A new method for determining speciated hydrocarbons in exhaust emissions of flex fuel vehicles using ethanol (E100)

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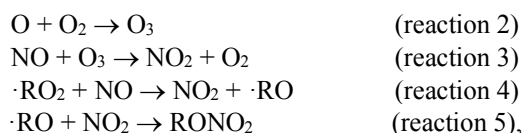**Pedro Vicentini**
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ABSTRACT

In urban environments, vehicle emissions are the main source of hydrocarbons (HC) which contribute to the formation of secondary pollutants like tropospheric ozone. However, the determination of HC in the exhaust emissions of vehicles fueled with ethanol is a great challenge, from the analytical point of view, due to the interference of several contaminants. In this project, sampling and analytical methods were implemented and optimized. Contaminations were minimized through a rigorous sampling and analytical procedure. Two flex fuel vehicles (PROCONVE L4 and L6 phases), using ethanol (E100) were tested. Vehicle exhaust samples were obtained during emissions testing with EPA-75 drive cycle (according to ABNT/NBR 6601) for each of the three phases: cold start, stabilized and hot start. The exhaust was collected in Tedlar® bags and transferred to electropolished stainless steel canisters. As in a previous study, C_4-C_{12} HC have been analyzed and considered negligible, in this one C_2-C_3 HC were analyzed using thermal desorption and gas chromatography with a mass spectrometry detector and a PLOT type chromatographic column and without using a cryogenic system. Ethene, acetylene and ethane represented 99% of measured non-methane hydrocarbons. The main improvements of the method are the sampling using inert canisters, the elimination of water vapor and ethanol through a dryer trap, the analysis of dilution air for each phase and the chromatographic analysis in the temperature interval from $25^{\circ}C$ to $250^{\circ}C$, avoiding the use of a cryogenic system. Since speciated HC emission results are required to calculate MIR (maximum incremental reactivity) and OFP (ozone forming potential) factors, these results can be useful for technical discussions about the ozone formation using Brazilian fuels.

INTRODUCTION

Tropospheric ozone is a criteria pollutant [1], formed in the atmosphere by photochemical reactions in the presence of sunlight and precursors pollutants, mainly oxides of nitrogen ($NO_x = NO + NO_2$) and volatile organic compounds (VOC). The photochemical processes related to tropospheric ozone formation have been extensively discussed in the literature [2]. In the troposphere, ozone is formed when NO_2 photodissociates into NO and oxygen atom (O (^{3}P)), as shown in reaction 1. The O (^{3}P) atom combines with O_2 to form O_3 (reaction 2). The reaction of O (^{3}P) with O_2 is the only known source of tropospheric ozone. In the absence of VOC, ozone reacts rapidly with NO to regenerate NO_2 (reaction 3) and its concentration depends on the NO_2/NO ratio and the rate of photolysis. However, in the presence of VOC, free radicals are generated in the process of VOC oxidation by hydroxyl radical ($\cdot$OH) and others photochemical oxidants, such as O_3 and NO_3, leading to the conversion of NO to NO_2 and a variety of potential reaction paths through the formation of another free radical (reaction 4). Radicals formed in reaction 4 may also react with NO_2 removing it from the system in a chain termination reaction (reaction 5). Thus, NO_x acts both to promote O_3 formation (reactions 1, 2 and 4) and to inhibit O_3 formation (reaction 3 and 5). Net photochemical formation of O_3 versus net photochemical loss of O_3 in the troposphere, therefore, depends primarily on the VOC/NO ratio (more than absolute concentrations of precursors) and on the reactivity of the VOC mixture [3]. At high VOC/NO_x ratios, the system becomes NO_x-controlled. At low VOC/NO_x ratios, the system is VOC-controlled, and ozone formation depends both on VOC concentration and speciation.

$$NO_2 \rightarrow NO + O \qquad \text{(reaction 1)}$$

$O + O_2 \rightarrow O_3$	(reaction 2)
$NO + O_3 \rightarrow NO_2 + O_2$	(reaction 3)
$\cdot RO_2 + NO \rightarrow NO_2 + \cdot RO$	(reaction 4)
$\cdot RO + NO_2 \rightarrow RONO_2$	(reaction 5),

where R stands for H or a hydrocarbon fragment.

Strategies to control tropospheric ozone and other photochemical oxidants focus on its precursor gas emissions. In urban areas, light duty vehicles and motorcycles are the main VOC emission sources. The knowledge of the composition of gas exhaust is important to estimate the Ozone Forming Potential (OFP) of emission sources and to develop effective control technologies. Data about speciated VOC emission sources is also useful for air quality modelling [4]. Previous studies have shown that the concentration and type of volatile organic compounds depend on the vehicle model, technology level, mileage, engine condition, fuel type, and operational factors such as speed, acceleration, gear selection and road gradient [5]; [6]. Among all the methods to measure emissions from vehicles, the chassis dynamometer is commonly employed and accepted by legislations worldwide to acquire a uniform source profile for vehicle evaluation and regulatory purpose [5]; [7]; [8]. The chassis dynamometer can simulate various engine operation conditions using different driving test cycles, which are fixed schedules of vehicle operation that allow an emission test to be conducted under reproducible conditions. In Brazil, the driving conditions are similar to the US test [9] and were established by the Brazilian Association of Technical Standards (ABNT), referred as ABNT NBR 6601 [7].

Analytical methods to determine hydrocarbons (HC, non-oxygenated volatile organic compounds) in automotive exhaust samples have been implemented by the California Environmental Protection Agency (CARB), using gas chromatography (GC) [10]; [11]. Briefly, two gas chromatographs (GCs) are used, one for analyzing the light end (C_2 to C_5) HC and the other for analyzing the mid-range (C_8 to C_{12}) HC. Each GC is equipped with a gas-sampling loop, cryogenic pre-concentrator and a flame ionization detector (FID). Samples are collected using small Tedlar® bags (typically 5 to 6 L in volume) [10]; [11].

However, the determination of HC in the exhaust emissions of vehicles fueled with ethanol is a great challenge, from the analytical point of view, due to the interference of several contaminants. In a previous study, a new method was described to determine HC in the interval C_4-C_{12}, emitted by flex fuel vehicles using gasoline (E22) and hydrous ethanol (E100), running on the ABNT NBR 6601 Brazilian Standard cycle and based on international procedures to analyze the organic compounds [12]. One of the main conclusions of that study was that the contribution of HC in the interval C_4-C_{12}, for vehicles using E100, represented approximately 1-2% of total non-methane hydrocarbons (NMHC) and was probably due to contamination. However, the determination of HC in the interval C_2-C_3 is extremely relevant since these compounds,

mainly ethene and propene, have high Maximum Incremental Reactivities (MIR).

The main goal of this study is to describe a method to determine the hydrocarbons in the interval C_2-C_3, emitted by flex fuel vehicles using hydrous ethanol (E100), based on the ABNT NBR 6601 Brazilian Standards and international procedures to analyze the organic compounds, as well as to calculate the ozone forming potential of the gas mixture due to HC. Weighted MIR and OFP values were also calculated for the C_2-C_3 HC fraction exhaust. The contribution of oxygenated species, such as ethanol and carbonyl compounds (CC) should also be considered in the calculation of the Non-Methane Organic Gases (NMOG) mass and in the OFP calculation but is not described here because specific methods are established [13]; [14]. This method can be also used to determine the C_2 to C_5 HC fraction for the exhaust of vehicles using E22.

MATERIAL AND METHODS

Vehicles, fuels and driving conditions

Two flex fuel light duty vehicles were used: PROCONVE L4 (PFI, 2.0L, 2008 model) and PROCONVE L6 (GDI, 1.6L, 2016 model). Fuel used in this study was commercial hydrous ethanol with up to 4.9% v/v of water (E100). For each vehicle, duplicate tests were performed. The driving conditions met the procedure published by the Brazilian Association of Technical Standards (ABNT), referred as ABNT NBR 6601 [7]. The driving cycle is the same that was established by the Code of Federal Regulations of USA (CFR), with the name Federal Test Procedure, FTP75 (also known as EPA75) [9]. The whole emissions test consists of the following steps:
1. Phase 1: Cold start transient phase, 0-505 s,
2. Phase 2: Stabilized phase, 506-1372 s,
3. Hot soak: a break of 10 minutes,
4. Phase 3: Hot start transient phase, 0-505 s.

Each vehicle was set on the chassis dynamometer with constant volume sampler (CVS 7200 series, HORIBA). Emissions from each phase were diluted and collected in separated Tedlar® bags. The exhaust of each phase and the dilution ambient air for each phase were analyzed by dedicated analyzers (CO, CH_4, THC, NO_x, CO_2). These tests were performed at the facilities of Petrobras Research Center (CENPES).

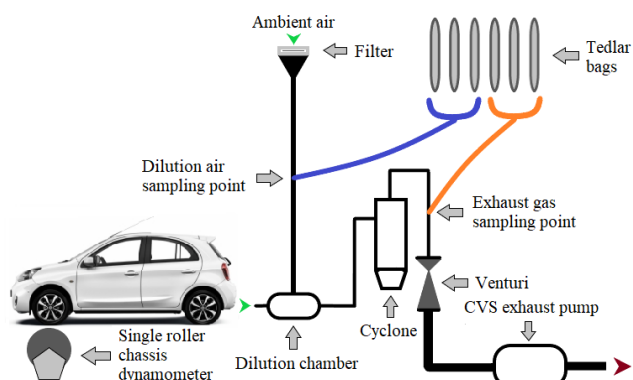In Figure 1, the chassis dynamometer, the constant volume sampler and the Tedlar bags are shown.

Figure 1. Schematic diagram of the constant volume sampler and method for sampling the diluted exhaust gas. Before performing the tests a strict fuel change procedure and analysis protocol was applied to avoid contamination. The fuel change was performed as follows: the fuel was drained, and the tank was flushed with 5 L of the new fuel. Then, this fuel was drained again and after filling the tank with 30 L, the vehicle was run for 30 km, before the pre-conditioning test, which was performed following the ABNT NBR 6601.

Hydrocarbons analysis (C_2-C_3)

The diluted exhaust and the dilution ambient air of each phase were collected in 6.0 L stainless steel canisters (Restek Silonite®) with TOV-2™ valves, by active sampling using a pumping device (Figure 2). The sampling line was previously purged with the sample contained in the Tedlar® bags to avoid contamination. Before sampling, the canisters were cleaned using a cleaning system (RM Environmental Systems Inc., model 960, CA, USA). Briefly, all canisters were evacuated to 500 mTorr at 120 °C and maintained in vacuum for 60 min. Then, the canisters were filled with humidified (50% relative humidity) helium (He) to 30 psig. This cycle was completed three more times for a total of four cycles; then, four additional cycles were completed with dry He. Blank samples were generated by pressurizing the clean canisters with He. The canisters were considered clean if less than 0.2 ng of each target compound was detected. Then, the canisters were evacuated below 5 mTorr prior to use. All canisters were labeled and were always used for the same type of sample (exhaust phase 1, exhaust phase 2, etc.).
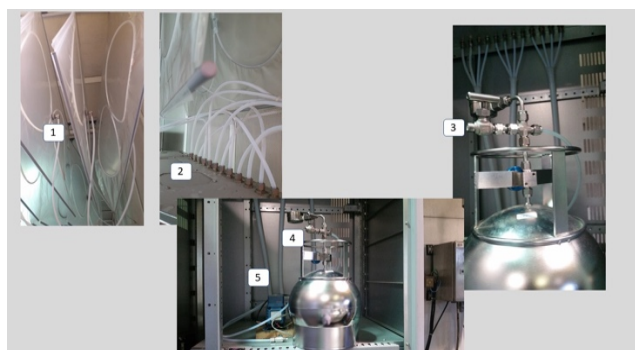

Figure 2. Tedlar bags and stainless-steel canister where the samples were transferred. The sample in the bag was transferred using a Teflon tube (connections 1 and 2) and a three-way valve (3). The system was previously purged using valve (4) and a small electrically powered pump (5).

After sampling at CENPES, the canisters were taken back to the Laboratory of Atmospheric Chemistry and Pollution/UFRJ and were kept at temperatures in the interval 20-22 °C. The samples were analyzed within 24 hours to avoid contamination, with thermal desorption coupled to a gas chromatograph with mass spectrometer detection (TD/GC/MS) system (Agilent, model GC 7890A, MS 5975C, CA, USA and Markes CIA Advanced, OH, USA). The method is an adaptation of the TO-15 Method [15], which has been previously optimized in the UFRJ laboratory for ambient samples [16]. In this study, some modifications were required to attend high pollutant concentrations and humidity of vehicular exhaust.

Samples were directed from the canister (flow rate of 20 mL min^{-1}) through a Nafion® dryer trap to reduce the water vapor and ethanol content below any threshold affecting the proper operation of the analytical system. It was then directed through a cold trap containing carbon molecular sieves (specific for compounds C_2-C_{12}) at -20 °C to retain the target compounds. The compounds were then thermally desorbed (300 °C) and transferred to a PoraPlot Q-HT column (25 m × 0.32 mm × 10 μm). He 5.0 (99.999%, ultra-high purity grade) was used as the carrier gas at a constant flow of 2.5 mL min^{-1}. The oven temperature program was set as follows: 25 °C for 5 min, 25 °C to 50 °C at 0.8 °C min^{-1}, 50 °C to 250 °C at 5 °C min^{-1} and 250 °C for 3 min. The injector temperature was 190 °C. This analytical method can be used for HC compounds in the interval from C_2 to C_5.
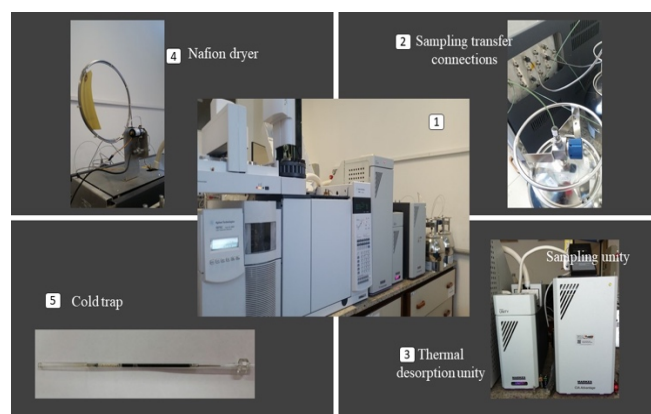

Figure 3. (1) Chromatographic system (TD/GC/MS), (2) Transfer connections, (3) Sampling and desorption Unities, (4) Nafion dryer and (5) cold trap used to transfer and analyze the samples (Laboratory of Atmospheric Chemistry and Pollution/UFRJ).

Each compound was identified by matching the retention time and mass spectrum of the unknown compound with those of a standard reference mixture (57 compounds,

Restek, 100 ppb, PO#127804, PA, USA). Both scan mode and selective ion monitoring (SIM) of the most abundant ions were used to ensure the correct identification of all compounds. Quantification was performed using selective ion monitoring (SIM) of the most abundant ions, based on an external analytical curve using the standard reference mixture that covered the entire concentration range of the samples. The calculated determination coefficients for all compounds were greater than 0.99. The analytical curve was constructed in triplicate, using five concentration levels and points were verified daily for quality control. The limits of detection (LOD) and quantification (LOQ), which were calculated from the noise standard deviation, were 0.2 ng and 0.6 ng, respectively, for all compounds.

All samples were measured in triplicate, and a difference of less than 25% was considered acceptable, as stated in the TO-15 Method [16]. The concentration determined in each exhaust phase was corrected by the dilution ambient air used in each phase. Since, as usual, the dilution air was pumped from the laboratory where the driving test was conducted, and no filters were used to retain the organic compounds, the composition of the dilution air changed during the test and the concentration of hydrocarbons was different in the three dilution bags.

The sample volume was adjusted for each test to obtain a chromatographic response consistent with the range of the analytical curve. Typically, 8 – 500 mL were analyzed. As sample concentrations covered a large range, two different volumes were analyzed.

The concentrations of each compound in the exhaust samples were calculated, for each phase in the driving cycle, using Equation 1:

$$CC_{ix} = EC_{ix} - [DAC_{ix} (1 - 1/DF_x)] \qquad \text{Equation 1}$$

where:
CC_{ix} = Calculated concentration of compound i in phase x
EC_{ix} = Compound i concentration determined in the vehicular exhaust (phase x)
DAC_{ix} = Compound i concentration determined in the dilution ambient air (phase x)
DF_x = Dilution factor reported for each phase in the test report (phase x)
x = phase 1 or phase 2 or phase 3
i = HC compound

The total mass emission (in mass/distance units) of each compound (i) emitted during the test was calculated using Equation 2, where the masses determined in each phase were weighted using the coefficients reported in the ABNT NBR 6601 document.

$$E_i = 0.43 \left[(E1_i + E2_i)/(D1 + D2) \right] + 0.57 \left[(E3_i + E2_i)/(D3 + D2) \right]$$
$$\text{Equation 2}$$

where:
E_i = calculated emission of compound i (in mass/distance units)
$E1_i$ = emission determined for compound i in phase 1 (in mass units)

$D1$ = distance in phase 1
$E2_i$ = emission determined for compound i in phase 2 (in mass units)
$D2$ = distance in phase 2
$E3_i$ = emission determined for compound i in phase 3 (in mass units)
$D3$ = distance in phase 3

Average Specific Reactivity (MIR Average) Methodology

The Maximum Incremental Reactivity scale (MIR) scale, created by William Carter and adopted by CARB, has been used to estimate the maximum equivalent ozone that would be produced by the various species found in this measurement [17]. Briefly, the reactivity scale is based on calculations of relative ozone impacts, expressed as mass of additional ozone formed per mass of VOC added to the emissions, for various compounds under various atmospheric conditions, given a chemical mechanism for the compounds and other relevant atmospheric species, models for various atmospheric conditions, and a modeling and reactivity assessment procedure. The values used in this work were calculated using the SAPRC-07 mechanism and were discussed in detail by Carter [18].

The speciation information, determined for each test, was further analyzed by calculating the composite ozone-forming potential of each species and of the total HC mixture. Multiplying the emission of the individual species by the MIR_i factor (of that compound) yields the maximum mass of ozone that might be produced by that mass of speciate (known as the ozone forming potential, OFP_i). These values can be calculated for each phase and for the weighted emission value for the complete test.

The "average reactivity" of the sample was calculated by summing all the individual OFP_i as shown in Equation 3.

$$\text{MIR average} = [\Sigma OFP_i] / \text{total emission} \qquad \text{Equation 3}$$

where:
MIR average = Average reactivity or specific reactivity
OFP_i = OFP for each compound

RESULTS AND DISCUSSION

For each test, the mean value of the GC triplicate analysis was previously calculated. The determined emissions for the two vehicles are shown in Table 1. Values are the means of the tests performed with each vehicle. The differences of results for the tests performed with the same vehicle were lower than 14% of the mean value, an excellent result considering all the variables and experimental procedures during the test, sampling and analysis. The concentration of C_3 compounds was lower than the LOQ.

The main contribution to emissions is due to phase 1 (cold start). Ethane was the only compound determined in phase 2, in small concentrations and with a contribution of 1.5 and 1 mg km^{-1} for vehicles PROCONVE L4 and L6, respectively. The most abundant compound is ethene, both in phase 1 and in the weighted gas mixture, with a contribution higher than 50%.

These results are in good agreement with the known chemistry of ethanol combustion [19]. Furthermore, Poulopoulos *et al.* studied the regulated and unregulated emissions from an internal combustion engine operated with ethanol-containing fuels and also found that ethene was the most abundant C_2 HC [20].

As detailed in the previous section and using Equation 3, the MIR average and OFP for each driving phase and the weighted value were calculated, as shown in Table 2.

Table 1. Emissions (in g km^{-1}) determined for vehicles PROCONVE L4 and L6 using E100 and the ABNT NBR 6601 driving test.

Compound	Vehicle L4		Vehicle L6	
	Emission (g km^{-1})	%	Emission (g km^{-1})	%
Phase 1				
Ethene	0.0331	56.4	0.00590	61.8
Acetylene	0.0144	24.5	0.00209	21.9
Ethane	0.0112	19.1	0.00156	16.3
Total	0.0587	100.0	0.00955	100
Phase 2				
Ethene	<LOD	0	<LOD	0
Acetylene	<LOD	0	<LOD	0
Ethane	0.0015	100	0.00001	100
Total	0.0015	100	0.00001	100
Phase 3				
Ethene	0.0013	0.0	<LOQ	0
Acetylene	0.0007	0.0	<LOQ	0
Ethane	0.0021	100.0	0.00011	100
Total	0.0041	100.0	0.00011	100
Weighted				
Ethene	0.0090	56.8	0.00123	60.6
Acetylene	0.0032	19.9	0.00043	21.5
Ethane	0.0037	23.3	0.00036	17.9
Total	0.0158	100.0	0.00202	100.0

Since the contribution of C_3-C_{12} HC is irrelevant [12], the MIR and OFP values for total HC is that of the C_2 fraction. OFP for PROCONVE L4 vehicle is approximately 7.4 times higher than the value for the PROCONVE L6 vehicle. The MIR values for both are in the interval from 5 to 6 , that were significantly higher than those calculated in two previous Brazilian studies when using ethanol: 3.99 for a PROCONVE L3 vehicle [21] and 3.18 for a PROCONVE L5 one [22]. High amounts of aromatic

hydrocarbons found in the NMHC exhaust composition of those vehicles (22% and 55% respectively) suggest a possible sample contamination.

Table 2. Weighted emissions (g km^{-1}), OFP (g O_3 km^{-1}) and MIR, determined for vehicles PROCONVE L4 and L6 using E100 and the ABNT NBR 6601 driving test.

Vehicle PROCONVE	Total C_2 HC Emission (g km^{-1})	OFP (g O_3 km^{-1})	MIR
L4	0.0158	0.0850	5.36
L6	0.0020	0.0115	5.69

The MIR results in this work also showed a significatively higher reactivity of ethanol than the one found for gasoline in other papers, which varies from 3 to 4 [21],[22],[23]. The total NMOG and MIR values were not evaluated since the emissions of ethanol and carbonyl compounds were outside the scope of the present study.

CONCLUSIONS

This study describes a method to determine the hydrocarbons, emitted by flex-fuel vehicles using ethanol (E100), measured on the ABNT NBR 6601 Brazilian Standard cycle. A strict sampling procedure protocol was applied to avoid contamination. The method can also be used to determine HC from C_2 to C_5 in the exhaust of vehicles using E22. The method is based on thermal desorption and gas chromatography with a mass spectrometry detector and without using a cryogenic system.

As previously determined, the contribution of C_4-C_{12} hydrocarbons using E100 was considered negligible (lower than 1-2% of the total non-methane fraction) [12]. In this study C_3 HC were lower than the limit of detection. The contribution of ethene is higher than 50% for phase 1 and for the weighted total emission. OFP values were 0.0850 and 0.0115 g O_3 km^{-1} for the PROCONVE L4 and L6 vehicles, respectively. The MIR values for the HC fraction from ethanol combustion were in the interval from 5 to 6, that were much higher than those ones calculated in two previous Brazilian papers [21],[22], but high amounts of aromatic hydrocarbons found in the exhaust composition of both studies suggest a possible sample contamination. The MIR results in this work also showed a significatively higher reactivity of ethanol than the one found for gasoline in other papers [21],[22],[23].

The main modifications, in comparison to CARB methods [10]; [11], are the sampling using inert canisters to reduce contamination, the elimination of water vapor and ethanol through a dryer trap to improve the chromatographic resolution and the analysis of dilution air for each phase. The chromatographic analysis in the temperature interval

from 25ºC to 250ºC, avoiding the use of a cryogenic system, which is very important to reduce costs and to simplify the method. Finally, the EM detector improves the identification and separation of similar compounds. In comparison the to our previous method [12], the main modification is the analysis of all C_2-C_3 hydrocarbons.

A new chromatographic method for the determination of C_2-C_{12} using one GC, without a cryogenic system, is being optimized in this project. The main improvement of the new method is the use of an unique CG and only one injection for the analysis.

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