoline price (65% in 1980 and 59% in 1982) and taxes on the sale of ethanol cars were significantly reduced.

In 1984, ethanol vehicles accounted for 94.5% of national production. The alcohol industry has replaced since 1976, over 1.44 billion barrels of oil [28]. Brazil was the first country to use ethanol on a large scale. The program was economically and technologically successful. [29]

In the early 90´s, with the fall in gasoline prices, the price of ethanol fuel, initially set at 64.5% of the price of gasoline reached to achieve a percentage of 80%, losing some of its competitive advantages. The Brazilian government has given incentives tax to the so-called "popular cars", that run on gasoline, which came to exert strong competition to the alcohol-fueled cars.

Alongside this, there was an increase in international prices of sugar and more profitable export market, which resulted in the decrease of ethanol production, generating a distrust of regular supply of this fuel. In 1990, the country was forced to import ethanol and methanol used in blending with gasoline. [28]

These factors contributed to the sale of alcohol-fueled cars in Brazil were close to zero in the mid-90s, dismantling the main program of biomass fuel in the world. Only taxis and rental cars continued to be manufactured with alcohol engine, although the mandatory blend to gasoline has been maintained. [28, 30]

Nowadays, the advent of flex-fuel vehicles allows the vehicle to be fueled with alcohol or gasoline, eliminating the uncertainty about the irregularity in supply. Initially developed in the United States and Europe, this technology was introduced in Brazil in 2003. The first Brazilian flex vehicle was the “Gol 1.6 full flex", released by Volkswagen. Then, flex vehicles technology was spread rapidly for nearly all automakers. Currently, there are in the Brazilian market more than 16 million flex-fuel vehicles of sixty different models produced by ten manufacturers.

There are also studies for ethanol use in heavy-duty engines. They have been introduced experimentally in a few numbers of buses (E95) in the city of São Paulo. Brazilian ethanol is considerate an ally to reduce GHGs emissions. Estimates based on analysis of the ethanol life cycle show that when produced from sugar cane can reduce GHG emissions in up to 90% [31]. Energy balance is also excellent for Brazilian ethanol, once for every unit of fossil energy used in the production of ethanol, 9.3 units of renewable energy are generated [32].

In Brazil, the first flex motorcycle was developed by Honda engineers, being considered as an important project by the Honda Research and Development Center in Japan [33].

In Botucatu (SP), Neiva Aeronautic Industry, manufacturer of aircraft components for agricultural and regional Embraer jets, started, on October 2004, the production of Ipanema, aircraft with the certification of the Aerospace Technical Center (CTA) and 100% powered by hydrated ethanol. The Ipanema is the first series production aircraft in the world to leave the factory certified to fly on this type of fuel. [34]

2.2. The Brazilian industry of sugarcane

The Report of the Food and Agriculture Organization (FAO) [35] estimates that in 2010, 23.8 million hectares of sugar cane were grown in over 90 countries worldwide, resulting in a world production of 1.69 billion tons of sugarcane. The report also shows that Brazil is the world largest producer of sugarcane, followed by India, China, Thailand, Pakistan and Mexico. Brazil has accumulated experiences with vehicles powered by biofuels over the past 30 years [4, 34, 35], including pure ethanol and ethanol blended with gasoline. The Brazilian sugar industry has experienced huge and technological developments. [36] Brazil is the world's largest producer of sugarcane, producing about 490 million ton per year in an area of 7.8 million hectares, which is 2.3% of the arable land in the country. Brazil also has the lowest production cost among the main contenders in the international market, and leads the knowledge of sugarcane biotechnology, with Australia and South Africa.

The Brazilian sugarcane industry has some peculiarities that differentiate it from other sugarcane industries around the globe. First, most industries produces a very high proportion of sugarcane that it processes. Only one-third of the raw material processed is acquired from third parties [29]. Another important factor is the diversity of commercial products that are made from the juice of sugar cane and from the solid and liquid waste grinding, beyond the co-generation of electricity by burning bagasse. Most of ethanol and sugar production comes from plants with attached distilleries, capable of designating a portion of the juice of sugar cane for sugar production and partly for the manufacture of the alcohol.

Another important aspect is the distribution of production units of cane sugar in the whole national territory. The provision of a large portion of land in the North-South provides a wide variety of microclimates that allow the production in economic scale of the majority of commercial crops in use worldwide. As a result of the distribution of production units and combining state of the harvest periods, the country maintains with different intensities, the sugar and alcohol production by virtually every month of the year [29]. The successful Brazilian ethanol program is now supported by 2 basic factors: The mandatory use of ethanol blend in gasoline, and expanding market for flex-fuel. The gasoline sold in Brazil has 20% to 25% of anhydrous ethanol, and approximately 90% of the new cars sold use flex fuel engines.

2.3. Environmental aspects: Pollutant emissions

Air pollution is a growing concern for all human society. Phenomena such as acid rain, photochemical smog, depletion of the ozone layer and global warming are directly linked to this type of pollution, with serious consequences to human health and climate change worldwide. The transportation sector is considered a major factor in the generation of air pollution, generating a large variety and quantity of polluting gases such as CO, CO_2, NO, NO_2, N_2O, C_2H_4, VOCs (Volatile Organic Compounds). According to data from the World Automotive Industry, the global fleet of motor vehicles reached in 2008 for the first time, the mark of 1 billion units. Considering that this number continues to grow significantly for many years, the transport will become increasingly relevant in greenhouse gas emissions.

Nowadays, in Brazil, there is a boom in sales of cars and motorcycles, which use various fuels such as gasoline, ethanol, diesel, biodiesel and natural gas. The environmental problem tends to rise with the new perspectives of the Brazilian economy.

The use of biofuels is surrounded by many international, scientific, technical and political controversies [4-6, 36, 37] about carbon dioxide emission, oil prices, fuel and food security, forest destruction, soil erosion, impacts on water resources, energy balance and energy security. Under the particular aspect of the greenhouse effect, it's necessary to consider not only the carbon dioxide content in the fuel, but also the entire chain of production. For the specific case of ethanol, we have to consider the industries of nitrogenous fertilizer, land use and emissions of nitrous oxides [9-11, 37, 38], agricultural machinery, cane transportation from the land to the plant, ethanol transportation to the consume centers, fermentation, generation of carbon dioxide at the plant (boilers) and, finally, we have to consider the source of energy that supplies the plant. All these criteria must be considered in order to ensure the sustainability of biofuels production chain.

3. Biodiesel in Brazil

3.1. Historical aspects

In Brazil, Count Francisco Matarazzo pioneered the use of biofuels. In the sixties, Matarazzo Industries sought to produce oil from the coffee beans. Ethanol from sugar cane was used to wash the coffee in order to remove impurities, unfit for human consumption. The reaction between alcohol and coffee oil resulted in the release of glycerol and ethyl ester, a product that is now called biodiesel [39].

In 1980, the project "PRODIESEL" was released at the Federal University of Ceará, by teacher Expedito Parente. The project was stalled due to disinterest of funding agencies, according to teacher Parente, responsible for the first patent for a process of Brazilian biodiesel in 1980 (PI - 8007957, requested the INPI - National Institute of Intellectual Property), produced from the mixture of castor oil and methanol [40].

The National Biodiesel Production and Use (PNPB) was established by the Decree of 23 December 2003. The production and consumption of biodiesel in Brazil were determined by Laws no. 11097 and 11116 in 2005. An important aspect of the law is assigned to the National Petroleum, Natural Gas and Biofuels Agency (ANP) the competence of the regulator of the biodiesel industry, as well as oil, natural gas and its derivatives.

The main thrust of the program is to implement a model of sustainable energy from the production and use of biodiesel produced from various oil sources, promoting social inclusion, ensuring competitive pricing, product quality and supply. According to PNPB, from January 2005, the addition of 2% biodiesel to diesel (B2) becomes mandatory. From January 2010, the addition of 5% biodiesel to diesel (B5) becomes mandatory.

3.2. Environmental and economic aspects

In 2011, Brazil produced 2.7 billion liters of biodiesel, moving 2.89 billion dollars. Brazil was the third largest producer, after the USA and Germany. In 2014, the Brazilian government provides for the addition of 10% biodiesel to diesel (B10) [41, 42]. Brazil is a tropical country, with a vast territory, intense sunlight, high biodiversity in oil plants, abundant water resources, regular rainfall and advanced agricultural technology, which generates economic advantages in the production of biodiesel.

The use of biodiesel provides excellent lubrication, maximizing engine life and low risk of explosion, facilitating transport and storage. The engines in trucks, tractors or machines generally do not require changes when using percentages to 20% of biodiesel added to diesel.

The use of biodiesel reduces dependence on petroleum and provides environmental benefits and life quality, improving public health in cities, due to the reduction of emissions of air pollutants, such as particulates, hydrocarbons (aromatic) and sulfur compounds. Moreover, unlike fossil fuels, the CO_2 released by burning biodiesel is recycled by absorption during the growth of oilseeds (photosynthesis) [43, 44]. Thus, the production of biodiesel is part of a cyclical process that assists in reducing the greenhouse effect, because there is a balance between the mass of carbon fixed and released into the atmosphere. Once it can be produced from vegetable oils used in cooking, biodiesel also helps reduce the problem of disposal of waste oils.

Biodiesel also provides interesting socioeconomic advantages, because it acts as a regulatory element of the vegetable oil markets, uses agricultural and industrial waste, reducing material sent to landfills and also reducing air pollution in large urban centers. Biodiesel production creates jobs, contributes to the establishment of man in the field and does not require major technological changes in engines [45, 46].

3.3. Ethanol and biodiesel: Gaseous emissions

Among the anthropogenic activities responsible for emissions, transport stands out due to large-scale increase in the number of motor vehicles that circulate everywhere on the planet. In this context, two noteworthy fuels: gasoline, fossil fuel hegemonic entire world's fleet of light vehicles and ethanol, which has gained importance with the advent of flex vehicles, especially in Brazil.

Due to the use of biodiesel (B5) in the Brazilian fuels matrix, studies of pollutant emissions from the combustion of biofuels blended with conventional diesel are required. We present an evaluation of emissions of an engine bench, with different mixtures of biodiesel and diesel.

For this, TEMPEST Electrochemical Analyzer to detect carbon monoxide (CO), the nitrogen oxides NO_x (NO+ NO_2) in the range of ppmv and the infrared analyzer (URAS), to detect carbon dioxide (CO_2). We also carried out the calibration of a photoacoustic spectrometer coupled to a CO_2 laser, which allows us to perform the detection of ethylene (VOCs) in the range of ppbv [23, 47-49].

4. Methodology

Photoacoustic technique presents a set of fundamental requirements to gas detection, such as high selectivity, multicomponent detection, high sensitivity, large dynamic range and good resolution time. This technique has been widely used in the detection of different gases in the concentration range of ppbv and sub-ppbv.

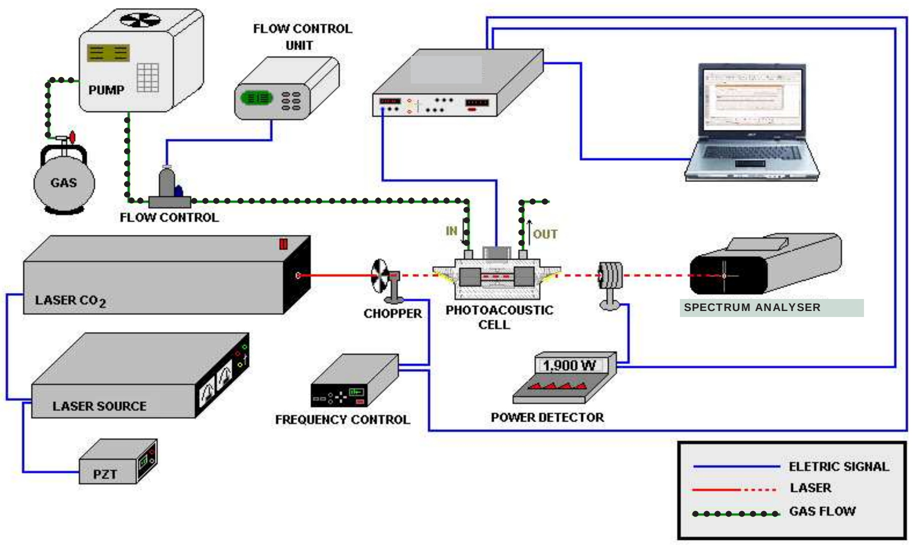

Figure 1. Scheme of the photoacoustic experimental setup

This methodology consists on the generation and detection of pressure waves (sound) inside a resonant cell, where the gas samples are placed. These samples are exposed to the incidence of modulated radiation, absorbing it at determined wavelengths. The resonant absorption of radiation generates rovibrational excitation in the gaseous molecules and a subsequent relaxation by collisions (heat). The modulate heating occurs in a constant volume, generating a pressure wave (sound), which can be detected by highly sensitive microphones inside the cell. These microphones convert this sound signal into an electric signal, which is filtered and detected. The Photoacoustic signal has a linear response with the concentration of the analyzed gas. The photoacoustic spectrometer (Figure 1) 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 teacher M. Sigrist (Swiss Federal Institute of Technology (ETH) – Zurich), flow meters 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 = 2.4kHz) of the photoacoustic cell were experimentally obtained. From these parameters we could determine photoacoustic signal of monocomponent sample by the relationship

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

where P is the power emitted by the laser, N is the density of molecules (≈2.5×10^{19} molecules/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.

4.1. 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.

The electrochemical techniques are powerful tools in the detection of gaseous species, especially because of some advantageous features, such as high sensitivity of the determinations, portability, easy of automation, the possibility of miniaturization and low cost. Currently, a wide variety of electrochemical sensors are being used to detect gas with numerous applications, among which we highlight the environmental application [22, 50].

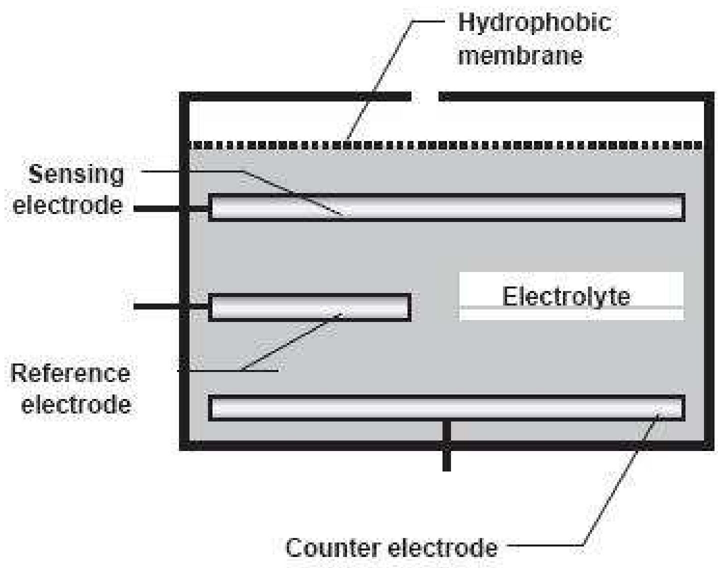

Figure 2. Detection scheme of an electrochemical sensor.

The electrochemical sensors (Figure 2) are composed of a sensing electrode, a counter electrode, a reference electrode and a reagent electrolyte inserted between the electrodes. Furthermore, a barrier permeable to gas, also known as hydrophobic membrane, must cover the sensor to avoid the entry of undesirable gases and water, and to control the amount of gaseous molecules that reach the electrode surface.

When the gas enters the sensor, it reacts with the electrodes and a process of oxidation-reduction occurs. As the electrodes are connected to a resistor, an electric current is generated between the cathode and the anode. The current generated is proportional to the gas concentration [50].

The Gas Analyzer URAS (Figure 3) uses a photoacoustic detection scheme capable of detecting a specific gas out of a multicomponent gas mixture avoiding cross interferences. [51] The selectivity of this instrument is achieved by comparing the direct absorption in a sample cell to that in a reference cell. After passing through the sample cell, each attenuated light beam enters a second detection cell filled only with the gas of interest as the detection cells are interconnected by a membrane connected to a capacitor. Since the dual beam is modulated, the difference in acoustic energy reflects the difference in absorption and thus the concentration difference between the sample cell and the reference cell. The species under investigation enables the wavelength to be selected in such a way that all wavelengths at which absorption occurs are simultaneously active. When there is no spectral overlap from other gases, additional absorptions in the sample cell do not contribute to the acoustic signal and the light passes the detection cell not attenuated. The photoacoustic instrument used in this work has been developed for gas detection concentrations in the ppmv range.

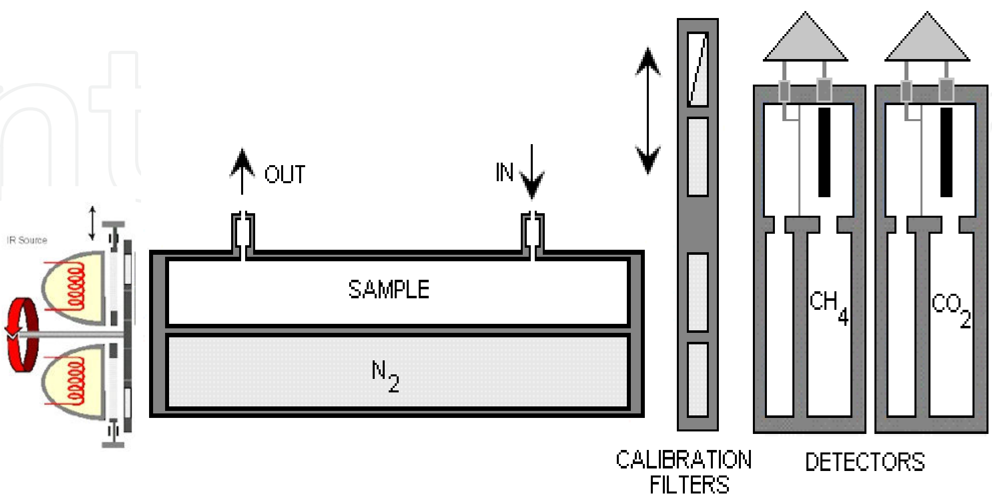

Figure 3. Detection scheme of Infrared Analyzer URAS

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5. Experimental procedure

The gas samples were collected from the exhaust of ethanol powered vehicles [52] and were stored in previously evacuated metallic canisters (SUMMA Andersen Instruments). The canisters are made of stainless steel and the samples were taken to the laboratory and coupled to our photoacoustic cell inlet. The gas sample was then pulled into this cell by a mechanical pump (Ambient Volatile Canister Sample AVOCS). Filters were used to remove the particulate matter larger than 2 μm. This collection was performed in two sequences in each vehicle: the first one with the bus engine turned on and without acceleration (*i.e.*, 1000 rpm of rotation speed) and the second one, with the bus engine turned on and with acceleration (*i.e.*, 3000 rpm of rotation speed). The gas samples were analyzed by a photoacoustic method at a pressure of 1 atm for detection of ethylene gas (C_2H_4). In conventional absorption spectroscopy, the absorption of the radiation power transmitted through the sample is measured. On the contrary, in photoacoustic spectroscopy, the absorbed power is determined directly via its heat and hence the sound produced in the sample.

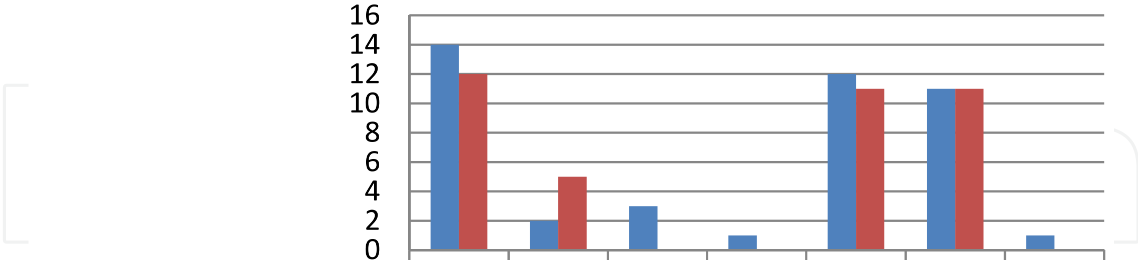
The Electrochemical Analyzer Tempest promosed the detection of CO, NO_x ($NO+NO_2$) from the exhaust of ethanol powered vehicles. The measurements were performed directly in the exhaust of these vehicles due to the portability of this equipment.

Other samples were collected from the exhaust of diesel engines (TOYAMA Model TD70F6.7 HP) and were stored in previously evacuated metallic canisters, similar procedure with the exhaust of ethanol powered vehicles. The sample collecting procedure was performed in two sequences: the first one with the bus engine turned on and at low rotation (3000 rpm) and the second one, with the engine turned on and at high rotation (9000 rpm). This procedure was adopted in the collection of samples from the diesel-biodiesel blends B5, B10, B15, B20 and B25 [53]. The measurements started in B5 because it is the diesel Brazilian standard. In this experiment, we used the soybean biodiesel and the gas samples were analyzed by the photoacoustic method at a pressure of 1 atm, for detection of ethylene gas (C_2H_4). The samples are also taken to Infrared Analyzer URAS was employed to detect CO_2 emissions. The Electrochemical Analyzer Tempest premised the detection of CO, NO_x ($NO+NO_2$) from the exhaust of diesel engines. The measurements were performed directly in the exhaust of these vehicles due to the portability of this equipment.

6. Results and comments

6.1. Ethanol engine

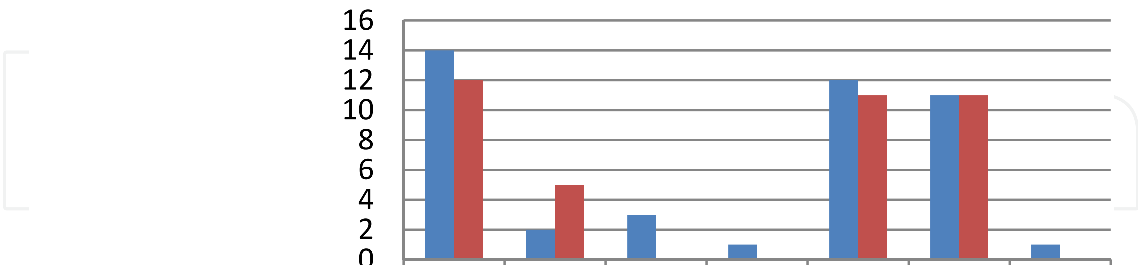
Figure 4 shows the emission of CO from the exhaust of ethanol powered. The measurements were performed in seven different kinds of vehicles manufactured in different years [51]. CO concentrations in the range 88-19240 ppmV were obtained. The CO emission was higher for vehicles under low engine speed. Probably, this mode of operation the combustion efficiency is smaller, so that the gases have been produced by incomplete combustion. We must also consider some variables such as manufacture year of the vehicle, make, model, power, maintenance, combustion temperature and rotation speed.



Vehicles	Astra 2006	Vectra 2007	Meriva 2007	Vectra 2007	Fiesta 2007	Focus 2007	Ford Ka 2008
NOx (ppmv) not accelerated	14	2	3	1	12	11	1
NOx (ppmv) accelerated	12	5	0	0	11	11	0

Figure 4. Emission of carbon monoxide by vehicles using ethanol engine

For the same group of ethanol vehicles, we carried out the measurement of nitrogen oxides (NO_x). In this case, the presence of nitrogen oxides is not related to the fuel, since the presence of nitrogen compounds cannot be observed in ethanol composition. The emission of NO_x is only due to oxidation of air nitrogen. We can notice (figure 5) a large fluctuation in the values of NO_x emitted by cars, which are not directly related to the model or year of manufacture of vehicles. This differential pattern is justified, since the temperature in the combustion chamber is the predominant factor in greenhouse gas emissions.



Vehicles	Astra 2006	Vectra 2007	Meriva 2007	Vectra 2007	Fiesta 2007	Focus 2007	Ford Ka 2008
NOx (ppmv) not accelerated	14	2	3	1	12	11	1
NOx (ppmv) accelerated	12	5	0	0	11	11	0

Figure 5. Emission of nitrogen oxides by vehicles using ethanol engine

Collection of gaseous samples was performed in another group of vehicles powered by ethanol, to identify the greenhouse gas CO, NOx and C_2H_4. CO concentrations in the range 350 to 7666 ppmv, NO_x concentrations in the range 1 to 464 ppmv [53] and C_2H_4 concentrations in the range 1 to 1198 ppmv were obtained.

6.2. Diesel-biodiesel engine

In the analysis of gas emissions from diesel engine exhaust, using binary mixtures diesel-biodiesel (B5, B10, B15, B20 and B25), CO_2 concentrations in the range of 1.95% and 3% were obtained in all mixtures tested. CO_2 emissions were higher in the accelerated mode of engine, and a reduction in the emission of this gas could not be observed with increasing percentages of biodiesel [52].

Moreover, CO concentrations in the range from 1400 to 2397 ppmv were obtained. A reduction in CO was not observed with the increase in the proportion of biodiesel. NO_x concentrations in the range 184-346 ppmv were also obtained. We observed an increase in the concentrations of NO_x to increase the proportion of biodiesel, especially for B15 and B25.

In the evaluation of C_2H_4 gas emissions, concentrations ranging from 67 to 123 ppmv were obtained in all mixtures evaluated. Emissions C_2H_4 were higher in an accelerated engine. A decrease in emissions of C_2H_4 with increasing percentages of biodiesel could not be observed [49].

7. Gaseous emissions in soils of sugarcane production

The use of fertilizer nitrogen-based synthetic has grown substantially in recent years, mainly in Brazil, which is the main agricultural activities in growing crops such as soybeans, corn, rice and beans, and large-scale cultivation of sugarcane sugar. In order to define the cycle of sustainability of ethanol production, we performed preliminary studies of the gas emissions of carbon dioxide (CO_2) and nitrous oxide (N_2O) from soils of sugar cane production in the region of Campos dos Goytacazes, RJ. [54]

The analyzes for the flow of nitrous oxide (N_2O) and carbon dioxide (CO_2) emitted from soils cultivated with sugarcane fertilized (urea and ammonium sulphate) and not fertilized, were made by the method known as "static dome." This method is the storage of gases within a dome made of PVC, glass, metal or acrylic, and may vary in size depending on the crop to be studied [55]. This method of static dome is the most commonly used and reported in the literature [56-58], because the gas concentrations vary linearly with time [59]. The gas samples are collected from the tanks and taken to be analyzed in the laboratory. The methods for determining gases concentration were previously described in methodology. CO_2 concentration was determined by Infrared Analyzer (URAS), N_2O concentration was determined by a photoacoustic spectrometer, similar to that described in Figure 1, but using a semiconductor quantum cascade laser (QCL) [20, 60-70] with an emission band ranging from 7.71 μm to 7.88 μm as the excitation source and a resonant differential photoacoustic (PA) cell as detector. The laser was fed applying pulsed current (26.2 mA) with a repetition rate of 400 kHz and a pulse duration of 50ns (duty cycle of 2%). With this methodology, it was possible to detect the emission of CO_2 gas from 500 to 1700 ppmv for the not fertilized area and concentrations from 600 to 1800 ppmv for the fertilized area. The N_2O emissions were from 84 to 321 ppbv for the not fertilized area and from 384 to 2066 ppbv for the fertilized area. The concentration value of the background region (380 ppbv) must be added to the N_2O concentrations.

8. Emission gases by the use of biofuels: Environmental problems

Air pollution generated by gases emitted by the use of biofuels (ethanol, diesel-biodiesel) and emissions from soils cultivated as sugar cane. It can produce serious environmental problems as produce a large amount of air pollutants [71], such as nitrogen oxide (NO_x), generators of acid rain and harmful to human health [72-76], carbon monoxide (CO), another pollutant emitted by ethanol and diesel-biodiesel engines, is not considered a direct greenhouse gas, but it is able to influence the production of methane and tropospheric ozone, which are important greenhouse gases [77-84]. Ethanol and diesel-biodiesel engines also produce volatile organic compounds (VOCs), such as ethylene [84-87].These chemical species are precursor for the generation of the tropospheric ozone [88-90], which is present in photochemical smog and directly affects human health. Tropospheric ozone can also trigger serious respiratory problems and cardiovascular effects [92-97]. Besides, it is a powerful greenhouse gas, whose formation is greatly potentiated by the incidence of sun radiation and the presence of nitrogen oxides (NO_x) [90, 91]. Other species, such as nitrous oxide (N_2O) and carbon dioxide (CO_2) are also present in the emissions studied, being considered important greenhouse gases.

9. Conclusion

The techniques presented, as photoacoustic spectroscopy, electrochemical sensors, and infrared analyzer (URAS) were sensitive and selective for the detection of gaseous pollutants in the range of ppmv and ppbv. Gases such as CO, NOx, CO_2, N_2O, C_2H_4 could be identified in our samples. Such gases are causing serious environmental problems, such as acid rain, global warming and the generation of tropospheric ozone, in addition to severe damage to human health. These gases are produced in the use of biofuels in the transport sector (engine exhaust) and in the cycle of sugar cane production (emissions from soil). We need to develop careful research in gas detection to identify the real contribution of the production chain of biofuels and biomass in general. Research should be encouraged in order to evaluate the real impacts on the use of biofuels. Thus, the use of new techniques, more accurate and selective, and the development of new methodologies for the identification of gases in trace level are essential.

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