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Ozone forming potential and sulfur effects on in-use vehicles of the metropolitan area of Mexico City

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Abstract: The largest urban areas of Mexico cities have witnessed high levels of air pollution in the past few decades. The most important air pollutants are ozone and particulate matter with levels that are still far above current air quality standard. In this work we studied exhaust and evaporative emissions of Mexico City metropolitan area (MAMC) vehicles using fuels in which sulfur content was varied from 89×10^{-6} to 817×10^{-6} , and calculated the ozone forming potential of emissions as well as the specific reactivity of the exhaust for each average fleet-fuel combinations. Data on emission levels were compared to those obtained in 2000 for the same vintage of vehicles. The almost twofold increase in emissions found could be due to degradation of the exhaust emissions control systems.

Key words: Fuel formulation, Ozone forming potential, Vehicles emissions, Mexicodoi:10.1631/jzus.2006.A0463Document code:ACLC number:S157.4

INTRODUCTION

Motor vehicles continue to be the dominant source of air pollution, despite tremendous advances in engine technology and pollution control. Vehicles are significant sources of CO, HC, and PM and comprise one of the most important sources of NO_x , which along with HC, are the essential precursors of ground-level ozone.

In view of emissions harm to human health, major efforts to control them have been made, both through improved emission control technologies and through gasoline reformulation (modifying of distillation properties, adding of oxygenated species, reducing sulfur content, etc.).

NRC (1999) reviewed many of the numerous studies addressing the effects of reformulation of gasoline on vehicle emissions. In general, reformulated and oxygenated gasoline is expected to reduce CO and VOC emissions, while the direction of the impact on NO_x emissions will depend on the details

of the reformulation.

Despite the efforts made in Mexico to curb pollution, the largest urban areas of Mexico cities have witnessed high levels of air pollution in the past few decades. The most important air pollutants are ozone and particulate matter with levels that are still far above current air quality standard. Table 1 shows the present status of Mexican cities with regards to fuel formulation, and main pollutants.

Two types of regular gasoline and one of premium are available, one for air quality non-attainment areas and the other for the rest of the country. Additionally, a premium gasoline is available in the country, representing about 16% of total sales.

It is projected that in the year 2007, car manufacturers in Mexico will begin introducing nationwide Tier 2 emission limits (1.31 g/km CO, 0.03 g/km non-methane hydrocarbons, and 0.04 g/km NO_x). Under Tier 2 requirement gasoline of much lower sulfur content will be necessary. Sulfur reduces the efficiency of catalytic converters, by far the most effective means of reducing harmful pollutants emitted by gasoline powered vehicles.

This paper addresses the need to reduce sulfur in fuels taking into consideration the impact that such measure will have on the in use fleet of vehicles of the largest metropolitan area in the country, i.e. the MAMC. Fig.1 provides information on the actual technological groups available in the mega city and the projected change in the percentage contribution for the year 2007.

We study not only the benefits that can be realized in terms of total pollutant emissions but also the potential of such emissions to produce ozone. In add-



Fig.1 Distribution of vehicles by technology in the MAMC and their projection to year 2007 (Annual growth=3.9%)

ition to what and how much is emitted, evaluating the ozone forming potential of various blends involves assessing how reactive the emitted pollutants might be in the chemical processes that form ozone in the lower atmosphere.

EXPERIMENTAL DETAILS

Test fuels

Gasoline blending stocks were brought to and stocked in our facilities from Mexican refineries streams with primary consideration given to hydrocarbon composition, and the actual blending process followed prescriptions reported by Pahl and McNally (1990). The inspection data for the fuels follow the American Society for Testing Materials procedures (ASTM, 2001).

The most important properties of the blending stocks are shown in Table 2. The fuels were blended using combinations (vol.%) of blending stocks shown in Table 3. In the course of this study five batches of each fuel were prepared and analyzed, each one approximately every three months; the ins-

Table 1 Fuel formulation and main pollutants in Mexican cities

	Reformulated	Oxygen	Sulfur	Sulfur ($\times 10^{-6}$)		Main
	gasoline	(wt.%)	Regular	Premium	(vol.%)	pollutants
3 major metropolitan areas	Yes	1.0~2.0	430	252	23.6	O ₃ , PM ₁₀
Middle size cities	No	No	733	202	30.9	CO, PM ₁₀
Northern border	No	No	798	152	28.2	O_3

Table 2 Analysis of blending components

B co	lending mponent	Catalytic cracking	Full range reformate	Light Alkylate	iC ₅ -C ₆ Isomerate	*MTBE	Hydrotreated gasoline	**TAME rafinate	Premium base gasoline
Grav	ity, 20/4 °C	0.737	0.78	0.703	0.7	0.683	0.734	0.681	0.773
RV	$P(lb/in^2)$	7.7	6.4	7.1	13	7.1	1.8	24.4	9.3
	RON	91.3	92.8	94.7	81.8	112	49.7	90.7	98
	MON	85.7	84.8	933.3	79	108	40.1	84.3	88.4
(ROI	N+MON)/2	88.5	88.0	94	80.4	110.8	44.9	87.5	93.2
D-86 dis- tillation	10% (°C)	59.1	75.7	72.5	44.3	55.1	104.5	26.1	55.5
	50% (°C)	83.7	125.9	99.6	51.7	56.7	125.7	34.3	114.6
	90% (°C)	151.9	173.8	123.8	77.4	57.3	160.3	40.7	156.4
	EP% (°C)	194.3	220.2	194.7	125.1	74.8	184	44.2	187.7
Aroma	atics (vol.%)	18.82	50.45	8.32			171.6	97	34
Olef	ins (vol.%)	28.5				3.1	1.7		48
Benz	ene (vol.%)	0.61	2.43				0.21	43.9	7
Sulf	fur (×10 ⁻⁶)	1530		23.3	243				0.98

* Methyl ter-butyl ether; **Ter-amyl methyl ether

pection average and 95% confidence intervals data of these fuels are shown in Table 4. Coded fuel 89-S was designated as the base gasoline from which other fuel parameters were varied. Coded fuel RC was blended to have industry average levels of sulfur, benzene, RVP, aromatics, olefins and distillation properties of the year 2002 gasoline sold outside of the ozone free non-attainment areas. Fuel-Metro simulates the average gasoline properties of gasoline sold in the ozone free non-attainment areas of the country.

The specifications in non-attainment areas have not changed since 1998, the oxygenation of the fuel $(1~2 \text{ wt.}\% \text{ O}_2)$ is mandatory and restricts the aromatic, olefins and sulfur content to limits in general close to those existing in the USA in 1990. Doping Metro fuel with thiophene yielded sulfur level of fuel coded 817-S. Twenty-six in-use units were randomly recruited in areas of the MAMC of different socioeconomic indicators. A description of the main characteristics of the fleet is given in Table 5. Tier 0 fleet refers to vehicles with emissions limits of 2.1 g/km for CO, 0.25 g/km for THC and 0.62 g/km for NO_x.

For the purpose of this work older vehicles (pre-1990) which do not have any emissions control devices, were not considered, it is difficult to characterize by sampling a small subset of the total population (Burns *et al.*, 1995).

Chassis dynamometer emissions testing

The objective of the test protocol was to define in a sound and repeatable way of measuring the short-term effect of fuels on regulated emissions; 2.1 g/km for CO, 0.156 g/km for non-methane hydrocarbons (NMHC), and 0.25 g/km for NO_x. In both cases the emissions limits refer to the vehicles when

Test vehicles

Table 3 Matrix fuel blends (vol.%) Fuels Blending components (vol.%) 89-S 209-S 817-S RC Metro Catalytic cracking 2.4 7.4 18.0 25.5 14.5 Full range reformate 11.7 23.6 22.4 30.8 33.0 Light alkylate 39.2 44.0 35.6 3.9 23.1 MTBE 5.5 5.5 5.5 2.0 6.7 iC_5-C_6 0.4 1.2 4.4 14.2 5.6 Hydrotreated gasoline 10.7 8.8 7.9 1.2 4.4 TAME rafinate 4.3 0.0 8.0 7.9 1.6 Premium base gasoline 28.5 5.2 6.2 14.4 4.8

Table 4 Test fuel properties from the five batches of gasolines

Droporty				Fuels		
	- Floperty	89-S	209-S	817-S	RC	Metro
Aromati	cs (vol.%)	19.84±1.85	19.95±0.83	19.77±1.21	27.95±0.41	24.14±1.98
Olefins	(vol.%)	4.97±0.96	7.41±1.44	6.12±1.19	13.51±1.03	8.98±1.62
Oxygen	, as MTBE (wt.%)	1.03 ± 0.08	$0.98{\pm}0.01$	1.05 ± 0.07	$0.34{\pm}0.016$	1.21±0.05
Benzene	e (vol.%)	0.59 ± 0.08	0.79±0.12	0.75±0.14	1.14 ± 0.08	0.99±0.26
Sulfur (×10 ⁻⁶)	89±3.31	209±10.43	817±26.2	724±17.80	403±9.66
RVP (lb/in^2)		6.62±0.28	6.7±0.25	6.6±0.28	6.87±0.11	7.66±0.13
RON		91.3±0.22	91.2±0.26	91.6±0.19	91.6±0.19	91.2±0.13
MON		83.7±0.49	84.1±0.35	83.5±0.33	84.6±0.46	83.5±0.27
(RON+	MON)/2	87.5±0.27	87.7±0.16	87.6±0.11	88.1±0.27	87.4±0.08
	IBP (°C)	40.5±1.70	39.2±3.92	37.8±2.61	35.94±1.54	37.9±1.13
D-86 distillation	10% (°C)	68.4±5.76	66.4±3.07	66.6±2.57	57.92±9.04	59.5±4.99
	50% (°C)	104.4±1.47	106.3±1.38	105.3±1.77	97.38±7.71	100.7±3.63
	90% (°C)	168.3±6.72	160.8±0.46	160.4±1.89	166.52±3.46	163.4±2.96
	EP% (°C)	204.8±1.46	200.8±1.87	199.6±1.99	203.12±2.48	204.6±9.42

Technological group	Maker	Model year	Displacement (l)	Fuel supply system	Emission control system	Odometer (km)
Tier 0	GM	Cutlass-93	2.8	MPFI [*]	TWC ^{**}	92784
	Chrysler	Spirit-93	2.5	MPFI	TWC	125500
	Nissan	Tsuru-94	1.6	MPFI	TWC	143348
	GM	Cavalier-94	3.1	MPFI	TWC	152788
	GM	Cavalier-94	2.2	MPFI	TWC	80658
	GM	Monza-95	1.6	MPFI	TWC	69047
	Ford	Pick-up-95	5.0	MPFI	TWC	26558
	Chrysler	Neon-96	2.0	MPFI	TWC	122321
	VW	Sedan-97	1.6	MPFI	TWC	60325
	Chrysler	Neon-97	2.0	MPFI	TWC	74654
	Nissan	Sentra-98	1.6	MPFI	TWC	26070
	Ford	Escort-98	2.0	MPFI	TWC	42347
	Chrysler	Stratus-98	2.2	MPFI	TWC	43198
	Nissan	Tsuru-99	1.6	MPFI	TWC	27386
	GM	Chevy-99	1.4	TBI	TWC	54639
	Chrysler	Stratus-99	2.2	MPFI	TWC	31574
	Dodge	Pick-up-99	3.5	MPFI	TWC	87151
Tier 1	Nissan	Pick-up-00	2.4	MPFI	TWC	56301
	VW	Pointer-00	1.8	MPFI	TWC	32000
	Nissan	Sentra-01	1.8	MPFI	TWC	36554
	GM	Monza-01	1.6	MPFI	TWC	7483
	Ford	Fiesta-02	1.6	MPFI	TWC	15064
	GM	Astra-02	1.6	MPFI	TWC	3034
	Ford	Focus-01	2.0	MPFI	TWC	54471
	VW	Jetta-01	2.0	MPFI	TWC	19320
	VW	Sedan-02	1.6	MPFI	TWC	23000

Table 5Test vehicles

*Multipoint injection; **TWC: Three way catalyst

Tier 1 fleet refers to vehicles with emissions of new, no mandate durability of emissions for the lifetime of the vehicles is still requested; therefore "Tier 1" vehicles do not have the technological advances of equivalent American counterparts, where the major modification/addition to older systems is the computer controls (On Board Diagnosis Systems).

The program included testing of each fuel over the exhaust emissions certification procedures and tolerances of the USA Federal Test Procedure (FTP-75) in three separate occasions in each vehicle (CFR, 1993).

The criterion used to determine if a new emissions test was necessary was based on those developed during the AQIRP (Painter and Rutherford, 1992), and CONCAWE (2003) programs. The re-test ratios used for FTP composite emissions results were: Total hydrocarbons (THC) greater than 1.175, CO greater than 1.336, and NO_x greater than 1.40. The ratio is defined as the larger test value divided by the smaller test value. It was anticipated that this degree of replication would render differences in fleet-average emissions of approximately 7% between the two levels of each design variable statistically significant at 95% confidence. Differences roughly twice this size would be needed for reject the null hypothesis in individual vehicles.

The fuels were tested from low to high sulfur content and a sulfur purge was implemented at each test as described in (Schifter *et al.*, 2004). The aim of sulfur purging was to cause the vehicle to transiently run at a high catalyst temperature in order to remove accumulated sulfur.

The Auto/Oil fuel change procedure was used before each emissions test (Burns *et al.*, 1992). The procedure is designed to minimize fuel carryover effects by thoroughly flushing the fuel delivery system and also to precondition the canister to the new fuel. Each time the fuel was changed, a cycle was performed on the dynamometer aiming to rid the vehicle engine and emissions system of sulfur effects as described by Schifter *et al.*(2003).The highest temperature recorded was 650 °C, measured using the Pre-Post Converter System.

Once the fuel changeover procedure was complete, the vehicles are placed on a chassis dynamometer and are operated over the FTP-75 standardized driving cycle. Throughout the study, a Horiba ECDM-48 electric dynamometer, coupled with a Horiba Constant Volume Sampler, CVS-45, was used along with a Horiba analytical bench system, which provided emissions analysis for CO, THC, CH_4 , CO_2 and NO_x .

The FTP protocol was followed by placing each one of the vehicles in the sealed housing for evaporative determination, which captures all vapor emissions from the vehicle during the diurnal and hot soak events. During the test, total hydrocarbons are monitored with a flame ionization detector. The results of these tests are generally expressed in grams of hydrocarbons per test, and later transformed to g/km according to Stebar *et al.*(1985). For that purpose, we considered that vehicles have at least one event of diurnal soak and three of hot soak and that 50 km is the average travel distance per day.

Evaporative emissions data during vehicles refueling were measured following California Environmental Protection Agency procedure (CEPA, 1996) and was performed on an instrumented service station located within our facilities (Schifter *et al.*, 2002). The equipment-adjusted flow was measured with the dispenser tip in its highest vertical position for at least one minute. The refueling was carried out using the fastest refueling speed and stopped when 80% of the tank capacity was reached. Vapor recovery efficiency was calculated with the five commercial vapor recovery units used in the MAMC gas stations.

Speciation/analytical procedures

The procedure for measuring the volatile organic compounds is described in (Bjordal *et al.*, 1996). Briefly, Tedlar bags containing sample exhaust gases were collected during the FTP and the bags were transferred to the chemical laboratory and analyzed using four Varian Star 3400 gas chromatographs and three HP 6890 equipped with flame ionization detectors. Over 170 C_1 through C_{12} species were identified and quantified using this procedure.

Carbonyls (aldehydes and ketones) were collected by diverting a small amount of diluted exhaust gas through a separate Horiba collection system to trap the carbonyls for later analysis by high performance liquid chromatography on a Hewlett Packard-1100 chromatograph (Bjordal *et al.*, 1996). The above analyses were combined to yield a single hydrocarbon speciation for each exhaust sample.

Ozone forming potential estimation of emissions

Speciated hydrocarbon data was used to estimate the potential of the emissions to form ozone and predict the impact of fuel changes on air quality. Carter (1994) developed 18 separate reactivity scales for quantifying VOC reactivity under different conditions. Of the 18 reactivity scales, the Maximal Incremental Reactivity (MIR) scale represents the incremental reactivity of a VOC computed for conditions in which the compound has its maximum incremental reactivity value. The California Air Resources Board (CARB) has adopted the use of ozone reactivities as a method for comparing the ozone forming potential of emissions from different types of fuels (CARB, 1991).

The MIR scale was also used to compare reactivities of vehicle emissions during various driving cycles as well as with the use of various reformulated gasoline in the Auto/Oil Study (AQIRP, 1993a; 1993b; 1997). Ozone Forming Potential (OFP) for a specific fuel was computed first by incorporating the MIR values expressed as grams of ozone per gram of the constituent measured in the exhaust from a particular fuel. Each compound was assigned an MIR value, which was multiplied by the mass of that compound to yield potential mass of ozone formed.

Specific reactivity (SR) is a measure of how much ozone could be produced by a unit mass of emissions and is typically expressed as grams of ozone per gram of non-methane organic gases (NMOG). When CARB implemented regulations for the low emission vehicles program, it introduced the concept of reactivity adjustment factors (RAFs) to provide a mechanism for manufacturers who build vehicles powered by alternative fuels (including reformulated gasoline) to take advantage of the lower ozone-forming potential of the emissions from these vehicles.

RAF is defined as the ratio of the specific exhaust reactivities of two fuels (per gram of emission of an alternatively-fueled vehicle to that of a conventionally fueled vehicle). If the alternative fuel's RAF is less than 1, then a proportionally greater amount of VOCs can be emitted, such that the RAF times the mass of emissions meets some total emissions standard.

Following the CARB concept, we define a reactivity adjustment factor as the ratio of the SR of one of the alternative fuels divided by SR of the base (reference) fuel, i.e. the RC fuel. If the alternative fuel's RAF is less than 1, then a proportionally greater amount of VOC's can be emitted and still meet a set ozone impact per km standard.

The sources and magnitude of the uncertainties in RAFs were investigated by various investigators (Yang *et al.*, 1996; McBride *et al.*, 1997). Briefly, it is believed that the uncertainties in reactivities can be minimized by focusing on relative as opposed to absolute reactivities.

The uncertainty of the relative reactivity of a composite set of VOCs arising from a single source, such as motor vehicles, tends to be somewhat smaller (i.e., about 15%~30%). Much of the uncertainty in this later case arises from potential errors in defining the speciation of the emissions as opposed to those associated with the chemistry of the species (NRC, 1999). If the formulated fuel's RAF is less than 1, then a proportionally greater amount of VOCs can be emitted and still meet a set ozone impact per km standard.

RESULTS AND DISCUSSION

Fleet arithmetic average emissions for each fuel were obtained by averaging results across all repeat tests with each fuel for each vehicle and then across all vehicles. Fig.2 shows a summary of the results for THC (2A), NO_x (2B), and CO (2C) exhaust average fleet-fuel combinations.

For the Tier 0 fleet, decreasing sulfur from 817×10^{-6} to 89×10^{-6} , lowers the CO, HCT and NO_x

exhaust emissions to 14%, 4.5% and 15.5% respectively. In 1991, the US Auto/Oil Air Quality Improvement Research Program (AQIRP) concluded that lowering sulfur levels from 450×10^{-6} to 50×10^{-6} decrease exhaust emissions in 1990 Tier 0 technology vehicles by 16%, 13%, and 9% respectively, for THC, CO, and NO_x emissions (Benson *et al.*, 1991).

In the case of Tier 1 fleet the decrease in emissions for the same pollutants was 10% CO, 15% THC, and 21% for NO_x. Data reported for Tier 1 vehicles in the USA (USEPA, 2001) claims that the percentages increase in emissions when sulfur varied



Fig.2 Pollutants exhaust emissions and fuel formulation (a) THC; (b) NO_x; (c) CO. (Unit: g/km)

from 30×10^{-6} to 330×10^{-6} was 24.2%, 20.8% and 10% for NMHC, CO and NO_x respectively.

Fig.3 shows results for the total toxic (benzene, 1, 3-butadiene, formaldehyde and acetaldehyde) emissions in mg/km. In all cases it was found that benzene was the main toxic emitted in terms of mass per kilometer, followed by formaldehyde. Lowering sulfur from 817×10^{-6} to 89×10^{-6} had no impact on the total toxic emissions.



Fig.3 Total toxic exhaust emissions in mg/km

Table 6 shows percentage distribution of exhaust VOCs emissions grouped by families for the exhaust emissions of Tier 0 and Tier 1 average fleet-fuel combinations respectively. It was noticed that compared to Tier 0 fleet, engine-out emissions in Tier 1 fleet had slightly more olefins.

 Table 6
 Percentage distribution of exhaust VOCs emissions

Fleet	Fuel	iso+n-Parafins	Olefins	Naphtenes	Aromatics
Tier 0	89-S	55	13	0.5	31
	209-S	59	12	0.7	28
	817-S	60	13	3.0	24
	RC	60	13	4.0	23
	Metro	59	14	2.6	24
Tier 1	89-S	49	17	0.4	34
	209-S	47	16	1.7	36
	817-S	59	15	1.0	25
	RC	57	16	1.0	26
	Metro	56	17	0.7	26

Fleet arithmetic average total non-exhaust VOCs emissions (diurnal, hot soak and refueling) in g/km are plotted in Fig.4. The regulated emission standard for evaporative emissions has not been changed in Mexico since 1993, when multipoint injection was introduced without fuel tank pressure sensors computer coupled to control systems. In general, vehicles control system work properly from 6.60 lb/in^2 to 8.64 lb/in^2 RVP values. Further increase in RVP makes the evaporative control system malfunction, when a two-fold increase in emissions was observed during the hot soak test.



Fig.4 Total non-exhaust emissions (g/km) with the study fuels

Fig.5 shows the calculated OFP of the engine out emissions for each average fleet-fuel combinations. Tier 0 vehicles are insensitive to the variation of sulfur in the fuel while Tier 1 vehicles 18% increase in the OFP value raises the sulfur content from 89×10^{-6} to 817×10^{-6} .



Fig.5 Calculated ozone forming potential (g ozone/km) for the different fuels

Fig.6 shows the means and 90% confidence intervals for the calculated SR (only exhaust emissions), for each of the average fleet-fuel combinations. Both Tier 0 and Tier 1 values are in general very high if one takes into account that in year 2000 we reported values of 3.12 for Tier 0 vehicles MY 1998 with average odometer readings of 36000 km for the gasoline used in the MAMC, and values of 3.1 for 30 new vehicles MY 1997 and 1998 using the same type of gasoline (Schifter *et al.*, 2000; 2001).



Fig.6 Calculated specific reactivity (mg ozone/mg NMHC) for the different fuels studied

For comparison purposes, three sets of studies conducted by Chevron, Arco, and the Society of Automotive Engineers using reformulated gasoline in American vehicles (MY 1984~1990) showed an average SR value of 2.7 (Boekhaus *et al.*, 1991; CARB, 1991). More recently Graham (2005) reported values of around 2.5 for two gasoline direct injection MY 2000 vehicles equipped with 3-way catalyst.

If the change in SR cannot be ascribed to the gasoline which has not been changed since 1998, it is suggested that the vehicle exhaust emission control system is no longer working efficiently. According to results of NRC (1999) an active catalyst should efficiently reduce olefin emissions by 92%~99%.

As no durability of emissions is required in Mexico, it is possible then that sulfur inhibition in catalysts is affecting the catalyst more than the American counterparts, taking into consideration that Tier 1 vehicles in USA certified emissions for at least 80000 km using a gasoline with sulfur content of as high as 320×10^{-6} . Therefore the results suggest that although Tier 1 OFP values are less than those of Tier 0, the SR of the emissions is of the same magnitude as that of the older vehicles (Tier 0).

Fig.7 shows calculated RAF average values for each of the average fleet-fuel combinations with Tier 0 and Tier 1 fleets using the RC fuel as reference.

It was apparent that improvement in fuel quality could be achieved by replacing the RC fuel by 89-S fuel but special attention should be paid to see to it that future vehicles sold in Mexico comply with the durability of emissions mandated in other countries.



Fig.7 Calculated reactivity adjustment factor for the different fuels

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