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Abstract

Particulate matter, mainly its finer fraction, is among the main atmospheric pollutants present in an urban environment. The relationship between the increase in the concentration of this pollutant and the harm to human health is well established. The main sources of particulate matter in urban areas are mobile sources, which includes the exhaust emission from light duty vehicles.

In Brazil since its advent in 2003, there has been great penetration in the market for bi-fuel or "flex" vehicles, which use ethanol, gasoline or their mixtures as fuel. More recently, with the introduction of public policies that led to the adoption of improvements in the energy efficiency of vehicles, the use of direct fuel injection technology (GDI), as a trend in downsizing for improved fuel economy, gained prominence. This technology optimizes the burning process in the combustion chamber of the engines, making their use more efficient. On the other hand, it has the side effect of a higher emission of particulate matter compared to engines that use indirect injection. This higher emission is aggravated by the fact that the particulate matter is extremely fine, precisely the most harmful fraction because it contains a large amount of inhalable particles.

This work measured the emission of particulate matter in light passenger vehicles, characterizing it in terms of emitted mass in "flex" vehicles with port fuel (indirect) injection (PFI), using ethanol and gasoline, and in a gasoline vehicle with direct fuel injection. For the four flex fuel PFI vehicles, the average emission of particulate matter was 1.1 ± 0.3 mg.km^{-1} for the tests running ethanol, and 1.0 ± 0.3 mg.km^{-1} for gasohol. For the vehicle equipped with GDI the average emission, with gasohol fuel was 2.8 ± 0.2 mg.km^{-1}.

Introduction

Particulate matter and public health

The particulate matter (PM) is a complex mixture of organic and inorganic compounds. When referring to PM, we generally do not specify its chemical composition, considering only the concentration, and mass for a given fraction established by the aerodynamic diameter. Numerical patterns are based on epidemiological evidence of the association between particle size concentrations, and an excess of mortality or cardio respiratory effects [1]

Studies, however, show a strong relationship between PM and the effects of short-term health with increasing rates of morbidity, lung cancer, cardiovascular and cardiopulmonary diseases. The size of the particles and their surface area determine the potential for biological damage that they can cause. In general, the lower the PM, the greater the toxicity through oxidative stress and inflammation mechanisms [2].

The World Health Organization (WHO) has estimated that the air pollution is the cause of approximately four million premature deaths annually across the planet [3]. Among the pollutants considered by WHO, particulate matter affects people more than any other atmospheric pollutant. Worldwide, it is estimated that particulate matter is responsible for about 16% of deaths from lung cancer, 11% of deaths from pulmonary obstruction diseases and more than 20% of deaths from heart disease [3]. Pollution from particulate matter is an environmental problem that affects people around the world, but countries with average and low income are the most affected.

Oberdörster [4] reported that even small concentrations can lead to harmful effects, since ultrafine particles (diameter less than 0.1 μm) contribute in little terms of mass, but are very numerous, and can reach urban atmospheres at hundreds of thousands per cm^3. Riva et al. [5] also indicated, in experiments with rats, that low doses of fine particulate matter can lead to lung inflammation. In this respect, a trend can be worrying. This option of using the direct fuel injection technology in the spark ignition light vehicles, leads to less fuel consumption, which is sometimes more important to be obtained by manufacturers. In contrast, there may be an important emission of fine particulate matter, a pollutant that until now had not been a cause for concern in this type of vehicle.

Many of the pre-existing conditions that increase the risk of death in people with viral respiratory infection are the same diseases that are affected by long-term exposure to air pollution. There was an indication that long-term average exposure to fine particulate matter ($PM_{2.5}$) was associated with an increased risk of COVID-19 death in the United States [6].

As well as predisposing the people who have lived with polluted air for decades, studies have also suggested that air pollution particles may act as vehicles for viral transmission [7].

Particulate matter origin

The aerosol can be defined as being solids and liquids suspended in the air, in the form of particles wich present a certain degree of mobility [8]. The particulate matter can be composed of a mixture of pollutants. It originates from a number of sources and differs in structure, size and composition, depending on the source from which it comes.

The diameter is usually used as a measure of the particle size, although the definition of diameter itself is not uniform. The most common, however, is to use as a particle size descriptor, the aerodynamic diameter, which depends on the particle density, and is defined as the diameter of a spherical particle (assuming a density of 1g/cm3), which has the same deposition rate of the particle being measured [9,10].

Whether emitted directly as particles (primary aerosol) or formed in the atmosphere by gas-particle conversion (secondary aerosol), atmospheric aerosols vary in diameter in the range of a few nanometers (nm) to tens of micrometers (µm).

A typical precursor gas is sulfuric acid that is produced in the atmosphere via oxidation of sulfur dioxide, which is emitted mainly by combustion. Sulfuric acid has a low vapor pressure and in the presence of water, it condenses to form aqueous sulfate particles. The composition of these particles can then be modified by the condensation of other gases including NH_3, HNO_3 and organic compounds.

The carbon particles in the atmosphere consist of two components - graphitic or black carbon (black carbon - BC) also called elementary (elemental) or free carbon; and organic material (organic carbon – OC).The term elemental carbon refers to carbonaceous material that does not volatilize below a certain temperature, usually around 550ºC [8].

Organic carbon represents most of the fine aerosol and is mainly caused by the condensation of hydrocarbons of both biogenic and anthropogenic origin. Figure 1 shows the different processes involved in the production, growth and eventual removal of particles in the atmosphere. The gas molecules are in a size range between 10^{-4} and 10^{-3} µm. The agglomeration of gas molecules (nucleation) produces ultrafine aerosol in the range of 10^{-3} to 10^{-2} µm. These ultrafine particles then grow to a size between 0.01 and 1 µm (fine aerosol) by condensing the gases and by coagulation (collisions between the particles during random movement). Growth beyond 1 µm is slower; as the particles are then large enough for random movement occurs more slowly, reducing the rate of coagulation. Particles originating from gas condensation tend to accumulate in the size range between 0.01 and 1 µm, which is why this range is called the accumulation mode.

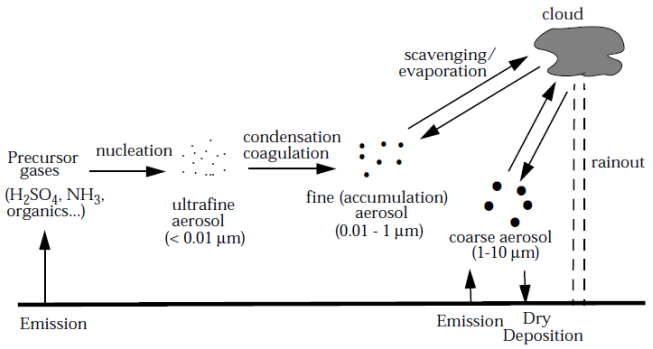

Figure 1 – Production, growth and removal of atmospheric aerosol
Source: [9]

It is usual to group the particles into three size classes, also referred as modes. A typical distribution, weighted by the volume of particles, in which they appear, divided into the following modes:

a) nucleation mode, also described as ultrafine, with size less than 0.1µm,

b) accumulation mode, also called fine, with a size of 0.1 to 1 µm,

c) coarse mode, in which the particles $PM_{2,5}$ and PM_{10} are found, with a diameter above 1 µm.

Particulate matter and Climate Change

Black carbon is a major component of particulate matter emissions from mobile sources and is believed to have a significant net atmospheric warming effect by enhancing the absorption of sunlight. Because of the combination of high absorption, the regional distribution and the capacity to form widespread atmospheric brown clouds in a mixture with other aerosol, emissions of black carbon are thought to be the second strongest contribution to climate change after CO_2 emissions [11]. It is estimated that 40% of gasoline PM emissions are black carbon. Removing black carbon emissions catched into immediate benefit to both global warming and public health.

Particulate matter standards and monitoring

In November 2018, the CONAMA Resolution 491 [13] was published, which established new national air quality standards for the main air pollutants, replacing the CONAMA Resolution 03 of 1990. The standards adopted for particulate matter were the same as those contained in State Decree of the State of São Paulo, 59113/2013 [14].

It was established new air quality standards for the parameters sulfur dioxide (SO_2), carbon monoxide (CO), inhalable particles (PM_{10}), fine inhalable particles ($PM_{2.5}$), total suspended particles (TSP), smoke, lead (Pb), nitrogen dioxide (NO_2) and ozone (O_3).

For the purpose of atmospheric measurement, establishment of atmospheric quality standards and subsequent planning of control measures, it was agreed to use the division only between particles up to 2.5 µm in diameter ($PM_{2.5}$), called fine or inhalable particles, and up to 10 µm (PM_{10}), called breathable particles [12].

With the exception of the parameters carbon monoxide (CO), total suspended particles (TSP) and lead (Pb), the new standards were established to be met in a stepwise manner in four stages, from an intermediate goal 1 (MI1) to a final standard (PF). Table 1 shows the new air quality standards for particulate matter, with their staggering intermediate targets up to the final standard.

Table 1 – Air quality standards for particulate matter

Standards	PM_{10} (µg/m^3)		$PM_{2.5}$ (µg/m^3)		TSP (µg/m^3)	
	24h	MAA	24h	MAA	24h	MGA
MI 1	120	40	60	20	240	80
MI 2	100	35	50	17	240	80
MI 3	75	30	37	15	240	80
PF	50	20	25	50	240	80

Source: [14]

Legend: MAA - annual arithmetic mean. MGA - annual geometric mean

The final standard, still with no defined date for implementation, is based on the recommendations of the World Health Organization (WHO).

Particulate matter vehicle emission

The combustion process in an engine is never complete. Thus, in addition to the characteristic combustion products of a hydrocarbon, which are CO_2 and water, other compounds will be formed. It is usual to classify these polluting compounds by grouping them in order to facilitate their measurement and control. The main groups of regulated pollutants are carbon monoxide (CO) and hydrocarbons (HC), which come directly from incomplete combustion and from transformations that occur both inside the combustion chamber of the engines and in the catalytic systems for after-treatment of emissions. The high temperatures in the combustion chamber are also responsible for the production of nitrogen oxides (NOx), through the chemical reaction of oxygen and nitrogen, the main constituents of air. In addition to these, another important pollutant formed is particulate matter, also caused by incomplete combustion of fuels.

During operation, numerous distinct technologies used in vehicles are at different levels of maintenance which also affect PM emissions. Even brand new vehicles emit PM from combustion but at low levels. The after-treatment system on most vehicles consists of a 3-way catalyst (TWC). The TWC was designed for simultaneous control of hydrocarbons, carbon monoxide, and nitrogen oxides.
Vehicles with 3-way catalysts would meet more stringent hydrocarbon and carbon monoxide emission standards while also meeting the first stringent nitrogen oxide standard. In oxidizing hydrocarbons, these systems also improved PM control decreasing emissions with increasing model year [15].
On the other hand Chen et al [16] note that although the TWC have the capability to extensively remove volatile and hydrocarbon compositions, it appears to be unable to capture the extremely tiny particles, below 10 nm in aerodynamic diameter.

Direct fuel injection

To face the challenges imposed by environmental legislation and in search of energy efficiency, the automotive industry has been developing and applying direct injection technology to spark ignition engines. Despite the known advantages, such technology has negative factors, with emphasis on the formation of particulate matter (PM).

Similar to diesel engines, in spark ignition engines with direct injection the fuel is injected directly into the combustion chamber and the specific power is controlled through the amount of fuel injected [17]. Figure 2 shows the schematic of the direct injection and pre-mixed engines.

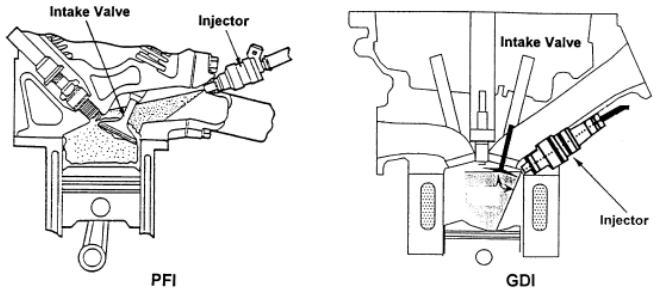

Figure 2 – Scheme of PFI and GDI. Source: [18]

With the injection of fuel under high pressure in the combustion chamber, the vaporization of the fuel occurs, therefore, the temperature in the chamber is reduced, thus allowing higher compression rates and poor operating condition. As a final result, it is possible to obtain lower specific fuel consumption values

Particulate matter emission control

Brazilian emission regulations, the PROCONVE – Control Program of Air Pollution from Motor Vehicles, was adopted in 1986 and had a succession of increasingly more stringent stage, denominated phases. For the light-duty vehicles it was implanted the phases L1 to L6, the later starting in the year 2014.
The PROCONVE standards are loosely based on early US regulations and on EU standards, but the respective PROCONVE phases are not directly equivalent to any of the US or Euro stages. Until the PROCONVE L6 phase it was not include any limit of PM for spark ignition light duty vehicles, just for the diesel ones. The L7 phase starting in 2022 will require a limit for particulate matter of spark ignition vehicles, when is used direct injection, equal to 6 mg.km^{-1}. In the next phase, L8, the final corporative limit foreseen for 2029 will be equal to 3 mg.km^{-1}.

Previous studies

There are many studies that show measurement results for particulate matter emission in light duty vehicles.

Chase et al. [19] reported that PM emissions from 11 LDVs had a mean FTP-weighted emission rate of 0.60 ± 0.17 mg.mi^{-1} for six low mileage vehicles and 0.67 ± 0.19 mg.mi^{-1} for five high mileage vehicles.
Maricq et al. [20] also reported measurements of LDV PM emissions at LEV III levels (limit 3.0 mg.mi^{-1}), finding that it is possible to measure PM emissions below 1 mg.mi^{-1} by the CVS dilution tunnel/gravimetric filter method. Nevertheless, they noted that using

a single filter to record PM emissions over an entire drive cycle may provide some improvement to the method.

Daemme et al [21] found a PM emission for a flexfuel GDI vehicle 0.63 ± 0.16 mg.km^{-1} when running with gasohol and 0.79 ± 0.11 mg.km^{-1} with ethanol fuel.

Saliba et al [22] testing 82 light-duty gasoline vehicles of in use California fleet, found that GDIs vehicles had, on average, a factor of 2 higher particulate matter (PM) mass emissions than PFIs due to higher elemental carbon (EC) emissions. For vehicles certified as LEV2 standard they found higher PM mass emissions from GDI vehicles (4.2 ±1.0 mg.mi^{-1}) compared to PFI vehicles (2.6 ± 0.5 mg.mi^{-1}).

Particulate matter emission rates

CETESB, the Environmental Company of the State of São Paulo, Brazil, is the body responsible for carrying out an inventory of motor vehicle emissions for the State of São Paulo. Currently, based on literature data, the particulate matter emission rate for gasoline and flex-gasoline cars used is: 2 mg.km^{-1} from 1982 to 1996 model year, and 1 mg. km^{-1} from 1997. No rate is used for ethanol vehicles.

MOVES – Motor Vehicle Emission simulator is the USEPA simulator for estimate and modeling the on road vehicle emissions. This software presents emissions rates for light duty vehicles separated by year of the vehicle, by particle size (PM $_{10}$ and PM $_{2.5}$), and for each size the fractions corresponding to organic carbon, black carbon and sulfates.
The emissions rates for total PM 10 vary from 27.7 mg.mi^{-1} for vehicle year 1990 to 2.5 mg.mi^{-1} for vehicle from the year 2004 to 2019 and 1.5 mg.mi^{-1} from 2020 onwards [23,24], as shown in Figure 3.

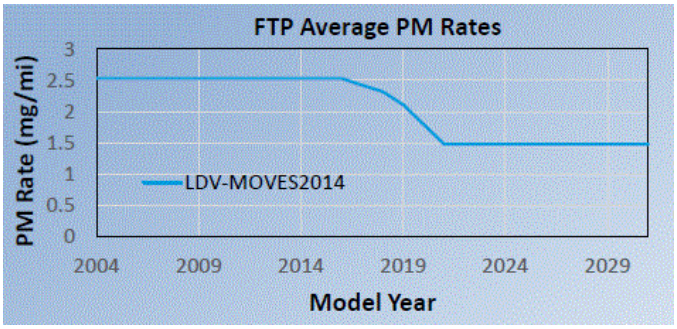

Figure 3 – MOVES 2014 PM rates for LDV.
Source: [24]

The latest version of MOVES is the 2014b one, and does not distinguish PFI and GDI vehicles. Since the data that guided the determination of that rates are from studies carried out in 2004/2005, modifications are being made, mainly to take into account the growing participation of GDI vehicles in the market.

Methodology

Characteristics of vehicles tested

Five in use vehicles were tested for the sampling of particulate matter. The tested vehicles were four automobiles with bi-fuel motorization ("flex"), and a gasoline car with gasoline direct fuel injection. Table 2 shows the main characteristics of the vehicles.

Tabela 2 – Vehicles tested

Veh. #	Fuel	Inject.	Displace-ment (L)	Year	Proconve phase	Odometer. (km)
# 1	Flex	PFI	1.4	2012	L5	150272
# 2	Flex	PFI	1.4	2012	L5	144122
# 3	Flex	PFI	1.4	2005	L4	169095
# 4	Flex	PFI	1.0	2014	L6	75950
# 5	Gasohol	GDI	1.6	2014	L6	76272

All tests were performed in duplicate and one of the vehicles (#4) could be tested in triplicate. The flex vehicles were tested with hydrated ethanol and gasohol (mixture of 22% anhydrous ethanol and 78% gasoline, by volume).

Test Methods

For the determination of particulate emissions from exhaust gas, the vehicles were tested by the method described in the standard ABNT NBR 6601 [25], which is similar to the procedure used by the US EPA (Code of Federal Regulation (CFR), 40 CFR part 86), through the use of the driving cycle FTP-75 - Federal Test Procedure. This standard prescribes the method for the determination of total hydrocarbons (THC) and non-methane hydrocarbons (NMHC), carbon monoxide (CO), nitrogen oxides (NO_x), carbon dioxide (CO_2) and particulate matter emitted by the engine through the tailpipe of light duty vehicles under simulated conditions of normal use in medium urban transit. FTP-75 is a three-phase cycle that simulates driving under cold-start conditions (phase 1), hot stabilized conditions (phase 2) and hot start conditions (phase 3) over an urban route (Figure 4).

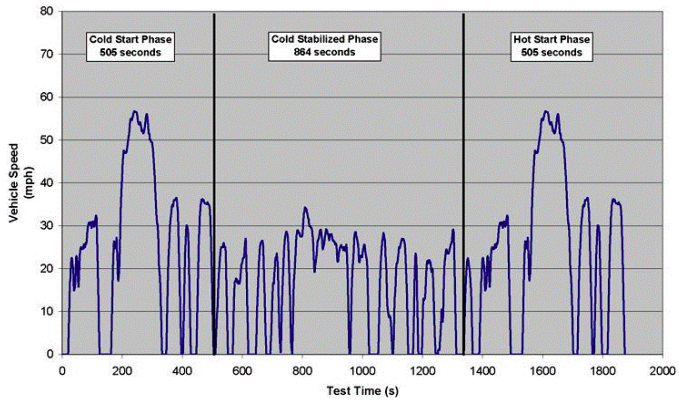

Figure 4 – Urban Drive Cycle – FTP-75. Source: USEPA, 2015

A single 48" roll electric dynamometer, model AVL Roadsim 2WD, was used to simulate the inertia and the resistance power of each vehicle tested (Figure 5). It was used the facilities of the vehicle emission laboratory of CETESB.

Figure 5 – Chassis dynamometer

Particulate matter sampling and analysis

The exhaust gases were diluted with ambient air of the laboratory using a constant volume sampler (CVS) model AVL CVS I60, and were then collected in Tedlar bags. This is the routine procedure for the method described in ABNT standard NBR 6601 (ABNT 2012). Another probe directs the exhaust gas to the filters holder. Three filters are disposed, one for each FTP test phase. According to that standard the filters are made of fluorocarbon with 47 mm in diameter. Figure 6 shows a diagram for the sample apparatus.

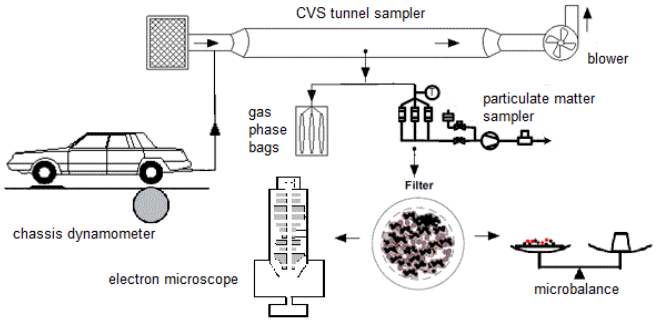

Figure 6 – Diagram of the sampling facilities

PM mass is then calculated by weighing the filters before and after the test. The filters collect all particle size fractions (nucleation, accumulation and coarse modes). To weigh the filters was used a micro balance model Sartorius CPA2P with a resolution of 1 µg.
For vehicles with modern after treatment technologies, the gravimetric method is reaching its detection limits [26]. A filter weighs about 150 mg, whereas the PM mass collected by the filter from new vehicles can reach as low as 10 µg or less. The increase in the measurement uncertainty of this method probably will led for looking into alternative detection techniques.
Despite this, CARB [27] found that repeat gravimetric measurements of FTP phase 2 and phase 3 PM emission rates for GDI vehicles and FTP weighted PM emission rates for PFI vehicles demonstrated that the gravimetric PM mass measurement method was capable of measuring PM mass emission rates at ~ 1 $mg.mi^{-1}$ (~ 0.6 $mg.km^{-1}$) or lower.

Microscopic imaging

Electron microscopy provides a means to examine the sizes and morphology of particles. This applies to solid particles. Semi-volatile particles are difficult to detect because they evaporate in the sample preparation and under vacuum and heating by the electron beam. Image analysis can provide a wealth of information about soot aggregates.
For this study it was used SEM – Scanning Electron Microscopy. The equipment and the analyses were provided by the Geosciences Institute of the University of Sao Paulo (USP). It was a scanning electron microscope Oxford model LEO 440I, showed in Figure 7.

Figure 7 – Scanning electron microscope

The same equipment is able to perform an Energy Dispersive Spectroscopy (EDS) analysis,It provided an elemental determination inside the samples in the SEM.
The images was obtained for filters sampled in the phase 1 only for the #3 vehicle, with magnification of 1000x, 2500x and 7500x, for gasohol and ethanol emission. The analysis planned for the filters of the other vehicles could not be obtained due to the occurrence of the global pandemic of COVID-19 that limited the activities of the laboratories involved. For the same reason it was not possible to obtain the results of the EDS analysis.

Fuels

For the tests with flex vehicles, when switching from ethanol to gasoline, before preconditioning, the fuel tank was drained and refilled with the test fuel. The fuels used in the tests follow the specifications prescribed by the Brazilian National Petroleum Agency - ANP. Tables 3 and 4 show the properties of the fuels used.

Table 3 – Standard gasohol for emission and consumption tests

Characteristic	Specification
Content of anhydrous ethanol	22% vol.
Density	735.0 to 765.0 $kg.m^{-3}$
Motor octane number (MON)	82.0 min.
Research octane number (RON)	93.0 min.
Reid vapor pressure at 37.8 °C	54.0 to 64.0 kPa
Sulfur (max.)	50 $mg.kg^{-1}$
Lead	5 $mg.L^{-1}$
Aromatics (max.)	35.0 % vol.
Olefins (max.)	15.0 % vol.

Note: According to the Petroleum National Agency (ANP) resolution number 764/2018

Table 4 – Standard commercial hydrated ethanol

Characteristic	Specification
Electrical conductivity (max.)	300 $\mu S.m^{-1}$
Density at 20 °C	805.2 to 811.2 $kg.m^{-3}$
Alcohol content (%)	92.5 to 94.6
pH	6.0 to 8.0
Evaporation residue (max.)	5 mg/100 mL
Sulfate ion (max.)	4 $mg.kg^{-1}$
Water content (max.) (%)	4.5
Methanol content (max.) (%)	0.5

Note: According to the Petroleum National Agency (ANP) resolution number19/2015

Results/Discussion

The individual results obtained for the mass emission of particulate matter for each test made are shown in the graph of Figure 8. The list of all the data obtained in the tests performed can be seen in the appendix tables.

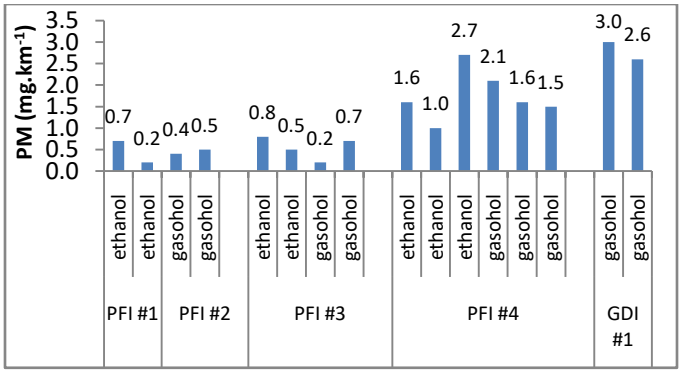

Figure 8- PM emissions for each test expressed in $mg.km^{-1}$

The graph of Figure 9 presents the average emission values obtained for each vehicle and each fuel used. Standard error was used as a dispersion measure, defined in equation 1:

Where:

S is the standard deviation of the sample,

n is the size (number of measurements) of the sample

$$s_x = \frac{s}{\sqrt{n}} \quad (1)$$

The standard error is indicating by the lines above each bar on the graph. For some vehicles this value was high, indicating that there was no good repeatability.

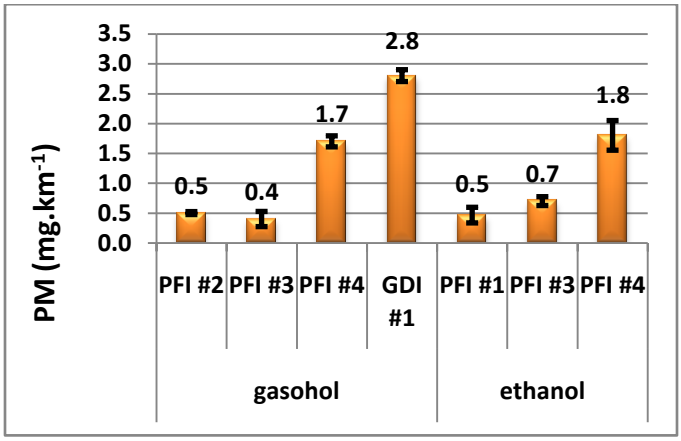

Figure 9- Average emissions of PM

On the other hand, a comparison of the averages obtained for each fuel, using a t-student statistical analysis showed that there was no difference in the PM emission when switching from ethanol to gasohol fuel.

For the four flex fuel PFI vehicles, the average emission of particulate matter was 1.1 ± 0.3 $mg.km^{-1}$ for the tests running ethanol, and 1.0 ± 0.3 $mg.km^{-1}$ for gasohol. For the vehicle equipped with GDI the average emission, with gasohol fuel was 2.8 ± 0.2 $mg.km^{-1}$.

As expected, the largest emission was in the vehicle equipped with GDI. In contrast, the newer flex vehicle (PFI # 4) was the one with

the highest emission among flex vehicles. The PFI vehicles # 1, # 2 and # 3, presented low PM emission, even though they are the oldest and with the highest accumulated mileage, having even surpassed the official warranty mileage (80,000 km).

Regulated pollutants emissions

Emissions values for regulated pollutants CO, THC and NOx were obtained for all tests. For the THC pollutant, there is a particularity in the control of vehicle emissions in Brazil. For flex vehicles when they are tested using ethanol as a fuel, the legislation allows the portion of ethanol emitted to be measured and discounted from the total emission.

The ethanol emission is usually high, especially in the cold phase of the test cycle, also increasing the THC emission value. This makes it difficult to compare this emission between the values obtained for the two fuels. The values obtained however are included in the list of all test values which can be seen in the appendix.

In the graph of Figure 10, the averages of the results obtained from the CO emission can be observed. The horizontal lines indicate the emission limits determined by legislation according to the year of the vehicle (Proconve phases 4, 5 and 6). The # 3 vehicle with the highest emissions is also the one with the highest age and the highest accumulated mileage, showing the expected influence of the deterioration in the emission of this pollutant. However, together with vehicles # 1 and # 2, it was the one that exhibited the lowest PM emissions, indicating that this direct proportionality between deterioration and emission may not apply to PM emissions. Note that these three vehicles had almost twice the manufacturer's warranty mileage.

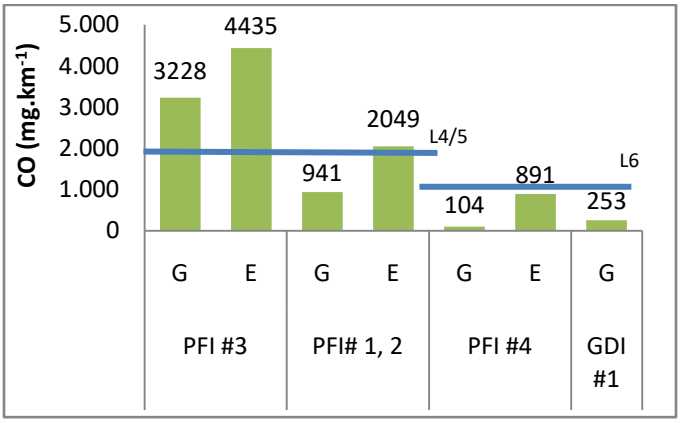

Figure 10 – Average emissions of CO
Legend: G = gasohol; E = ethanol

In the graph of Figure 11, the averages of the results obtained from the NOx emission can be observed. Also in this case, the horizontal lines indicate the emission limits determined by the legislation according to the year of the vehicle (Proconve phases 4, 5 and 6). Vehicle # 3 also had the highest emissions for NOx, showing the influence of deterioration in the emission of this pollutant. However, vehicles # 1 and # 2, with similar accumulated mileage, were the ones that exhibited the lowest NOx emissions, even lower than those for vehicles # 4 and GDI # 1, precisely the newest and still within the manufacturer warranty period of 80,000 km. As with CO, there was also no significant correlation with the emission of PM for this pollutant.

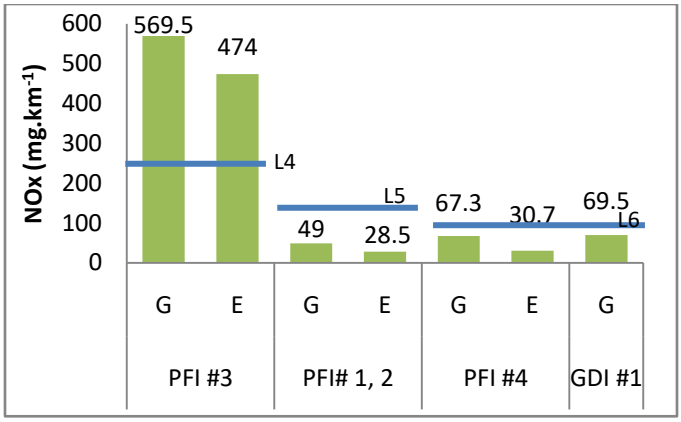

Figure 11 – Average emissions of NOx

PM emissions in relation to the cycle phases

It is known that, in general, emissions of particulate matter tend to be higher in the first phase of the FTP-75 driving cycle, because it is the phase in which the engine starts cold [15]. Total emission was considered to be the simple arithmetic sum of the emissions from the three phases and not the weighted average predicted by the standard for reporting the final result of a test.

The results obtained in this study, however, showed a great difference in this expected behavior, between the two fuels. The relationship between the emission obtained in the first phase of the cycle and the total PM emission when flex vehicles used ethanol as fuel was 49%, whereas for tests in which the vehicle used gasohol, this relationship was 79%. It was a similar value found by USEPA [15], of 84% in tests with 9 GDI vehicles.

The values obtained in the three phases of all tests performed are listed in the appendix.

Analysis of microscopic images

Figures 12 and 13 show the images obtained with scanning electron microscopy for gasohol and ethanol fuels, respectively, in the filters sampled in the first phase of the test with vehicle # 4.

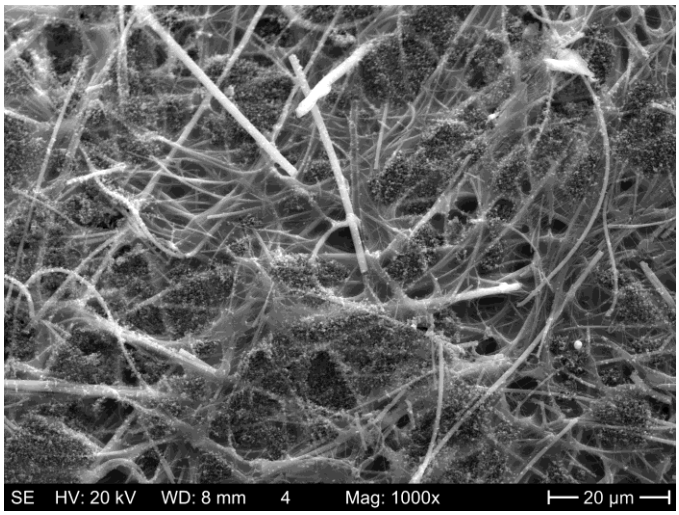

Figure 12 – SEM image with magnification of 1000x for gasohol emissions

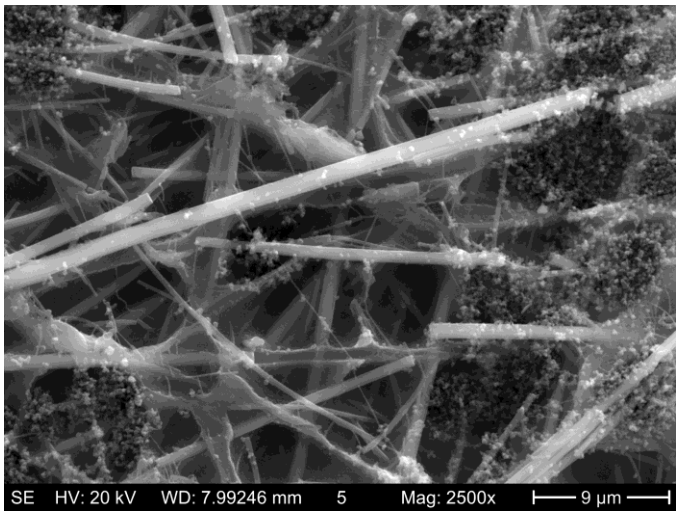

Figure 14 - SEM image with magnification of 2500x for gasohol emissions

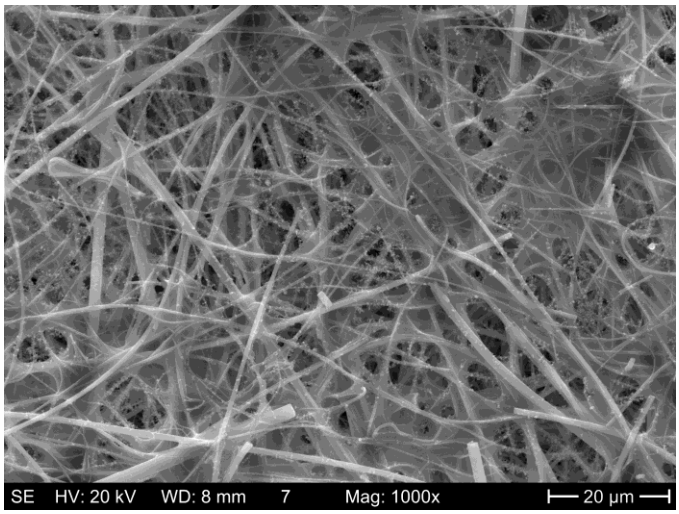

Figure 13 – SEM image with magnification of 1000x for ethanol emissions

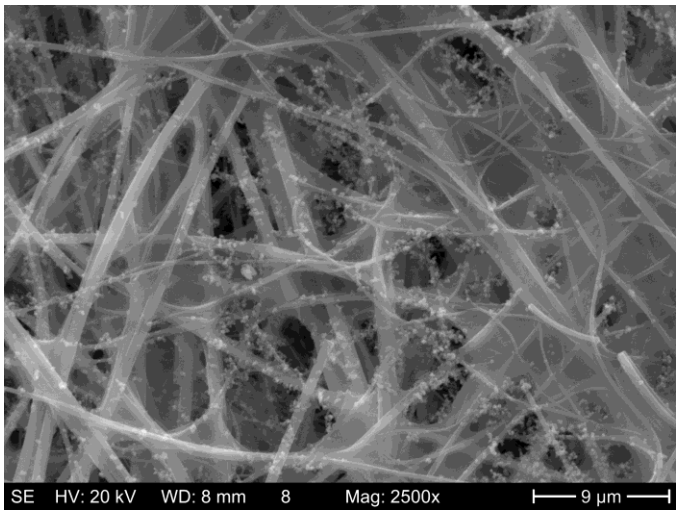

Figure 15 - SEM image with magnification of 2500x for ethanol emissions

Figures 14 and 15 show the images obtained with the scanning electron microscopy of the same filters but with a magnification of 2500x.

Although in terms of mass the emissions these tests did not show much difference (2.1 $mg.km^{-1}$ for gasohol and 1.7 $mg.km^{-1}$ for ethanol), it is possible to observe a greater agglomeration of particles in the filter corresponding to the gasohol test, as well as a larger number of particles.

Figure 16 shows the image obtained with a 7500x magnification for the gasohol test filter.

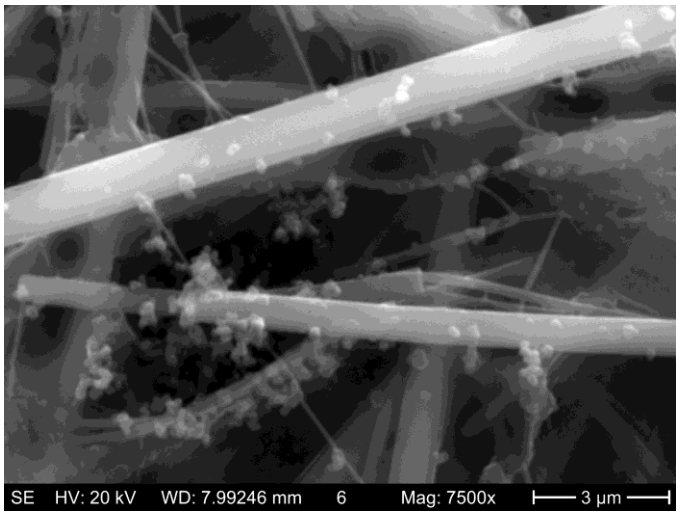

Figure 16 - SEM image with magnification of 7500x for gasohol emissions

From this image it is possible to estimate that the smallest particles are on the order of 0.5 microns or smaller, already within the scope of nanoparticles.

Summary/Conclusions

It can be seen, as expected, that the emission of particulate matter from the vehicle equipped with GDI technology was higher than the emission of PFI technology vehicles.

There was no significant difference in the PM emission between gasohol and ethanol fuels in flex vehicles. However, the images obtained by microscopy showed that there is a greater agglomeration of particles for the gasohol fuel, with the particles forming a kind of web between the fibers of the filter, which may indicate a greater amount of organic compounds of larger chains than those emitted when ethanol is used.

Regarding the emission of legislated pollutants, it can be observed that there was an excessive emission of CO and NOx in relation to the limits for one vehicle, but despite this, it did not present PM emission very different from the others.

In the tests in which gasohol was used, most of the PM emission was concentrated in phase 1 of the driving cycle, as expected and mentioned in the literature. However, when ethanol was used, there was not much difference between the emissions of the three phases of the cycle. Further investigation will be needed to confirm this behavior.

Even though images were obtained only for a vehicle with PFI technology, they showed that in the emission of these vehicles particles of nanometer size are formed and released to the environment. Because they are very thin, these are the particles that can cause the most damage to health. Further studies should be conducted to consolidate this understanding as well as to extend it to the emissions of vehicles equipped with GDI technology, in which the emitted particles are expected to be of an even smaller size.

Further studies are needed to determine the number of particles emitted and the compounds present in the particulate matter, including the separation of the carbon fractions present in this pollutant.

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Definitions/Abbreviations

ABNT	Technical Standards Brazilian Association
BC	Black Carbon
CETESB	Environmental Company of the State of São Paulo
CFR	Code of Federal Regulations
CO	Carbon Monoxide
CO_2	Carbon Dioxide
CONAMA	Brazilian National Environment Council

COVID-19	Corona Virus Disease 2019
CVS	Constant Volume Sampler
EDS	Energy Dispersive Spectroscopy
FTP-75	Federal Test Procedure
GDI	Gasoline Direct Injection
HNO_3	Nitric acid
NH_3	Ammonia
NO_2	Nitrogen Oxides
O_3	Ozone
OC	Organic Carbon
PFI	Portal Fuel Injection
PM	Particulate Matter
PROCONVE	Control Program of Air Pollution from Motor Vehicles
SEM	Scanning Electron Microscopy
SO_2	Sulfur Dioxide
THC	Total Hydrocarbon
USEPA	United States Environmental Protection Agency
USP	University of São Paulo
WHO	World Health Organization

Appendix

Table 5 – Pollutant values in mg.km-1 for each test made

Vehicle		Fuel	PM	NOx	CO	THC
2012, 1.4 PFI	PFI #1	ethanol	0.7	33	2175	150
		ethanol	0.2	24	1922	133
	PFI #2	gasohol	0.4	45	989	43
		gasohol	0.5	53	893	36
2005, 1.4 PFI	PFI #3	ethanol	0.8	477	4380	360
		ethanol	0.5	471	4490	459
		gasohol	0.2	588	3685	220
		gasohol	0.7	551	2771	165
2014, 1.0 PFI	PFI #4	ethanol	1.6	28	772	154
		ethanol	1.0	31	626	119
		ethanol	2.7	33	1276	79
		gasohol	2.1	53	106	0
		gasohol	1.6	42	99	30
		gasohol	1.5	51	107	27
2014, 1.4 GDI	GDI #1	gasohol	3.0	69	271	17
		gasohol	2.6	70	234	15

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Table 6 – PM values for each phase of the FTP-75 driving cycle

Vehicle	# test	Phase 1	Phase 2	Phase 3	Average
PFI #1	06.01-20U	0.9	0.0	1.9	0.7
	06.02-20U	0.2	0.0	0.5	0.2
PFI #2	03.03-20U	0.9	0.3	0.3	0.4
	03.04-20U	1.0	0.3	0.5	0.5
PFI #3	04.01-20U	1.6	0.5	0.7	0.8
	04.02-20U	1.0	0.3	0.5	0.5
	04.03-20U	0.5	0.2	0.0	0.2
	04.04-20U	1.0	0.5	0.7	0.7
PFI#4	018.01-19U	1.7	1.3	1.9	1.6
	018.02-19U	0.7	1.1	1.2	1.0
	018.03-19U	6.7	1.4	2.1	2.7
	018.04-19U	4.5	1.3	1.6	2.1
	018.05-19U	4.0	1.1	0.7	1.6
	018.06-19U	4.0	0.3	1.7	1.5
GDI #1	023.01-19U	7.1	1.4	2.6	3.0
	023.02-19U	6.4	1.3	2.1	2.6

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