

# Catalyst and Noncatalyst Exhaust Aldehydes Emissions from Brazilian Ethanol-Fueled Vehicles

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Foi realizado um estudo de dois anos para determinar a composição de aldeídos em gases de exaustão de dois veículos brasileiros típicos movidos a etanol hidratado, para avaliar o desempenho de catalisadores de três vias recobertos com Pt/Rh (5/1) na redução das emissões de aldeídos, e o efeito do envelhecimento dos catalisadores em seu desempenho. As emissões médias ponderadas (em g/km) de formaldeído e acetaldeído do veículo GM Opala sem o uso do catalisador foram, respectivamente, 0,046 e 0,246. Para o veículo VW Gol foram 0,019 and 0,143. Para ambos veículos, sem catalisadores, as concentrações (em ppmv) estavam na faixa entre 1,10 e 4,13 para formaldeído e entre 5,77 e 14,0 para acetaldeído. Com a instalação dos catalisadores, para ambos aldeídos, foram observadas reduções ponderadas superiores a 70%. Entretanto, após aproximadamente 5.000 km de uso do catalisador, as emissões de acetaldeído aumentaram acima dos níveis observados antes da instalação do catalisador.

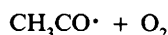
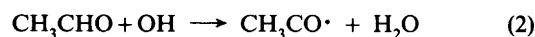
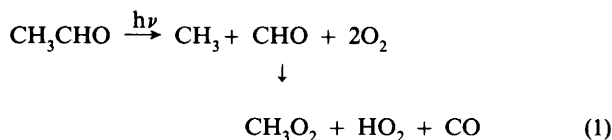
A two-year study was conducted to determine the aldehydes composition of exhaust emissions from two typical Brazilian ethanol-fueled vehicles, and to evaluate the effectiveness of three-way Pt/Rh (5/1) catalytic converters in the reduction of aldehydes emissions as well as the effect of aging on the performance of the catalysts. The weighted average emissions (in g/km) of formaldehyde and acetaldehyde by a GM Opala passenger car without the catalytic converter were 0.046 and 0.246, respectively. For a VW Gol vehicle they were 0.019 and 0.143. For both vehicles, the concentrations (in ppmv) without catalytic converters ranged from 1.10 to 4.13 for formaldehyde and from 5.77 to 14.0 for acetaldehyde. Upon installation of catalysts, weighted reductions of over 70 % were observed for both aldehydes. However, approximately 5,000 km after catalyst installation, acetaldehyde emissions increased beyond the levels observed without catalyst.

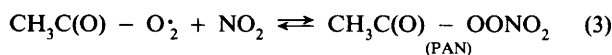
**Key words:** aldehydes, ethanol fuel, catalyst, exhaust emissions.

## Introduction

In the past two or three decades, aldehydes and other atmospheric carbonyl compounds directly emitted or formed in the atmosphere received much attention in regional air pollution studies because of their well known participation — as precursors — in atmospheric photochemical reactions that lead to the formation of important smog components such as nitric acid (HONO<sub>2</sub>), peroxyacetyl nitrate (PAN), and several others<sup>1,2</sup>. Enhanced PAN formation resulting from the use of ethanol-fueled vehicles may proceed via reactions 1-3<sup>2</sup>.

Trends in regional use of biomass-derived fuels — such as alcohols and agricultural residues — as a control measure proposed for elevated carbon monoxide levels in urban areas have expanded into a global scale. General interest in bio-fuels obviously results from economic considerations but, more recently, increased interest in these fuels have also resulted by the role that their



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combustion products may have on the question of global warming.

Economic and strategic considerations around the time of the 1973 "petroleum shock" lead several countries to consider bio-mass as an alternative solution to the use of fossil fuels. In the case of Brazil, partly due to traditional agricultural practices but, and especially, due to economic strategy, the choice fell on the use of both hydrous ethanol and gasohol (today in São Paulo  $22 \pm 2\%$  v/v ethanol in gasoline) as automotive fuels. Older models of ethanol-fueled brazilian vehicles emit 400% more aldehydes than their gasoline-fueled counterpart<sup>3</sup>. Newer models still emit over 200% more. It is clear that the quantification of the exhaust aldehyde emissions of ethanol-fueled vehicles is of paramount importance.

Furey and Jackson<sup>4</sup> measured exhaust emissions from a 1974 Brazilian Chevrolet Opala fueled by gasoline, and ethanol-gasoline mixtures up to 20% ethanol (v/v). They reported increased total aldehydes and nitrogen oxides ( $\text{NO}_x$ ) emissions with increasing ethanol content in the mixture. In their study, total aldehydes concentrations were obtained using a spectrophotometric procedure which does not allow speciation<sup>5</sup> and provides results which are 16% lower than those obtained by HPLC or capillary column gas chromatography<sup>6</sup>.

In this study we report on the results of a two-year study designed to: i) determine the aldehydes composition of exhaust emissions from Brazilian ethanol-fueled vehicles; ii) evaluate the effectiveness of three-way catalytic converters (designed for gasoline vehicles) in the reduction of aldehydes emissions; and iii) evaluate the effect of aging on the performance of the catalyst.

## Materials and Methods

Organic solvents used were chromatography grade (Grupo Quimica, Rio de Janeiro), further redistilled with 2,4-dinitrophenyl hydrazine (2,4-DNPHi). Hydrazone standards (2,4-DNPHo) were precipitated in chromatographic grade 2,4-DNPHi following a method described elsewhere<sup>7</sup>. Hydrazone working standards were prepared in acetonitrile. Microimpingers (25 ml capacity) adapted with coarse porous frits were used for sampling. Reverse phase Sep Pak C-18 cartridges (Waters Associates) were used to retain the hydrazones in the collection.

A high performance liquid chromatograph (HPLC, Waters Associates) equipped with a U6K injector and a Waters model 240 UV/VIS variable wavelength set at 365 nm and 0.1 AUFS was used. The analytical column was a spherical C-18  $5 \mu\text{m}$ , 15 cm x 3.9 mm i.d. (Waters Associates). Isocratic separation of the hydrazones was achieved with a methanol/water 57:43 (v/v) mobile phase ran at 1 ml/min. 20  $\mu\text{l}$  aliquots were injected. Further details are described elsewhere<sup>8,9</sup>.

A Clayton model ECE-50 chassis dynamometer equipped with a Horiba Instruments model 20-B constant volume sampler (CVS) was used for the simulation of the urban driving conditions as prescribed by the Brazilian Norm<sup>10</sup> which is the same as the US Environmental Protection Agency<sup>11</sup> urban dynamometer driving schedule for light-duty vehicles. Briefly, the driving schedule consists of a non-repetitive series of idle, acceleration, cruise and deceleration modes of various time sequences and rates. The dynamometer run consists of two tests, a "cold" start test after a 24 hr soak period and a "hot" start test following the "cold" start test by 10 min. The "cold" test is represented by two phases: phase 1 which represents the transitory period ends at the end of a deceleration

period which is programmed to occur at 505 s of the cycle. Phase 2 of the "cold" start represents the stabilized phase and concludes the first test. The engine is then turned off for 10 min. The "hot" test also consists of a transitory and a stabilized phase. Phase 3 represents the transitory phase of the "hot" start test. It starts exactly 10 min after the end of the "cold" start stabilized phase and ends when the 505 s deceleration period is completed. Because the stabilized phase of both tests are identical, no samples are collected during the stabilized phase of the "hot" start. Thus, in the three separate phases described, it simulates an average trip in an urban area of 12.1 Km (7.5 miles). A proportional part of the diluted exhaust (30 fold) is collected continuously in separate Tedlar bags, during the three phases, for subsequent determination of the aldehydes.

Two passenger fleet automobiles designed to operate with hydrous ethanol fuel were tested. Both had four cylinder engines and four-speed manual transmissions. One was a 1980 General Motors Opala, equipped with a 2.5 L (151 cubic inch) engine with 110,400 Km and the other a 1982 Volkswagen Gol equipped with a 1.6 L (97 cubic inch) engine with 43,946 Km. Both vehicles had standard carburetors (no fuel-injection!). These vehicles represent typical compact and medium size cars in the brazilian light duty vehicular fleet.

After testing without catalytic converters, each vehicle was equipped with an Engelhard Industries Division monolithic three-way (TWC) catalyst, first introduced in the United States on the 1977 gasoline-fueled model year Volvo automobiles sold in California. The converters were installed in the vehicle's exhaust line as shown in Figure 1. The TWC consists of a Pt/Rh 5/1 catalyst

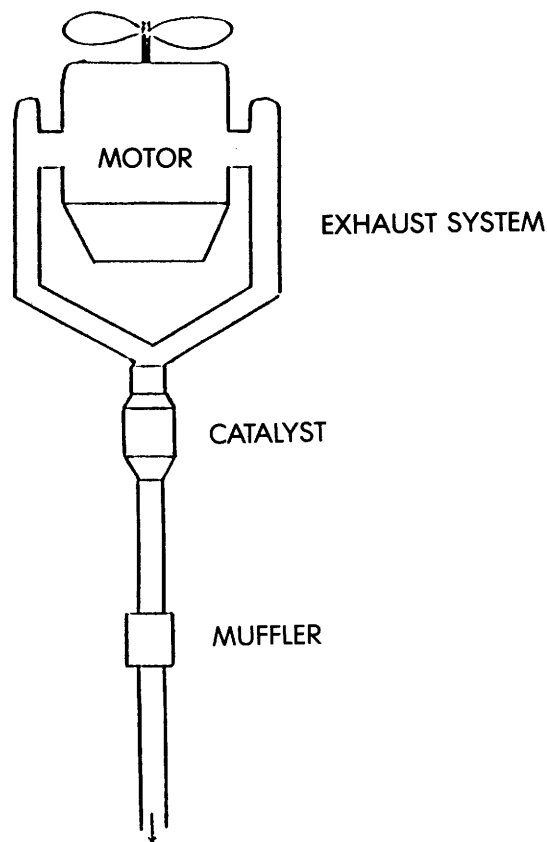


Figure 1. Schematic indicating the location of the catalyst in the exhaust system.

containing promoter base metal oxides to achieve simultaneous control of hydrocarbons (HC), carbon monoxide (CO) and oxides of nitrogen ( $\text{NO}_x$ ).

Aldehydes contained in the exhaust gases were sampled from the Tedlar bags using two impingers connected in series, each containing 10 ml of cyclohexane and 15 ml of an aqueous solution of 2,4-DNPHi (2 N HCl). After sampling, the two phases were separated. The organic phase was injected directly in the HPLC system. The entire aqueous phase was passed through Sep Pak cartridges (using a 30 ml glass syringe) at an approximate flow rate of 3 ml/min. The retained hydrazones were then eluted with acetonitrile to a final volume of 10 ml. Further details of this analytical protocol are reported elsewhere<sup>8,9</sup>.

### Results and Discussion

The weighted aldehyde emission factors for the ethanol vehicles operated under the urban driving cycle without catalytic converters were in the range of 0.019 to 0.046 g/km for formaldehyde and 0.143 to 0.246 g/km for acetaldehyde (Tables 1 and 2). For the GM vehicle, formaldehyde and acetaldehyde emissions were markedly higher during the transitory phase of the "cold" start (phase 1) of the test; during the second and third phases they were similar (Figure 2). For the VW vehicle, slightly higher emissions were observed for formaldehyde in the third phase with similar values obtained in the first and second phases; acetaldehyde emissions were similar in all three phases (Figure 3). Formaldehyde:acetaldehyde mole ratios for ethanol cars (0.13 and 0.19 Tables 1 and 2) are significantly lower ( $7.5 \pm 2.2$ ) than for noncatalyst US gasoline vehicles (1, quoting J. M. Heuss, personal communication).

**Table 1.** Noncatalyst and catalyst exhaust emission rates for the 1980 Chevrolet Opala operated under the Urban Driving Cycle.

Phase of the Cycle	g/km			
	HCHO		CH <sub>3</sub> CHO	
	Non-Catalyst	Catalyst	Non-Catalyst	Catalyst
1	0.065	0.004(94)	0.322	0.213(34)
2	0.050	0.023(54)	0.260	0.000(100)
3	0.023	0.004(83)	0.167	0.009(95)
Weighted	0.046	0.014(70)	0.246	0.044(82)

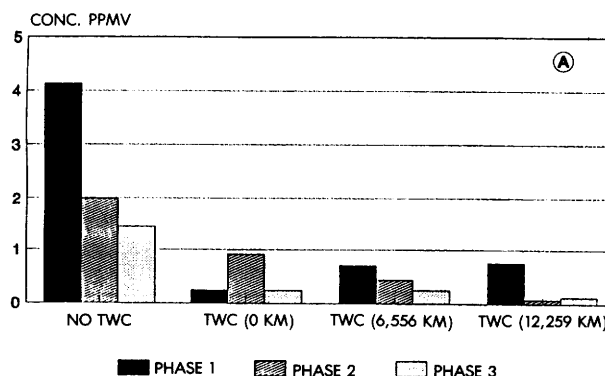
Values in parentheses represent the observed percent reduction

**Table 2.** Noncatalyst and catalyst exhaust emission rates for the 1982 Volkswagen Gol operated under the Urban Driving Cycle.

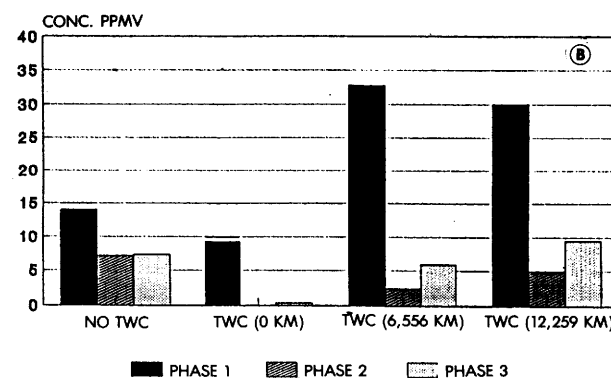
Phase of the Cycle	g/km			
	HCHO		CH <sub>3</sub> CHO	
	Non-Catalyst	Catalyst	Non-Catalyst	Catalyst
1	0.065	0.002(83)	0.100	0.083(17)
2	0.022	0.008(64)	0.175	0.000(100)
3	0.019	0.000(100)	0.113	0.029(74)
Weighted	0.019	0.005(74)	0.143	0.023(84)

Values in parentheses represent the observed percent reduction

### TWC Aging: Chevrolet Opala 1980 Formaldehyde



### TWC Aging: Chevrolet Opala 1980 Acetaldehyde



**Figure 2.** Aging of the Three-Way Catalyst of the 1980 GM Opala vehicle. A) formaldehyde, B) acetaldehyde.

Using the weighted factors obtained in this study, we estimated that the ethanol fleet alone (36% of light duty vehicles) circulating throughout the metropolitan region of São Paulo (8,000 km<sup>2</sup>) emits between 12 and 22 ton/day of both carbonyls (Table 3).

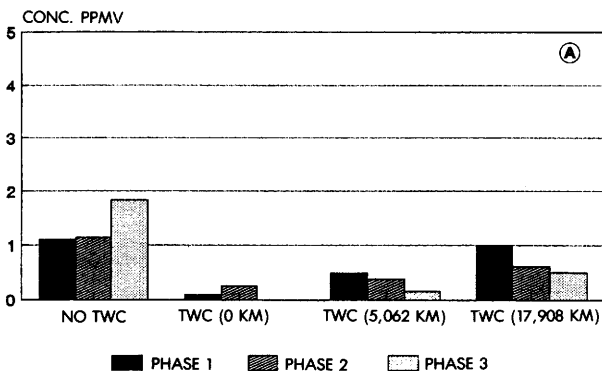
**Table 3.** Estimates of the exhaust emissions of formaldehyde and acetaldehyde to the atmosphere of the metropolitan region of São Paulo by ethanol-fueled light duty vehicles

Vehicle	Ton/day <sup>a</sup>		
	Formaldehyde	Acetaldehyde	Total
VW Gol	1.41	10.6	12.0
GM Opala	3.41	18.2	21.6

<sup>a</sup>based on 1.8 million vehicles, 15,000 km/year/vehicle and weighted aldehyde emissions data from Tables 1 and 2.

Immediately after installation of the Pt/Rh converters, substantial reductions were observed for the average weighted emissions of formaldehyde and acetaldehyde: 72% and 83%, respectively (Tables 1 and 2). Considering the three phases separately, for both vehicles, the highest reductions were observed for formaldehyde in the first phase of the "cold" start. In the second phase, the hottest

### TWC Aging: VW GOL 1982 Formaldehyde



### TWC Aging: VW GOL 1982 Acetaldehyde

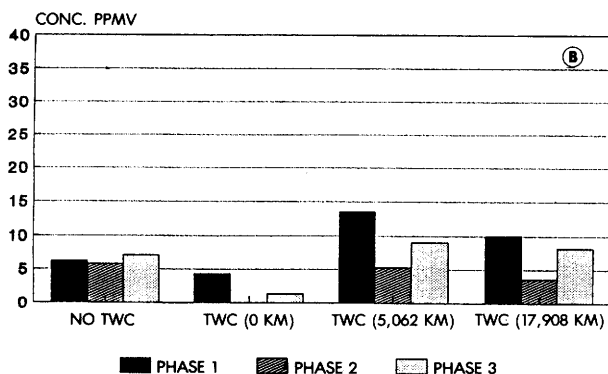


Figure 3. Aging of the Three-Way Catalyst of the 1982 VW Gol vehicle. A) formaldehyde, B) acetaldehyde.

of all three phases, for both vehicles, acetaldehyde reductions were 100%. In the third phase, for both aldehydes, the reductions were higher than 70% for both vehicles (Tables 1 and 2).

For both vehicles, catalyst aging was faster for acetaldehyde than for formaldehyde. It is worth noting that the catalysts employed were designed for gasoline cars where formaldehyde exhaust emissions are much higher than acetaldehyde<sup>1</sup>. After catalyst operation during normal vehicle use over 5,000 km, acetaldehyde emissions for both vehicles were in general higher than for the noncatalyst case, especially during the first phase where average actual increases of 124% and 91% were observed, respectively, for the GM and the VW vehicles (Figures 2 and 3). These increases may have resulted from conversion of unburned ethanol into acetaldehyde on the surface of the aged catalyst.

In addition, the decreased efficiency may have resulted from catalyst poisoning. After the last test period of the VW vehicle (over 17,908 km), the catalyst was removed and a section of the honeycomb inlet analyzed using an X-ray microprobe spectrometer. Of the particulate mass deposited over the front part of the catalyst surface, approximately 12% consisted of lead. Since the ethanol fuel was supposed to be free of lead, at this time, we can not ascertain as to the origin of the lead contamination.

## Conclusions

Formaldehyde and acetaldehyde emissions are markedly higher during the transitory phase of the "cold" start of the test. Installation of the Pt/Rh converters provided substantial reductions on the average weighted emissions of formaldehyde and acetaldehyde. Catalyst aging was faster for acetaldehyde and, after 5,000 km of operation, acetaldehyde emissions for both vehicles were higher than without catalysts, probably due to catalytic conversion of unburned ethanol into acetaldehyde.

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