Speciated hydrocarbons in exhaust emissions of Proconve L7 flex fuel vehicles using E22 gasohol and hydrous ethanol

Rogério Nascimento de Carvalho
Douglas Guerreiro Ribeiro
João Maximino de Souza
Tadeu Cavalcante Cordeiro de Melo
Pedro Caffaro Vicentini
Petróleo Brasileiro S.A.

ABSTRACT

This paper addresses the speciation of hydrocarbons from the exhaust emissions of Proconve L7 flex fuel vehicles using standard E22 gasohol and hydrous ethanol, which is necessary to obtain the Maximum Incremental Reactivity (MIR) coefficients applied in the NMOG (non-methane organic gases) emissions calculation. NMOG combined with NOx (nitrogen oxides) in the presence of sunlight are the main precursors of ozone in the troposphere and are regulated in Brazil from the Proconve L7 phase since 2022.

Hydrocarbons speciation, in the range of C_2 to C_{12}, were performed in a gas chromatograph coupled to a mass spectrometer detector and a flame ionization detector (FID), using inert metallic spheres for sampling and a standard reference gas mixture for calibration. Proconve L7 flex-fuel vehicles with port-fuel (PFI) and direct fuel injection systems (GDI) were evaluated with the canisters saturated with butane, following the NBR 6601 standard urban driving cycle. Results were consistent with previous studies of Petrobras with Proconve L4 to L6 vehicles, presenting typical hydrocarbons species of gasohol combustion in the tests with E22 and for the hydrous ethanol tests around 98% of C_2 compounds (ethene, ethane and acetylene) with no evidence of samples contamination.

INTRODUCTION

The Brazilian mobility sector is undergoing significant advancements in emission control and energy efficiency programs. For light-duty vehicles, the Proconve (Air Pollution Control Program by Motor Vehicles) initiated its L7 phase in 2022, presenting new challenges in emission limits followed by the L8 phase, started in 2025, introducing more stringent corporate emission limits [1]. These include, for instance, extending emission durability to 160,000 km and implementing new standards for evaporate emissions and Real Drive Emissions (RDE). Additionally, the establishment of combined "NMOG + NOx" emission limits is a significant advancement in regulatory measures to mitigate the formation of tropospheric ozone.

Elevated concentrations of tropospheric ozone contribute to photochemical smog formation and can lead to adverse effects on human health and the environment. The complexity of ozone formation process and its interactions with other pollutants make it a challenging issue to address.

NMOG (non-methane organic gases) are a subset of VOCs (volatile organic compounds) that include all organic compounds that can evaporate into the atmosphere. NMOG specifically excludes methane, focusing on other organic gases emissions (ethanol, aldehydes and non-methane hydrocarbons - NMHC). NMOG stands out, primarily due to their involvement in complex processes of tropospheric ozone formation [2 – 9].

In the Proconve L7 phase, the "NMOG + NOx" limit for passenger cars was set at 80 mg/km. For the Proconve L8 phase, this limit was reduced, as a corporate target, to 50 mg/km in 2025, with further reductions to 40 mg/km in 2027 and 30 mg/km in 2029.

To determine vehicle emissions of NMOG, Ibama (Brazilian Institute of Environment and Renewable Natural Resources), through Normative Instructions 22/2020, 21/2021, and 15/2022 [10 – 12], established a methodology based on procedures from CARB (California Environmental Protection Agency - Air Resources Board) [13 – 14]. In this methodology, the weighted NMOG emissions, in mg/km, are calculated from the emissions of non-methane hydrocarbons, aldehydes, and unburned ethanol from vehicle homologation tests as well as the average MIR (maximum incremental reactivity) of exhaust gases resulting from the use of different fuels, as stated in Equation 1.

$$NMOG = NONMHC_{Fuel} \cdot \frac{MIR_{NONMHC_{Fuel}}}{MIR_{NMOG_{E22}}} + ETOH.\frac{MIR_{ETOH}}{MIR_{NMOG_{E22}}} + $$
$$+ HCHO.\frac{MIR_{HCHO}}{MIR_{NMOG_{E22}}} + CH_3CHO.\frac{MIR_{CH_3CHO}}{MIR_{NMOG_{E22}}} \qquad (1)$$

where: $NONMHC_{Fuel}$ is the weighted non-oxygenated non-methane hydrocarbons emission for each fuel, $ETOH$ is the unburned ethanol emission, $HCHO$ is the weighted formaldehyde emission, and CH_3CHO is the weighted

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acetaldehyde emission. As can be noted in this formula, the emission of each hydrocarbon component is weighted by the respective ratio of its MIR value to the MIR of NMOG based on the use of reference E22 gasohol ($MIR_{NMOG\ E22}$).

The Maximum Incremental Reactivity - MIR is used to quantify the potential of a VOC to form ground-level ozone. The concept is based on the incremental reactivity of a VOC, which is defined as the amount of additional ozone produced when a small amount of the VOC is added to the atmosphere, divided by the amount of VOC added.

The MIR value is calculated using detailed chemical mechanisms that simulate the atmospheric reactions of VOC with nitrogen oxides (NOx) under sunlight. These simulations consider various environmental conditions and complex interactions between different chemical species [2].

The MIR scale was developed by Willian Carter [15] and ranks VOC according to their ozone-forming potential, with higher MIR values indicating greater reactivity and a higher propensity to contribute to ozone formation. This scale represents scenarios with high concentrations of NOx, making ozone formation more sensitive to VOC emissions and providing the greatest increase in ozone concentration due to variations in VOC levels [2].

This scale is well-established and widely used by environmental organizations. Both the US EPA (Environmental Protection Agency) and CARB rely on the MIR scale to assess the relative impact of VOCs on ozone formation, particularly those from vehicular emissions [13 – 18].

To determine the MIR_{NONMHC} of each fuel, it is necessary to perform the speciation of non-oxygenated non-methane hydrocarbons (NONMHC) present in the exhaust gases from the use of various fuels in combustion vehicles. Previous studies conducted with vehicles from the Proconve L4 to L6 phases provided these values [19 – 23]. Based on these studies, Ibama has established the following values (Table I) to be applied in each Proconve phase for the NMOG calculation using standard gasohol (E22) and hydrous ethanol for vehicle homologation [10 – 12].

Table I. MIR for Standard Gasohol (E22) and Hydrous Ethanol at Proconve L7 and L8 phases.

Proconve	MIR_{NONMHC}		MIR_{NMOG}
	E22	**Ethanol**	**E22**
L7 (2022)	4,70	3,16	4,86
L8 - Tab. 2A (2025)	4,20	4,37	4,39
L8 - Tab. 2B (2028)	3,69	5,57	3,91

This paper presents new results for the speciation of hydrocarbons in the exhaust gases of flex-fuel vehicles, using hydrous ethanol and standard gasohol (E22), which is a blend of 78% v/v gasoline and 22% v/v anhydrous ethanol. Results were obtained with two vehicles from the Proconve L7 phase, one with PFI (Port Fuel Injection) technology and the other with GDI (Gasoline Direct Injection) system.

METHODOLOGY

The method for VOC speciation applied in this study was initially proposed in a previous joint project between Petrobras and the Federal University of Rio de Janeiro (UFRJ) [2, 20–23]. This method is an adaptation of the US EPA TO-15 [24] and is based on a heart-cutting gas chromatography approach. It aims to obtain a complete NONMHC (C_2–C_{12}) speciated analysis of combustion gases using standard E22 gasohol and hydrous ethanol, mitigating any significant contamination when using ethanol as fuel in vehicles from the Proconve L4 to L6 phases.

This method was proposed as an alternative to the analytical methods implemented by the California Air Resources Board (CARB), which uses two gas chromatographs (GCs): one for analyzing the C_2 to C_5 range of hydrocarbons (HC) and the other for analyzing the C_6 to C_{12} HC range. These CARB methods are currently being adopted in the USA and are recommended for Brazil [10–14]. In these methods, Tedlar® bags are used for gas sampling, which are then transferred to the GCs by means of a gas-sampling loop and cryogenic pre-concentrator, where they are analyzed through flame ionization detectors (FID) [22].

The speciation method developed at UFRJ was successfully replicated in the laboratories of the Petrobras Research Center and applied to address the hydrocarbons (HC) speciated profiles of Proconve L7 vehicles.

The analytical system employed a gas chromatograph with two columns:

1) a DB-624 Ultra inert column (60 m x 320 μm x 1.8 μm), connected to a mass spectrometer (MS);

2) a PoraPLOT Q column (25 m x 320 μm x 10 μm), connected to a flame ionization detector (FID).

After injection, the analytes were eluted through columns 1 and 2, where C_2 to C_3 compounds were separated and detected on FID. At a run time of 9.2 minutes, a switch valve is closed and the outflow from column 1 is redirected from column 2 to the mass spectrometer, for detection of C_4 to C_{12} compounds.

The GC oven temperature program for each run was set as: 20ºC for 10 min, 20 to 240ºC at 5 ºC/min and post run at 250ºC for 5 min.

The sample collection system involved cleaning the inert steel spheres with 20 cycles of vacuum and pressurization at 80 ºC using humidified nitrogen.

A standard gas containing 57 ozone precursor compounds, with calibration traceable to the National Institute of Standards and Technology (NIST), was used as quantification standard.

This standard gas mixture was injected 10 times at GC-MS system for methodology validation, reaching maximum standard deviations lower than 10% for the 57 analytes. The literature repeatability acceptance is up to 25%. Also, the response linearity was verified with $R^2 > 0.99$ for all analytes.

After that, pilot emissions tests were conducted on a Proconve L7 flex-fuel vehicle to generate samples for VOC speciation: the results were satisfactory, and the methodology was considered implemented.

VEHICLES AND FUELS – Two flex-fuel vehicles representative from the Proconve L7 phase were used in this study with different propulsion technologies to verify their potential impacts on the VOC speciation profiles. Vehicles are identified as "PFI" and "GDI" and their main characteristics are listed in Table II.

Table II. Main characteristics of test vehicles.

Characteristic	PFI Vehicle	GDI Vehicle
Fuel System	Port Fuel Injection	Direct Injection
Air Intake System	Naturally Aspirated	Turbocharged
Engine Displacement	1.3-liter	1.0-liter
Accumulated km (approx.)	6,500 km	13,500 km
Year of Fabrication	2024	2022
Fuel Preheating System for Cold Start	Yes	No
Testing Sequence	Ethanol → E22	E22 → Ethanol

Both vehicles were tested with Brazilian standard fuels, E22 gasohol and 100% hydrous ethanol, in accordance with Resolution No. 864/2021 [25] from the National Agency of Petroleum, Natural Gas and Biofuels (ANP).

These fuels are used in fuel consumption and vehicle emissions testing for the homologation of new motor vehicles, in compliance with the Proconve L8 phase regulations. The components with contents greater than 1% m/m of the standard E22 gasohol (22% v/v of ethanol) used in this work are listed in Table III.

Table III. Composition of the standard E22 in % m/m gasohol used for tests.

Compound	Content *(% m/m)*
ethanol	24.67
toluene	22.26
2,2,4-trimethylpentane (iso-octane)	6.20
n-hexane	5.29
isopentane	5.26
n-pentane	4.81
3-methylpentane	2.64
2-methylpentane	2.31
methyl cyclopentane	1.92
branched-chain olefin c6	1.75
2,4-dimethylpentane	1.74
2,3,4-trimethylpentane	1.72
n-decane	1.19
Others (individual content < 1% m/m)	18.24

TEST PROCEDURES – Emission tests were performed in accordance with the Brazilian standards ABNT NBR 6601, NBR 12026, and NBR 15598 [26–28], as applied for vehicle homologation in the country. The NBR 6601 procedure is based on the EPA FTP-75 urban driving cycle, which consists of three phases: a cold start transient phase (phase 1), a stabilized phase (phase 2), and a hot start transient phase after a 10-minutes soak (phase 3). During each phase of conduction, ambient air and tailpipe gases diluted in ambient air are collected in Tedlar® bags, totaling six bags per test.

At least two tests were conducted for each fuel in both vehicles. Before each sequence, the vehicle tanks were fully drained and cleaned with a 5-liter flush of the new test fuel. After refueling, the vehicles were driven under urban conditions for approximately 30 km to adapt the electronic system to the new fuel. As defined by the NBR 6601 procedure, the pre-conditioning cycle (FTP-75 phases 1 and 2) was performed between 12 and 36 hours before the first test.

Additionally, before each test repetition, the vehicle vapor canister was fully saturated with butane to prevent any contamination from the previously used fuel in each vehicle. The primary function of the vapor canister is to capture and store fuel vapors from the fuel tank, preventing them from being released into the atmosphere, as a component of the evaporative emission control system.

Figure 1 shows the vehicle vapor canister in the conditioning system during the saturation procedure, as defined in the NBR 16927 [29].

Figure 1. Vehicle vapor canister in the conditioning system during the saturation procedure.

Promptly after each emission test, the samples of dilution air and diluted exhaust gas from each phase were transferred from Tedlar® bags directly to inert steel spheres, totaling six samples per test. To prevent contamination, the sampling line was pre-purged with the gas sample before proceeding with the transfer. The steel spheres were then transported to the laboratory for VOC speciation and the sample analysis was quickly initiated to minimize the risk of decomposition. Figure 2 presents a detailed view of the sampling point in the emission laboratory and Figure 3 illustrates the transfer process for each steel sphere.

Figure 2. Detailed view of the sampling point in the emission laboratory.

Figure 3. Sample transfer process for the steel spheres.

MIR CALCULATION – As stated in Equation 1, the determination of NMOG emissions from a vehicle using any fuel is based on the relationship between the MIR values of NONMHC, ethanol, and aldehydes, and the MIR of the NMOG with standard E22 gasohol. Ethanol, formaldehyde, and acetaldehyde MIR values were available at the Carter's scale [13 – 15] as 1.53, 9.46, and 6.54, respectively.

The MIR_{NONMHC} value of a fuel can be obtained by the share of its Ozone Formation Potential (*OFP*), in mg O_3/km, and the total emission of the speciated VOCs ($NONMHC_i$), in mg/km, as shown in Equation 2 [20].

$$MIR_{NONMHC} = \frac{OFP}{\sum NONMHC_i} \tag{2}$$

While the *OFP* is calculated by summing the emissions of each speciated VOC, weighted by its respective MIR_i value, as defined in the MIR Carter's scale (Eq. 3) [20].

$$OFP = \sum NONMHC_i . MIR_i \tag{3}$$

The values are computed for each phase of the urban drive cycle and subsequently weighed up to obtain the result, in accordance with the ABNT NBR 6601 standard.

The $MIR_{NMOG\ E22}$ value is calculated similarly to other MIR values, by considering the *OFP* and emissions of NMOG that include NONMHC, ethanol, formaldehyde, and acetaldehyde when using standard E22 gasohol. Table IV displays the Maximum Incremental Reactivity (MIR) values for various volatile organic compounds (VOCs) that act as ozone precursors, as determined by Carter's scale.

Table IV. Main VOCs MIR values – Carter's Scale [13].

Compound	MIR
ethene	9.00
acetylene	0.95
ethane	0.28
propene	11.66
propane	0.49
1-butene	9.73
n-butane	1.15
n-hexane	1.24
benzene	0.72
2,2,4-trimethylpentane	1.26
n-heptane	1.07
2,3,4-trimethylpentane	1.03
toluene	4.00
ethanol	1.53
formaldehyde	9.46
acetaldehyde	6.54

RESULTS AND DISCUSSIONS

In the previous joint project between Petrobras and UFRJ [2, 20–23], vehicles from the Proconve phases L4, L5 and L6 were assessed. The following average MIR_{NONMHC} with E22 gasohol and hydrous ethanol results were obtained, as shown in Table V.

Table V. Results of MIR_{NONMHC} with E22 gasohol and hydrous ethanol in Proconve L4 to L6 vehicles from the previous Petrobras-UFRJ joint research [2, 20–23].

Vehicle	E22	Ethanol
L4	3.9	5.4
L5	3.5	6.2
L6	3.6	5.7

The subsequent results present newly obtained MIR_{NONMHC} values from the assessment of two Proconve L7 vehicles using both E22 gasohol and hydrous ethanol.

Figure 4 illustrates the speciated distribution of VOCs in the emission gases collected from both L7 Proconve PFI and GDI vehicles using standard E22 gasohol. Results of two tests per vehicle are expressed as mass percent (% m/m) for each hydrocarbon species with concentrations exceeding 1% m/m. Other VOCs with concentrations below 1% have a combined maximum sum of 2.6%.

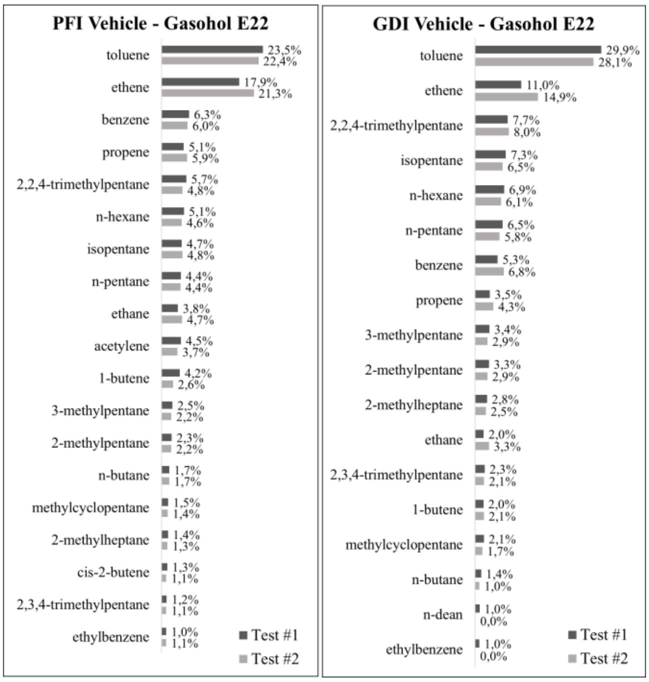

Figure 4. Speciated distribution of VOCs collected from PFI and GDI vehicles using E22 gasohol.

As observed, the results were highly consistent between duplicate tests and across both vehicles. The VOC species identified align with the gasohol composition and no unexpected hydrocarbons were detected. Toluene and ethene are the predominant species in the VOC composition of exhaust gases, accounting for more than 40% in all tests. Comparing the exhaust gases to the E22 gasohol main composition in Table III, there is a high correlation between them, with the elevated ethene levels being attributed to the ethanol content in the fuel.

The distributions of emitted VOCs sampled from the PFI and GDI vehicles using standard hydrous ethanol are presented in Figure 5. In these cases, 100% of the speciated hydrocarbons are included.

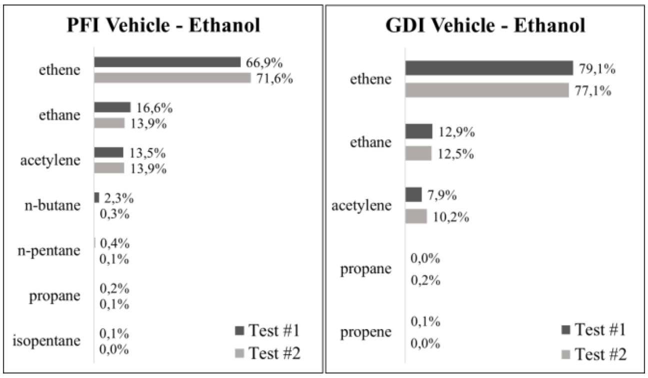

Figure 5. Speciated distribution of VOCs collected from PFI and GDI vehicles using hydrous ethanol.

Similarly to E22 gasohol, the results between duplicates and across both vehicles fueled with ethanol were quite consistent. Around 98% of the VOCs are hydrocarbons with two carbon atoms (C_2) – ethene, ethane, and acetylene – as expected from ethanol combustion without contamination by heavier compounds. Ethene (C_2H_4) concentrations ranged from approximately 67% to nearly 80%, contributing to elevated MIR_{NONMHC} values with ethanol, considering that ethene has a MIR value of 9.0 according to Carter's scale (Table IV).

Tables VI and VII display the hydrocarbon emission from each test conducted on L7 vehicles using E22 gasohol and ethanol and their respective MIR_{NONMHC} results. The data includes total hydrocarbons (THC), non-methane hydrocarbons (NMHC), the sum of speciated volatile organic compounds ($\sum$NONMHCi), and the ozone forming potential (OFP).

Table VI. HC emissions and MIR_{NONMHC} with E22 gasohol in Proconve L7 vehicles.

L7 Vehicles	E22 Gasohol					
	PFI			GDI		
	Test #1	*Test #2*	Average	*Test #1*	*Test #2*	Average
THC *(mg/km)*	*8.0*	*9.2*	8.6	*32.6*	*21.3*	27.0
NMHC *(mg/km)*	*5.5*	*6.5*	6.0	*27.6*	*15.1*	21.3
$\sum$ $NONMHC_i$ *(mg/km)*	*3.7*	*3.6*	3.6	*13.4*	*7.6*	10.5
OFP *(mg_{O3}/km)*	*16.2*	*16.6*	16.4	*46.6*	*28.8*	37.7
MIR_{NONMHC}	*4.4*	*4.6*	**4.5**	*3.5*	*3.8*	**3.6**

Table VII. HC emissions and MIR_{NONMHC} with hydrous ethanol in Proconve L7 vehicles.

L7 Vehicles	Ethanol					
	PFI			GDI		
	Test #1	*Test #2*	Average	*Test #1*	*Test #2*	Average
THC *(mg/km)*	*39.9*	*31.1*	35.5	*18.8*	*42.7*	30.7
NMHC *(mg/km)*	*20.9*	*19.6*	20.3	*10.5*	*27.0*	18.7
$\sum$ NONMHC$_i$ *(mg/km)*	*3.9*	*3.4*	3.7	*3.7*	*4.7*	4.2
OFP *(mg$_{O_3}$/km)*	*24.3*	*22.6*	23.4	*26.5*	*33.1*	29.8
MIR_{NONMHC}	*6.2*	*6.6*	**6.4**	*7.2*	*7.1*	**7.2**

The MIR_{NONMHC} results align well with the previous study, as shown in Table V. The mean values for both vehicles are 4.1 with E22 gasohol and 6.8 with hydrous ethanol. As anticipated, the values obtained with ethanol are higher than those with E22 gasohol. This can be attributed to the high ethene content in the speciated VOCs (Figure 5), which has a MIR coefficient of 9.0 on the Carter's scale.

CONCLUSIONS

The procedure for VOC speciation of ozone precursors from vehicle exhaust emissions, initially developed in collaboration between Petrobras and the Federal University of Rio de Janeiro (UFRJ), has been successfully implemented at the Petrobras Research Center. This method effectively determines the hydrocarbon profile within the C_2 to C_{12} range, essential for calculating Maximum Incremental Reactivity (MIR) coefficients used in NMOG (non-methane organic gases) emissions assessments with various fuels.

The analytical system employed a gas chromatograph coupled with a mass spectrometer (GC-MS). Compounds in the C_2 to C_3 range were detected using a flame ionization detector (FID) and in the C_4 to C_{12} range, using mass spectrometry (MS). A standard gas containing 57 ozone precursor compounds, with calibration traceable to the National Institute of Standards and Technology (NIST), was used.

Two L7 Proconve vehicles employing different technologies (PFI and GDI) were tested in accordance with the emission homologation procedure in Brazil, as outlined by the ABNT NBR 6601 standard. This included saturating vapor canisters with butane prior to each test. To prevent cross-contamination, exhaust samples were collected directly from the emission measurement system into inert steel spheres previously cleaned with cycles of vacuum and pressurization using humidified nitrogen. Samples were promptly injected into the speciation system to prevent deterioration of the species.

The results were consistent between duplicate tests and aligned with expected emissions profiles for E22 gasohol and hydrous ethanol, with no evidence of contamination. The VOC profiles were consistent with those obtained in previous UFRJ studies on Proconve L4 to L6 vehicles, showing a predominance of toluene and ethene in E22 gasohol tests and C_2 compounds (mainly ethene) in hydrous ethanol tests. The average MIR_{NONMHC} values for the tested vehicles were 4.1 with E22 gasohol and 6.8 with hydrous ethanol.

These results can contribute to enhance the understanding of the reactivity of vehicle emissions and their potential for ozone formation with different fuels, a pertinent issue in the current Brazilian emission regulation landscape.

REFERENCES

[1] CONAMA - National Council for the Environment, **Resolution No. 492/2018**: *Establishing PROCONVE L7 and L8 phases for light-duty vehicle emission standards*. 2018.

[2] BARROS, B. S. R., *Avaliação do potencial formador de ozônio de hidrocarbonetos emitidos pelo escapamento de veículos flex*. (PhD Thesis) – Chemical Institute, Federal University of Rio de Janeiro, Rio de Janeiro, 2024.

[3] CARTER, W. P. L., *Development of Ozone Reactivity Scales for Volatile Organic Compounds.* Journal of the Air and Waste Management Association, v. 44, p. 881-899, 1994.

[4] WHO - World Health Organization, **WHO global air quality guidelines.** *Particulate matter (PM2.5 and PM10), ozone, nitrogen dioxide, sulfur dioxide and carbon monoxide,* 2021.

[5] ATKINSON, R. *Atmospheric chemistry of VOCs and NOx*. Atmospheric Environment, v. 34, p. 2063-2101, 2020.

[6] FINLAYSON-PITTS, B. J.; PITTS, J. N. *Chemistry of the Upper and Lower Atmosphere. Theory, Experiments and Applications.* 3rd Ed. Academic Press: San Diego, USA, 2000.

[7] SEINFELD, J. H.; PANDIS, S. N. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, 3rd Ed. John Wiley & Sons: Hoboken, New Jersey, USA, 2016.

[8] DANTAS, G.; SICILIANO, B.; SILVA, C. M.; ARBILLA, G. *A reactivity analysis of volatile organic compounds in a Rio de Janeiro urban area impacted by vehicular and industrial emissions*. Atmospheric Pollution Research, v. 11, p. 1018-1027, 2020.

[9] SICILIANO, B. *Determinação de hidrocarbonetos (C_4-C_{12}) no escapamento de veículos flex*, 2020. (M. Sc. Thesis) – Chemical Institute, Federal University of Rio de Janeiro, 2020.

[10] IBAMA - Brazilian Institute of Environment and Renewable Natural Resources, **Normative Instruction No. 22/2020**, 2020.

[11] IBAMA - Brazilian Institute of Environment and Renewable Natural Resources, **Normative Instruction No. 21/2021**, 2021.

[12] IBAMA - Brazilian Institute of Environment and Renewable Natural Resources, **Normative Instruction No. 15/2022**, 2022.

[13] CARB - California Air Resources Board, *California non-methane organic gas test procedures for 1993 through 2016 model year vehicles*, 2015.

[14] CARB - California Air Resources Board, *California non-methane organic gas test procedures for 2017 and subsequent model year vehicles*, 2015.

[15] CARB - California Air Resources Board, *Tables of Maximum Incremental Reactivity (MIR) Values*, 2009

[16] CARTER, W. P. L., *Development of Reactivity Scales for Volatile Organic Compounds*, 2013. Available: <https://intra.engr.ucr.edu/~carter/pubs/AQMDtalk2.pdf> Access: May 14th, 2025

[17] CARTER, W. P. L., *Development of Ozone Reactivity Scales for Volatile Organic Compounds*. Journal of the Air and Waste Management Association, v. 44, p. 881-899, 1994.

[18] VENECEK, M. A.; CARTER, W. P. L.; KLEEMAN, M. J., *Updating the SAPRC Maximum Incremental Reactivity (MIR) scale for the United States from 1988 to 2010.* Journal of the Air & Waste Management Association, v. 68, n. 12, p. 1301-1316, 2018.

[19] GRANER, L.; GARCIA, I. S.; JOSEPH Jr., H., *Estudo comparativo dos hidrocarbonetos emitidos pelo gás de escapamento de um veículo flex quando abastecido com E22 e com E100*, XXI International Symposium on Automotive Engineering – SIMEA 2013, v. 1, n. 1, p. 89-101, 2013.

[20] SICILIANO, B.; SILVA, C. M.; LOUREIRO, L. N.; VICENTINI, P. C.; ARBILLA, G., *Hydrocarbon emissions in flex fuel vehicles using ethanol: Preliminary results using a method implemented in Brazil*. Fuel, v. 287, p. 119506, 2021.

[21] ARBILLA, G.; SILVA, C.M.; SICILIANO, B.; VICENTINI, P.; LOUREIRO, L., *A new method for determining speciated hydrocarbons in exhaust emissions of flex fuel vehicles using ethanol (E100).* XXVIII International Symposium on Automotive Engineering – SIMEA 2021, v. 8, p. 429-435, 2021.

[22] SICILIANO, B.; SILVA, C. M.; DE MELO, T.; VICENTINI, P.; ARBILLA, G., *An analysis of speciated hydrocarbons in hydrous ethanol (H100) and ethanol-gasoline blend (E22) for vehicle exhaust emissions*. Atmospheric Environment, v. 285, p. 119248, 2022.

[23] SILVA, C. M.; SICILIANO, B.; DANTAS, G.; ARBILLA, G., *An improvement of method TO-15A, aided by heart-cutting multidimensional gas chromatography, for the analysis of C_2-C_{12} hydrocarbons in atmospheric samples*. Microchemical Journal, v. 183, p. 108008, 2022.

[24] U.S. EPA – United States Environmental Protection Agency, **Method TO-15A** – *Determination of volatile organic compounds (VOCs) in air collected in specially prepared canisters and analyzed by gas chromatography-mass spectrometry (GC-MS)*, 2019.

[25] ANP - National Agency of Petroleum, Natural Gas and Biofuels, **Resolution No. 864/2021**: *Specifications of reference fuels for the approval of new motor vehicles*, 2021.

[26] ABNT - Brazilian Association of Technical Standards, **NBR 6601:2021** – *Light duty road vehicles - Determination of hydrocarbons, carbon monoxide, nitrogen oxide, carbon dioxide and particulate material on exhaust gas*, 2021.

[27] ABNT - Brazilian Association of Technical Standards, **NBR 12026:2021** – *Light duty road vehicles - Determination of aldehydes and ketones in exhaust gas by liquid chromatography - DNPH method*, 2021.

[28] ABNT - Brazilian Association of Technical Standards, **NBR 15598:2022** – *Light road vehicles - Determination of unburned ethanol in exhaust gas by gas chromatography or photoacoustic analysis*, 2021.

[29] ABNT - Brazilian Association of Technical Standards, **NBR 16927:2021 Ed. 2** – *Light duty vehicles with spark ignition engines - Measurement of evaporative emission under diurnal, hot soak and refueling conditions*, 2021.