EXPERIMENTAL STUDY OF OZONE-FORMING POTENTIAL FROM EXHAUST EMISSIONS OF VEHICLES FUELED WITH REFORMULATED GASOLINE IN MÉXICO CITY

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Key words: smog chamber, exhaust emission, reformulated gasoline, ozone-forming potential

ABSTRACT

Several experiments using outdoor smog chambers were carried out to determine the ozone-forming potential from exhaust emissions of reformulated gasolines compared with a reference gasoline. The objective of this experimental study is to select a reformulated gasoline which has the lowest impact on ozone formation, by using automobiles equipped with technology that complies with the Euro4 regulation. This gasoline will substitute the one used in vehicles technologically equipped to comply with the Tier 1 regulation in México City. The smog chamber method showed that the reformulated gasoline with the lowest impact on ozone formation, in automobiles that comply with Tier 1, was F3, and the one for Euro4 vehicles, was F5. These gasolines have lower benzene and sulfur concentrations than the reference gasoline used in the experiments. Also, after 9 runs carried out in a dynamometer and using the reference gasoline in both types of automobiles, the one equipped to comply with Euro4 emitted less pollutants (mg/km) and toxic species to the atmosphere, than the one equipped to comply with Tier 1. This is a preliminary study, and it is necessary to carry out further tests with these fuels using representative vehicles of the MCMA, with and without catalytic converter.

Palabras clave: cámaras de esmog, emisiones de escape, gasolina reformulada, potencial de formación de ozono

RESUMEN

Se llevaron a cabo experimentos usando cámaras de esmog exteriores para determinar el potencial de formación de ozono de emisiones de escape de gasolinas reformuladas, comparándolas con una gasolina de referencia. El propósito de este estudio experimental se enfoca a seleccionar una gasolina reformulada con el más bajo impacto sobre la formación de ozono, utilizando automóviles equipados con tecnología para cumplir con la regulación Euro4, la cual sustituirá a los equipados para cumplir con la regulación

Tier 1 en la ciudad de México. El método de cámaras de esmog mostró que la gasolina reformulada con el menor impacto sobre la formación de ozono en automóviles con Tier 1, fue la gasolina 3 (F3) y para el vehículo con Euro4 fue la gasolina 5 (F5). Dichas gasolinas tienen menor concentración de benceno y azufre que la gasolina de referencia utilizada en los experimentos. También, después de 9 corridas llevadas a cabo en un dinamómetro y utilizando gasolina de referencia en ambos tipos de automóviles, el equipado para cumplir con Euro4 emitió menos contaminantes (mg/km) y especies tóxicas a la atmósfera que el equipado para cumplir con Tier 1**.** Este estudio es preliminar y es necesario llevar a cabo una mayor cantidad de pruebas con los mejores combustibles, utilizando vehículos representativos del Área Metropolitana de la Ciudad de México (AMCM) con y sin convertidor catalítico.

INTRODUCTION

Air pollution has become a problem in the main urban cities of the world, as due to energy demand of transportation and the satisfaction of population's needs. In addition, a lot of forest or agricultural areas have been dedicated to urban use, thus breaking up the ecological balance with disastrous consequences in some regions of the planet.

México is included in this environmental problem. Main cities and industrial areas continuously produce dangerous air pollutants. This is the case of México City's Metropolitan Area (MCMA), Guadalajara and Monterrey. Due to this problem, in 1986, the government of México City began the construction of a network for atmospheric monitoring throughout the MCMA, to record the ozone levels and those of other pollutants (PICCA 1990). This allowed to define the real level of ozone contamination affecting the population. During the winter of 1990 and the spring of 1992, the worst days of environmental contingency were registered (PROAIRE 1996).

In the last two decades, among all polluting sources, automobiles have had the highest impact. They contribute with 75 % of total emissions (PROAIRE 1996). Therefore, pollution from vehicles is a serious and complex problem due to its several causes: the automotive technology, the total amount of circulating vehicles, the quantity and type of fuel utilized, the average circulation speed, the average distance covered per day, the mechanical condition of vehicles, the different types of vehicles, and the driving ways, among others (Díaz-Gutiérrez 2002, Shifter *et al.* 2003). In order to improve the air quality, a standard that establishes the properties of liquid and gas fuels utilized in MCMA, was issued in 1994 (INE 1994).

The reduction of ozone levels by replacing current fuels, is one of several plans made to continuously decrease pollution. This replacement includes reformulated gasolines to improve air quality by reducing ozone-generating emissions. But the exhaust emissions of a vehicle are directly related to the composition of the fuel it burns (Schuetzle *et al.* 1994). Therefore, it is necessary to experimentally evaluate the emissions of reformulated gasolines to assure that their marketing does not represent a more serious threat for the environment than those commercially available. However, there is another problem to consider besides of reducing emissions. Every substance emitted after fuel combustion has a different reactivity toward secondary pollutants, as ozone (Carter 1994). Therefore, it is necessary to be aware of what is emitted to the atmosphere, and to determine its relation with the fuel used.

In order to select the fuels that produce emissions with the lowest reactivity, the reactivity factors of each one of the more relevant species were determined based on the photochemical reactions they undergo (CARB 1991). These reactions occur when volatile organic compounds (VOC) and nitrogen oxides (NOx) are emitted to the atmosphere and irradiated by the natural light of the sun during the day, giving place to ozone formation in the troposphere. Particularly, in México City high contents of ozone are related to the intensive use of gasoline vehicles. Despite the strong efforts of local and federal authorities, oriented to reduce the emission of VOC and NOx from new and in-use vehicles, ozone levels are still high (Isaac Schifter *et al.* 2000). This fact has an important relationship not only with the total hydrocarbon mass emitted by vehicles, but also with the specific reactivity of fuels.

MATERIAL AND METHODS

Reactivity using smog chambers

Recently, different methods are used to define the reactivity for ozone-forming potential from non-methane hydrocarbon (NMHC) emissions. The method of incremental reactivity (IR) is among them (Carter and Atkinson 1989). IR was defined as the additional ozone formed, ΔO3, that each volatile organic compound (VOC) tested forms when added to a base urban mixture of VOC and NOx, divided by the amount of the test VOC, ΔVOC. Thus, IR is defined by the following equation:

$$IR = \Delta O_3/\Delta VOC \quad (1)$$

Carter's IR factors provide a simple method to determine reactivities in exhaust mixtures. However, another method can be used to characterize the photochemical process that occurs during reactivity experiments. It is called smog produced (SP) (Johnson 1984) and is defined by:

$$SP = O_3(t) + NO(0) - NO(t) \quad (2)$$

where $O_3(t)$ and NO(t) are the respective concentrations of O_3 and NO at the time t, and NO(0) the initial NO. The variable SP includes the NO oxidation and ozone formation from the atmospheric oxidation processes. This method is the one used in this paper.

Exhaust emissions

In order to select the reformulated gasoline with the lowest impact on ozone formation compared with a reference gasoline, some reformulated gasolines were evaluated. **Table I** shows the formulation of each one of them. To evaluate the potential, Carter's IR factors were applied to the species of exhaust emission of the test automobiles and the SP in the smog chambers designed for this work. The vehicles used were provided by GM: a vehicle equipped to comply with Tier 1 regulation, which is being used in México, and another one equipped to comply with Euro4 regulation, that will be introduced in the near future. The characteristics of both vehicles are shown in **table II**. These automobiles were subjected to similar tests of FTP-75 cycle. The test cycle is called Urban-Mex, and it was designed by the Mexican Petroleum Institute (MPI) according to the driving conditions of México City. The parameters of the Urban-Mex cycle and the graphic comparison with the FTP-75 cycle, are shown in **figure 1**.

Testing of each fuel was carried out in two days. The first day, a vehicle was evaluated with the test fuel and the other vehicle with the reference fuel. The next day, the same cars were used, but fuels were exchanged. In this way, information of the exhaust emissions from each vehicle was gathered, both with test fuel and reference fuel. Constant volume sampling (CVS) tests were carried out in a dynamometer Horiba of 48 inches, model LDV-46-86-125HP-AC, using the Urban-Mex cycle. Before carrying out each CVS test, the vehicles were conditioned according to the NMX-AA-11-1993-SCFI (DGN 1993) standard "Test method for the evaluation of exhaust emissions of new vehicles that use gasoline as a fuel."

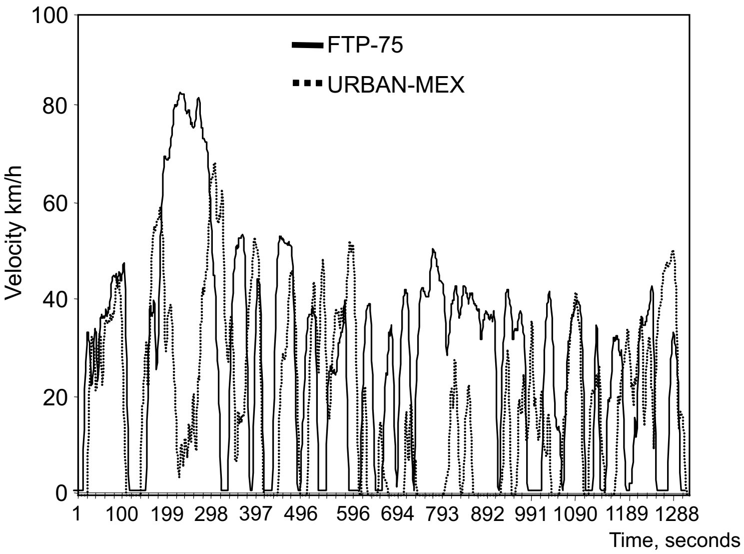
TABLE I. REFORMULATED GASOLINES

Fuel	RF	F1	F2	F3	F4	F5
Sulfur (ppm)	720	440	400	420	370	415
Aromatics (Vol %)	28	17.2	19	19.9	18	22.6
Olefins (Vol %)	13	7.2	6.6	6.9	7.2	15.2
RVP (psi)	8.8	6.8	6.6	8.3	10.7	10.8
O_2 (W %)	0.3	0	$2_{(MTBE)}$	$1_{(MTBE)}$	$1_{(MTBE)}$	$1_{(MTBE)}$
T_{90} (°C)	172	163	164	163	164	164

Note: T_{90} represents the temperature related to 90 % distillation, as a result, it has a strong relationship with fuel economy after engine warm-up and minimal fuel dilution in oil crankcase, at the same time, T_{90} is adjusted to reduce volatile organic compounds (VOC) exhaust emissions, and to avoid engine deposits

TABLE II. CHARACTERISTICS OF EURO 4 AND TIER 1 VEHICLES

	Euro 4	Tier 1
Engine	4 cylinders. Dual overhead cam	4 cylinders. Dual overhead cam
Displacement	2.0 l	1.8 l
Fuel management system	Multiport fuel injection	Multiport fuel injection
Power	150 hp	125 hp
Compression ratio	9.1 to 1	9.0 to 1
Catalytic converter	TWC, close coupled Palladium-Rhodium	TWC, under-body Platinum-Rhodium
Metal total charge	2.5081	1.5585
Metal ratio (Pt/Pd/Rh)	0/6.5/1	5/0/1



PARAMETERS	MCMA
LENGTH (km)	8.8
TIME (sec)	1360
AVERAGE VELOCITY (km/h)	23.4
MAX VELOCITY (km/h)	73.6
CONSTANT VELOCITY (% time)	5.3
ACELERATION (%)	38.0
DEACELERATION (%)	31.4
MIN MARCH (%)	24.7
STOPS (km)	2.3

Fig. 1. Urban-Mex vs FTP-75 Cycle

During the CVS tests, an exhaust sample was taken in a teflon bag of fluorinated ethylene propylene (FEP). This bag was covered with a black plastic material to prevent the content to contact light. Then, the bag was brought to the place where the experimental system of smog chambers was located, which was 200 meters away.

Experimental chambers

The experiments were carried out in teflon bags FEP type A, with a thickness of 0.051 mm and a capacity of 600 liters. Each bag was fitted with two teflon connections of 0.635 cm; one of them had fill and evacuation functions, the other was used to take the samples to the analyzers. The bags were linked, through Teflon lines, to a 2 liter Pyrex bulb.

For NOx and O_3 measuring, Thermo Environmental analyzers models 42 and 49 were used. The analyzer model 42 was calibrated several times throughout the study by using a dynamic calibrator coupled to a clean air generator (EPA gas protocol). This system allowed to make dilutions of gas with a precision of ± 1%. The ozone analyzer was calibrated with an ozone photometry calibrator Thermo Environmental model 49-PS. The solar radiation was measured with an Eppley radiometer, which had been previously calibrated in the Centro de Ciencias de la Atmósfera of the Universidad Nacional Autónoma de México. The radiometer was installed close to the experimental test rig. The temperature of the control bag was measured with a thermocouple Type "J", calibrated in the Metrology Laboratory of the MPI; which has the T-14 accreditation of the National System of Calibration.

Figure 2 shows a scheme of the experimental system. Six bags were used to carry out the experiments, and bag 7 was used as a control. All six bags were linked, through Teflon lines, to an automatic system of valves lodged in a device to open a specific valve of each bag to be analyzed. The chamber's operation was described by Jaimes-López *et al.* (2003).

The electric signals from the analyzers, the temperature sensor, and the radiometer, were sent to a data acquisition equipment in order to capture data.

Experimental procedures

The experiments began in the morning at 6.00

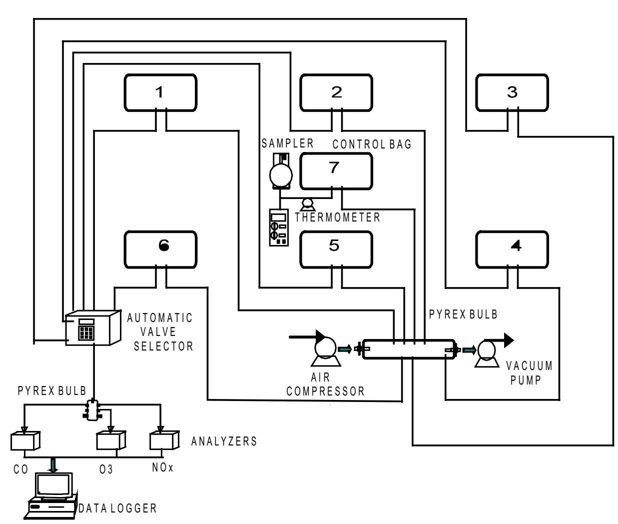


Fig. 2. Experimental system of outdoor smog chambers

o'clock, just before sunrise. First, the bags were emptied and filled with 500 liters of ultra-pure air to flush them. Then, all bags were filled with 500 liters ultra-pure air. Bags 1, 2 and 3 were injected a volume of the exhaust emission from the Tier 1 automobile, adjusting the injection to obtain 0.400 ppmC of VOC in each one of the bags. This same operation was repeated for bags 4, 5 and 6, except that these bags were injected with the exhaust emissions from Euro4 the vehicle. Finally, the bags were exposed to natural solar irradiation. During the day, samples of gas were taken from the bags every hour to follow the ozone formation. Once the experiments were finished, the bags were evacuated and flushed with ultra-pure air, to avoid masking the next day's results.

Ozone-formation potential

Potentials of ozone formation from vehicular emissions were calculated by using the maximum incremental reactivity (MIR) determined by Carter (1994), and the data from smog chambers. To evaluate the reactivity of the fuels, MIR was calculated as follows:

$$R_{MIR} = \sum_{i}^{n} (MIR)_i F_i \quad (3)$$

where MIR_i is the MIR for the species i (mg O_3/mg HC_i), and Fi the fraction of the species i in the vehicular emission (mg HC_i/km). Therefore, equation 3 determines the reactivity of the test fuels and the reference fuel, in mg O_3/km. In this way, when the reactivity of the test fuel is related to the reference fuel, the relative potential of the reformulated fuel is determined by

$$P = \frac{R_{MIR(Test\ fuel)}}{R_{MIR(Reference\ fuel)}} \quad (4)$$

The reactivity from smog chambers data was calculated by using the concept of smog produced given by equation 2. It was obtained from the maximal slop of the curve of ozone concentration versus time. **Figure 3** shows one example of that kind of curve.

The relative potential of ozone formation, was calculated from chambers data by

$$P = \frac{SP(test\ fuel)}{SP(reference\ fuel)} \quad (5)$$

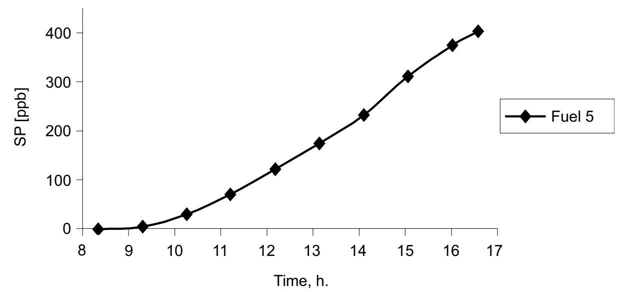


Fig. 3. Measuring of the smog produced in Euro4 versus irradiation time

RESULTS AND DISCUSSION

Since the experimental methodology includes the comparison of each tested gasoline with the reference gasoline, the number of repetitions carried out with this gasoline allowed to calculate the average of total exhaust emissions, which are showed in **table III**. It shows the emission composition of the automobiles equipped to comply with Tier 1 and Euro4 regulations. The data correspond to the average of nine tests carried out in a dynamometer with the reference gasoline in each one of the automobiles. Generally, the results show that the emissions of hydrocarbons, carbon dioxide, nitrogen oxides and methane, are higher for Tier 1 than for Euro4. But Euro4 emits a quantity lightly higher of carbon monoxide. However, this automobile's emissions of NOx showed to be substantially lower. The reduction of this pollutant will be a good benefit for the air quality when Euro4 automobiles are marketed in México City.

These tests also allowed to compare the emission of some toxic compounds in both types of automobiles. **Figure 4** shows the average emissions. The graph shows that there is a higher emission of most of the toxic compounds in the automobile equipped to comply with Tier 1 when compared to Euro4. Although benzene emission has a contrary behavior, it would not be a problem when Euro4 is introduced in México City. The reference gasoline used in the tests

TABLE III. EURO 4 VS TIER 1 AVERAGE EMISSIONS

Emissions	TIER1 (g/km)	EURO 4 (g/km)
THC	0.218	0.131
CO	1.739	1.893
CO_2	240.757	207.956
NOx	0.264	0.084
CH_4	0.020	0.016

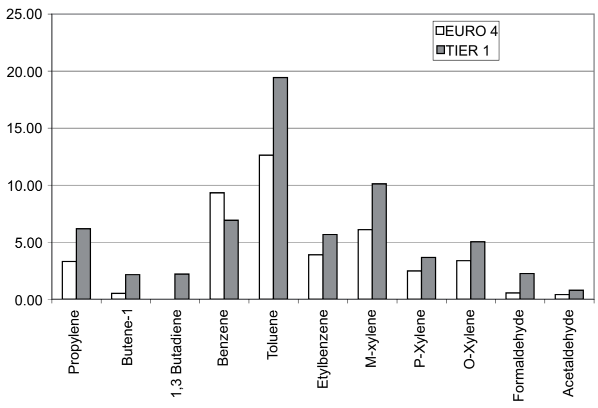


Fig. 4. Toxic compounds emitted by the reference fuel

of this study will not be for sale, and the five reformulated gasolines did not have a benzene emission higher than 1 mg/km in the automobile equipped to comply with Euro4 regulation (EPA 1994).

Figures 5 and **6** show the results of ozone potentials for Euro4 and Tier 1 during the tests. The calculations were carried out with the data obtained in the smog chambers, by applying equation 5. These results were compared with the potential calculated by equation 4 using the Carter's factors. The order of distribution of ozone potentials of each reformulated gasoline with both methodologies were similar. However, the order for fuels was different in each one of the automobiles. Based on ozone potentials, the order for Euro4 was found to be F5 > F1 > F4 > F3 > F2, while for Tier 1 the result was F3 > F5 > F2 > F1.

Sulfur concentration of F5, F3 and F1 was similar (430 ppm). This value can be considered high, and sulfur level in gasoline can significantly damage the emission control devices of vehicles, never the less, the Palladium–Rodium close coupled TWC from Euro4 vehicle can support better the poisoning than the Platinum–Rodium from the Tier 1 vehicle. Sulfur blocks sites on the catalyst were designed to store the oxygen necessary for a highly efficient NOx conversion reactions.

The Mexican standard NOM-086-SEMAR-SENER-SCFI-05 (SEMARNAP 1996), "Specifications of Fuels for the Environmental Protection", establishes the sulfur limits for the Mexican gasolines. Related to México City, the premium gasoline has 250 ppm average limit and a maximum of 300 ppm. In Magna gasoline, the average sulfur content is 300 ppm with a 500 ppm maximum. Sulfur in gasoline inhibits the emission control performance of catalytic converters, but a variety of factors establishes the degree of impact and the reversibility of this impact. Factors include the catalyst composition and location, engine calibration, fuel metering technology and the way a vehicle is driven. Related to the precious metal charge in the catalytic converter, during years, platinum base was selected like the most efficient metal. However, it´s inconvenience is the price and its susceptibility to be inhibited by sulfur. In the other hand, the palladium base catalytic converter has more resistance to deterioration with high sulfur levels.

The Euro4 vehicle use close coupled TWC technology for better light off catalyst performance focused in

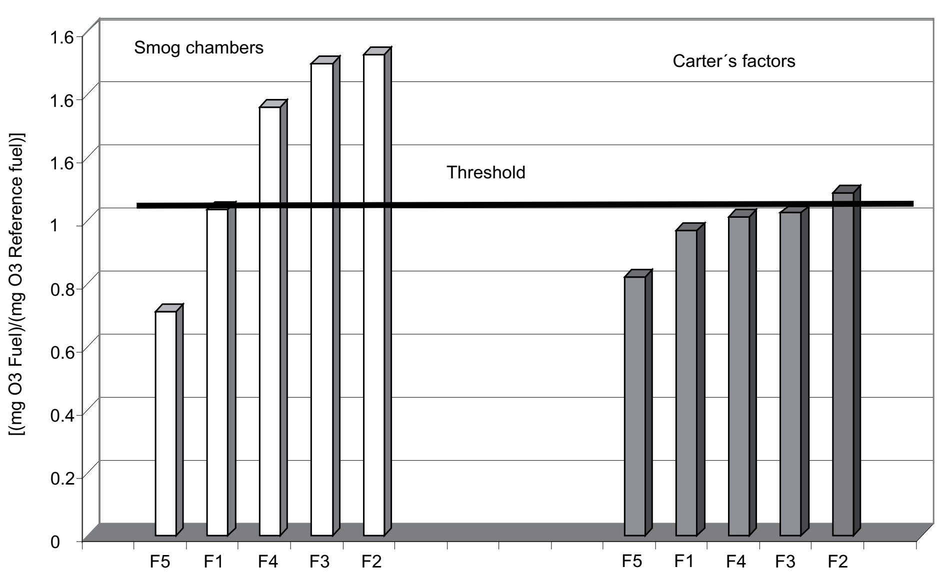


Fig. 5. Ozone potential from reformulated gasolines tested in Euro 4

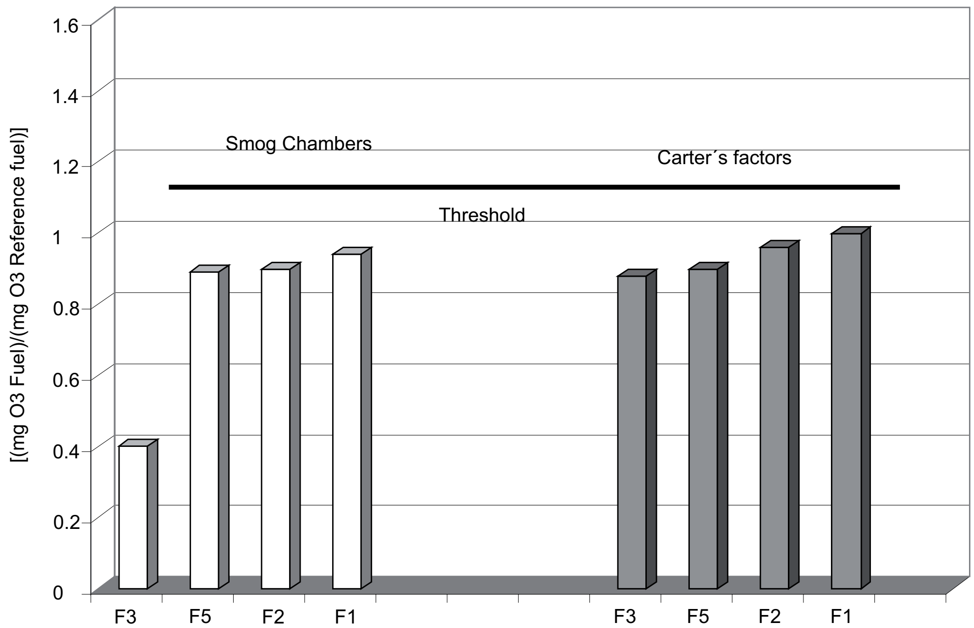


Fig. 6. Ozone potential from reformulated gasolines tested in Tier 1

lower THC emissions. Additionally, the Euro4 vehicle uses Palladium-Rhodium catalytic converter with higher metal contents than Tier 1 vehicle, generally focused in strong NOx emissions control. For these two vehicles it is possible to contemplate a reduction in catalyst activity by means of sulfur level in gasoline, but the regeneration is possible by means of hot cycle in rich calibration. The Tier 1 vehicle looks more sensible to sulfur level in gasoline than the Euro4.

CONCLUSIONS

These results allowed the selection of the formulation with the lowest impact on ozone formation. In the case of the automobile equipped to comply with Euro4, the reformulated gasoline F5 showed the lowest ozone potential. For Tier 1, the reformulated gasoline F3 was found to have the lowest potential. On the other hand, if both types of automobiles shall circulate in México City, the reformulated gasoline F5 would be the choice.

The introduction of the automobile equipped to comply Euro4 regulation in México City will help to improve the air quality, as its emissions are lower than to those of Tier 1.

The method of smog chambers employed allows the selection of the reformulated gasoline with the lowest impact on ozone formation. Formulation F5 had the lowest potential for Euro4 regulation, and formulation F3 for Tier 1. However, formulation F5 may be used in both automobiles to decrease the impact of ozone.

Due to the discrepancy of ozone potential found between smog chambers and Carter’s factors, it is necessary to carry out further experimental work, in order to improve the smog chamber method and to find a correlation between both methods.

This is a preliminary study, and it is necessary to carry out more repetitions with the fuels that showed the best performance, with the aim of increasing the statistical validity. We also recommend to carry out more tests with these fuels utilizing MCMA representative vehicles, with and without catalytic converter, in order to evaluate its emissions and their possible impact on air quality.

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