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Evaporative volatile organic compounds from gasoline in Mexico City: Characterization and atmospheric reactivity

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Abstract

In 2016, only 4% of energy consumption in transportation came from renewables; then, use of fossil fuels will continue by several decades, with their corresponding evaporative and combustion emissions. Volatile organic compounds (VOCs) from gasoline evaporation were determined in Mexico City in order to know the emission of each compound to the atmosphere, as well as their ozone formation potential. Headspace technique was used to characterize the VOC evaporated mixture from different gasolines consumed in the city. Analyses of VOCs were carried out by chromatography with flame ionization detector. Composition of gasoline vapors was 18.40 ± 4.43 for paraffin, 52.4 ± 2.09 for iso-paraffin, 11.8 ± 3.71 for olefins, 3.1 ± 1.09 for naphthenes, and 12.1 ± 3.23 for aromatics (% w/w), which is quite different of exhaust emissions from gasoline vehicles. The content of carcinogenic VOCs was 0.44 ± 0.07 and 0.02 ± 0.01 (% w/w) for benzene and 1,3-butadiene, respectively, but despite the small content, they should be reduced as much as possible to protect inhabitants health. Despite i-sopentane, methylpentanes, n-pentane, and the sum of trimethylpentanes, had the greater abundance in evaporative emissions, the major contributors to reactivity were the olefins contributing with 62% for the potential ozone formation, estimated with the maximum incremental reactivity.

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Keywords: Benzene; Evaporative emissions; Gasoline; Ozone; Reactivity; VOC

1. Introduction

International regulations on emissions from vehicles with internal combustion engines that obtain their energy from the combustion of fossil fuels are becoming more stringent, aiming to reduce impacts on human health and environment, both from evaporation emissions of fuel as well as from combustion emissions from engines [1]. Most light duty vehicles used in developing countries are fitted with spark ignition engines that employ gasoline

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as a fuel, emitting currently copious amounts of toxic and greenhouse gases [2]; among them, volatile organic compounds (VOCs) are important pollutants since in addition that some of them are harmful to health, they are also ozone formation precursors. Ozone concentration in Mexico City exceeds the Mexican air quality 1-h standard of 0.095 ppm more than 200 days, and additionally this secondary pollutant has been reported as a short-living climatic pollutant contributing to global warming; thus, decreasing of VOCs in the atmosphere is mandatory [3], and although the purchase of electric and hybrid vehicles has increased, vehicles with internal combustion engines using hydrocarbon fuels will continue to be the important transportation system for decades [4,5]. Although more than 200 VOCs species emissions from vehicles have been reported, not all these species have the same ozone formation ozone because they have different atmospheric reactivities as has been studied by Carter [6], then is important to know the gasoline compositions in order to design control strategies.

The VOCs exhaust profile of light duty vehicles in Mexico City tunnels, and the VOCs atmospheric concentration have been investigated previously [7,8], but not the VOC profiles from gasoline evaporation. Evaporative emissions are present after vehicle operation (hot soak emissions), during the diurnal temperature cycle by pressure changes in the vapor space on top of liquid fuel into gasoline tanks, by leak of liquid gasoline in gas stations as well as in the course of transportation and distribution of fuels into the city. The main objective of this research was to determine the composition of evaporative emissions from gasoline vehicles, as well as the estimation of the ozone potential formation that will provide decision makers valuable information to design strategies for ozone level reductions trough decisions based in the gasoline composition.

2. Experimental methods

Liquid regular Magna gasoline samples were acquired directly during the 2018 fall in fourteen service gas stations, which represent the gasoline brands in Mexico City; samples were immediately refrigerated at 4 °C in the sites and then translated to the laboratory refrigerator. Vapor gasoline analyses were carried out in triplicate for each brand of gasoline with a static headspace device and a gas Perkin Elmer chromatograph model CLARUS 690 equipped with a flame ionization detector (FID), using a 100 m DHA Perkin Elmer capillary analytical column of 0.25 ID and DF 0.60. The chromatograph was cooled with liquid carbon dioxide applying the international ASTM D6733 method, to quantify the percentage of type groups: paraffin, i-paraffin, olefines, naphthenes and aromatics (PIONA), as well as those of the different VOCs. After sample injection, the oven temperature was increased at 2.2 °C per minute from 5 to 150 °C.

Ozone formation potential was estimated multiplying the concentration in mass by the maximum incremental reactivity developed by Carter [6] of each VOC. Statistical analyses were performed with STATISTICA 10, for Spearman correlation of different brands of gasolines and Mann Whitney tests in the comparison of different groups.

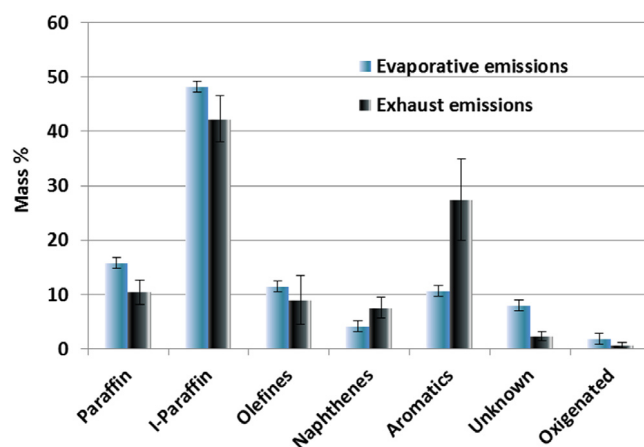


Fig. 1. Comparison of evaporative and exhaust gasoline emissions.

3. Results and discussion

Most abundant compounds were the isomerized paraffin (i-paraffin) followed by paraffins and olefins, and the less abundant were the oxygenated (Fig. 1). With the exception of oxygenated compounds, the composition of evaporative emissions of each group did not present significant differences ($p > 0.05$) among the different gasolines, which had a calculated octane number of 85.6 in average. Evaporative emission composition presented high differences with the exhaust emissions composition [8], especially in paraffins that were two times higher in evaporative emissions while aromatic species had a content up to six times lower than in liquid gasoline. Regarding carcinogenic compounds, benzene and 1–3 butadiene accounted with 0.44 ± 0.12 and $0.02 \pm 0.01\%$ respectively.

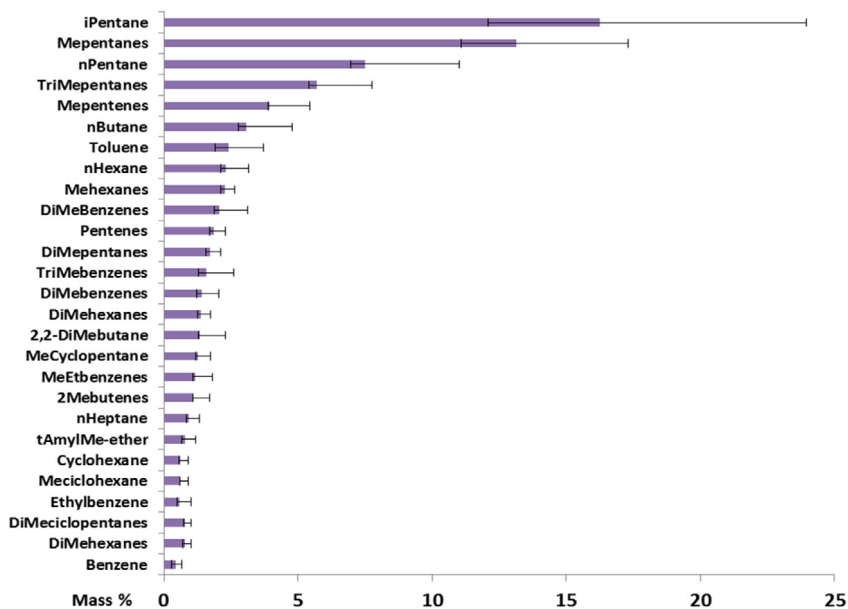


Fig. 2. VOC profile of evaporative emissions of Mexican gasolines.

More than 200 organic compounds were identified in the evaporative emissions. Fig. 2 shows the evaporative VOC composition of the most abundant compounds which contributes with 77% of total emissions; it is possible to observe that major contributions were due to i-pentane, methylpentane isomers, n-pentane, trimethylpentane isomers, methylpentene isomers and -butane, which are also the most important compounds in gasolines.

Most abundant olefins were 4-methyl-pentene-2 and 2-methyl-butene; methylcyclopentane was the main naphthene contributor, whereas toluene, xylenes (dimethylbenzenes) and trimethylbenzenes were the main aromatic species. As was expected, the lowest evaporative emissions corresponded to the heavier components of gasoline (C10–C11) such as tridecane, undecane and dodecene (not shown in Fig. 2).

Oxygenated compounds presented low content of 1.99% in average, and their contribution to evaporative emissions were very variable, since gasolines are oxygenated in Mexico City (NOM-016-CRE-2016), due to its high altitude of 2200 masl. The oxygenated compounds were different in the evaluated evaporative emissions, some had tert-Amyl methyl ether (TAME), others had methyl-t-butylether and low quantities of alcohols, such as methanol and t-butanol whereas the presence of ethanol was lower to 0.02% in all cases.

Reactivity, or ozone formation potential was expressed per unit mass of VOC emissions using Eq. (1), where R is the normalized reactivity in g of O_3 formed per g of VOC emitted, MIR_i is the maximum incremental reactivity for species i [g of O_3 formed per g of species i emitted], and W_i is the weight fraction of species i in total VOC emissions [6].

$$R = \sum_{i=1}^n W_i \times MIR_i \quad (1)$$

Fig. 3 presents the comparison between atmospheric reactivity for ozone formation of different VOC groups with the abundance of evaporative emissions. It is evident that although olefins contributed with only 12% of evaporative

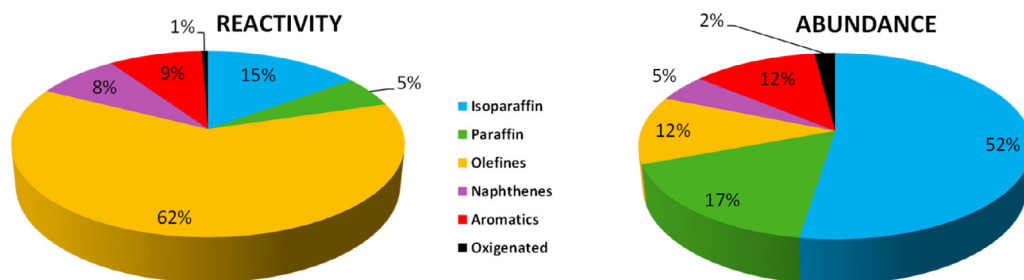


Fig. 3. Ozone formation potential (reactivity) and abundance of different VOC groups in evaporative emissions.

emissions of identified compounds, the contribution to reactivity is 62% since they have the highest MIR; in the case of aromatics which are responsible of 9% of the mixture reactivity, their abundance is 12%. Considering that the Mexico City government reported in its last Emission Inventory 1352 ton of evaporative emission of VOCs only due to gasoline transportation [9], 581 ton per year would correspond to reactive olefins. As Mexico City has an ozone formation VOC limited regimen [10], then the reduction in fuel formulation of some compounds, especially the most reactive species combined with the reduction on gasoline vapor pressure (resulting in lower mass emissions) should be implemented to achieve ozone decreasing. Regarding benzene, although its content is around 0.7% and has a reactivity ranking of 56, its reduction is needed in order to decrease the inhabitant's cancer risk.

Table 1 shows that 4-methyl-pentene-2 had the ranking 1 for ozone potential formation, because this specie is very reactive with a high MIR and was the fourth compound more abundant, whereas i-pentane had the ranking 2 due to is the most abundant emitted compound, although it is not very reactive. Para xylene presented also a high ozone formation potential with the ranking 4 due to its high MIR, although it was the number 10 in abundance. These results show that not only abundance, but also maximum incremental reactivity of each species should be considered when gasolines are formulated.

In comparison with reactivities for exhaust emissions they are quite different since in this last case the greater highest reactivity corresponded to ethylene, propylene, 1-butene, xylenes and propane [8]. Mexican regulations have established that olefins maximum content should be 10% which is fulfilled in gasoline formulations [11], but the findings of this study show that is necessary taking in account the individual reactivities not only of total olefins but also of aromatic compounds to decrease the high levels of ozone in Mexico City without octane number decreasing. This research shows the species that should be reduced in the fuel to diminish the reactivity of evaporated VOCs mixture in the atmosphere.

4. Conclusions

Despite the development of electric transportation, light duty vehicles will still get their energy from the combustion of gasoline for many years, emitting consequently volatile organic compounds from the fuel evaporation as well as from the combustion system.

Characterization of evaporative emissions from gasolines expended in Mexico City, showed that the abundance of organic groups of VOCs is: i-paraffin > paraffin > aromatics > olefins > naphthenes > oxygenated.

VOCs evaporative emissions profile was very different to VOCs exhaust profile; i-pentane, npentane, methylpentanes, nbutane, nhexane, methylbutanes and 2,2,4 trimethylpentane were the most abundant species are related with gasoline composition. Benzene and 1–3 butadiene, which are carcinogenic compounds represented 0.44 ± 0.07 and $0.02 \pm 0.01\%$ respectively.

Reactivities of each VOC were estimated using the maximum incremental reactivity, showing the highest ozone formation potential for 4-methyl-pentene-2, i-pentan2, 2-methylpentane, meta-xylene and 2-methyl-butene-2.

Olefins presented the highest reactivity of all groups with 62% followed by i-paraffin despite the first group only contributes to the total evaporative emissions with 12%, whereas the second group accounted with 52%.

Since in Mexico City ozone formation regimen is VOC limited, reduction of vapor pressure as well as most reactive species such as olefins and aromatics could result in a more effective reduction in ozone levels. Additionally, benzene reduction is important for its carcinogenic character.

Table 1. Reactivity (ozone formation potential, OFP) of evaporative VOCs [g of O₃ formed per g of VOC].

Compound	MIR	Reactivity	OFP Ranking
n-butane	1.08	3.3	18
t-butene-2	14.79	4.4	13
1,2-butadiene	9.03	1.2	30
i-pentane	1.36	22.1	2
Pentene-1	6.97	5.2	11
2-methylbutene-2	13.72	13.4	5
n-pentane	1.23	9.2	7
t-pentene-2	10.25	7.2	8
c-pentene-2	10.07	4.3	14
3-methylbutene-1	6.8	0.9	38
Cyclopentene	6.55	1.8	22
2-methylpentane	1.41	15.5	3
3-methylpentane	1.7	3.7	17
2-methylpentene-1	5.12	0.8	42
4-methylpentene-2	7.9	30.1	1
Methylcyclopentane	2.1	2.6	20
n-hexane	1.15	2.7	19
c-hexene-3	8.02	1.1	34
c-hexene-2	8.41	1.0	35
2-methylpentene-2	10.7	1.4	27
2,2-dimethylbutane	1.1	1.5	22
2,3-dimethylpentane	1.2	1.3	31
3,3-dimethylpentene-1	4.71	0.845	29
1-methylcyclopentene	12.11	2.2	21
Cyclohexane	1.16	0.611	34
2,4-dimethylpentane	1.5	1.2	33
3-methylhexane	1.51	1.7	24
n-heptane	0.99	0.9	39
2,4-dimethylhexane	1.6	1.0	36
3-methylhexene-1	47.24	5.5	9
Methylcyclohexane	1.58	0.9	37
2,2,4-trimethylpentane	1.2	4.1	15
2,2,3-trimethylpentane	0.95	1.2	32
1,3-dimethylcyclopentane	1.82	0.9	40
Toluene	3.88	9.4	6
Ethylbenzene	2.93	1.7	23
m-xylene	9.52	13.4	4
p-xylene	5.69	3.8	16
o-xylene	7.44	5.5	10
1,4-methylethylbenzene	4.31	1.7	25
1,3,5-trimethylbenzene	11.44	4.5	12
1, 4-diethylbenzene	8.64	0.9	41
Tert-amyl-methyl-ether	1.69	1.4	28

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