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ALCOHOL AS AN AUTOMOTIVE FUEL, AND ITS ROLE ON ATMOSPHERIC
POLLUTION

Engº Gabriel Murgel Branco

Engº Manoel Paulo de Toledo

Engº Paulo Tetuia Hasegawa

ARQUIVO TECNICO

Companhia de Tecnologia de Saneamento Ambiental

São Paulo - Brazil

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ALCOHOL AS AN AUTOMOTIVE FUEL, AND ITS ROLE ON ATMOSPHERIC POLLUTION

1. INTRODUCTION

At the end of 1979 Brazil's crude oil reserves totalled 1264 mn barrels (52,8% offshore, 47,2 onshore) and natural gas deposits of 45,1 mn m³, representing increases of 10,6% and 1,8% respectively over and 1978 figures. (10) Despite this growth, global projections of petroleum reserves show that even with future constraints of consume it will not be useful for more than four decades.

Nowadays huge quantities of money are being applied in the viability studies for the use of alternative energy sources such as methane, coal gasification and liquefaction, hydrogen, methanol, ethanol etc...

In Brazil, the expansion of cane production aided by government incentives under the national alcohol program seems to be an irreversible path. At the present the combination of 20% alcohol with gasoline represents a savings of U.S.\$ 300 million/yr. The federal target for ethanol production for the country is about 2,77 billion gallons in 1985 and at the present, efforts are being concentrated for increase the output of alcohol (11). In other words, it can be said that ethanol is already chosen as a good alternative fuel. Now Brazil has just entered in the second phase of the process, i.e, the adaptation of gasoline vehicles for adequate use of gasoline-alcohol blends and at the same time a second generation of engines, especific for optimal alcohol use is begining to grow.

However, the problem of fuel changing is not only related to engine design, the Administrator must regard, among other



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items, the environmental impact.

The contribution of vehicular emissions at the São Paulo Metropolitan Area (SPMA) is the following according to the 1978 Cetesb SPMA Source Inventory: 76% of hydrocarbons, 96% of carbon monoxide, 84% of nitrogen oxides, 18% of sulfur oxides and 8% of particulate matter, corresponding to a total gasoline and Diesel powered fleet of $1,9 \times 10^6$ units. These figures were based on pure gasoline and Diesel emissions factors.

The following items briefly resume the properties of alcohol, its uses and the environmental aspects involved.

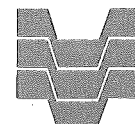
2. FUEL PROPERTIES

Properties which make ethanol distinct from gasoline include: lower heat of combustion, lower stoichiometric air-fuel ratio, leaner flamability limit, higher heat of vaporization, higher octane number in relation to non blended brazilian gasoline and a single boiling point, rather than a full destilation range.

The substitution of gasoline by ethanol without any carburetor adjustments does not change the meterd air-fuel ratio a great deal since the densities are similar.

On the other hand since the stoichiometric air-fuel-ratio is considerably lower for ethanol than gasoline, the addition of ethanol to gasoline causes the equivalence ratio leaner (2) and this is one of the most important mixture characteristics related to engine running and to exhaust emissions, as shown in figure 1.

Because of its high heat of vaporization the neat ethanol requires additional heating to the mixture and design revisions have to be made in intake manifold. The single boiling point of ethanol instead of a wide distillation



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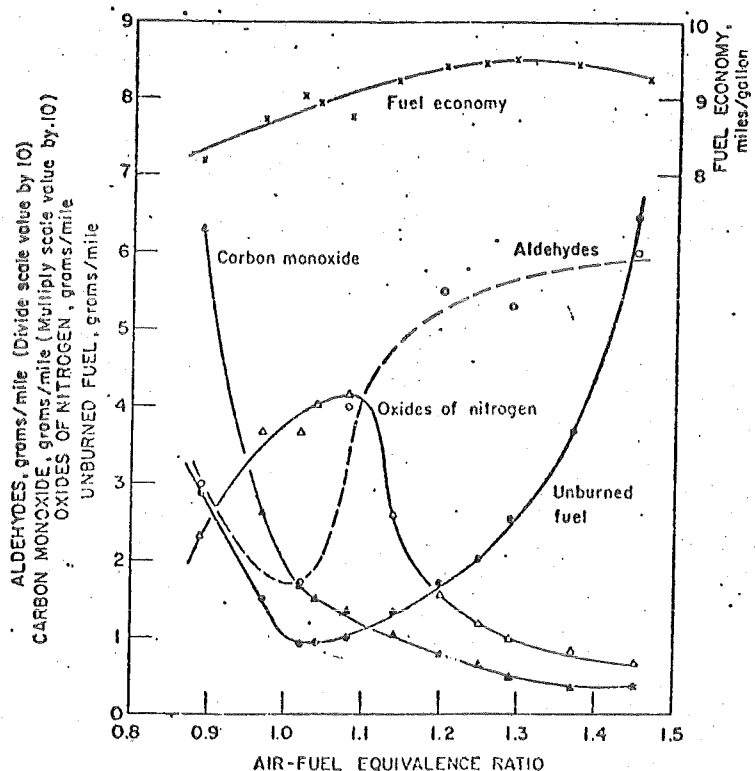


FIG. 1 - Mixture ratio effect on emissions and economy (ref. 3)

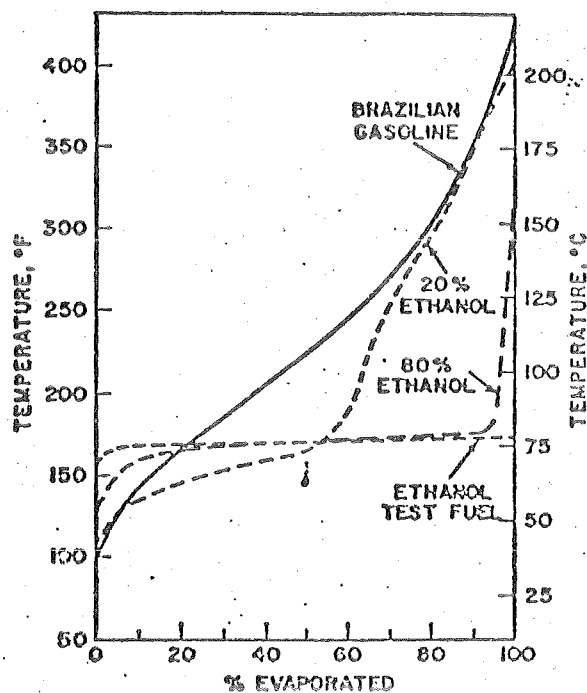


FIG. 2 - Distillation of Brazilian gasoline and its blends with ethanol (ref. 2)

range of gasoline (fig. 2), difficults some more the cold start and cold running in addition to vapor lock problems in temperatures higher than 80°C, (2). However the constant molecular composition of this fuel will permit a better control of the air fuel ratio, so resulting in a better CO control.

For diesel engines application, ethanol has a low octane



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number which difficults the expontaneous ignition. However this problem can be solved as described in item 5.

3. THE USE OF A GASOLINE BLEND WITH 20% OF ETHANOL

As it was shown in item 2, the addition of ethanol to gasoline increases the equivalence ratio and the anti-knock property of blended fuel. Since Brazilian vehicles manufactured before petroleum crisis were calibrated rich to have the best power and having the ethanol a leaner flamability limit, it had been possible to use the 20% ethanol/80% gasoline blend as automotive fuel, without any change in the vehicles calibration, as well as the addition of tetra-ethyl-lead can be reduced, which is a lead emission control mean. This practice has been used in Brazil since 1977 providing a better air fuel-ratio, so that carbon monoxide and hydrocarbon emissions have decreased, although aldehyde emissions have increased.

In relation to NO_x emissions two effects must be regarded. First, emissions have the tendency to be increased due to change in the mixture air-fuel ratio, secondly they have the opposite trend due to the lower combustion heat of ethanol which decreases the combustion chamber temperature. Finally, it is expected a small global increase in NO_x emissions, as shown in some reports (2 - 4)

Cetesb in its auto emission laboratory has sampled vehicles using some alcohol-gasoline blends (0; 5; 10; 15; 20 and 25%) (6). NDIR was used for analysis of carbon monoxide and hydrocarbons. For aldehydes it was used the adapted sodium bissulfide method.

The data was gathered with three vehicles in an electrical dynamometer used to simulate two modes: unloaded (free horizontal road and loaded (5% inclined road) and are presented in tables 1 to 6.

TAB. 1 - AVERAGE VALUES OF CARBON MONOXIDE (CO), IN PERCENT (%), OBTAINED WITH A CHEVETTE AT IDLE AND SEVERAL SPEEDS ON UNLOADED*AND LOADED*MODE IN DYNAMOMETER

% Alcohol	km/h	IDLE	20		30		40		50		60		70		80	
			UN-LOADED	LOADED	UN-LOADED	LOADED	UN-LOADED	LOADED	UN-LOADED	LOADED	UN-LOADED	LOADED	UN-LOADED	LOADED	UN-LOADED	LOADED
0		4.9	8.4	9.7	9.5	7.7	7.5	4.9	5.4	3.0	4.4	1.6	2.9	0.8	1.1	0.4
5		4.3	8.0	9.7	9.7	7.1	7.3	4.1	4.9	1.5	2.5	0.5	1.4	0.3	0.4	0.3
10		3.9	7.3	8.2	8.5	7.0	6.9	4.0	4.4	1.5	2.3	0.7	1.4	0.3	0.5	0.2
15		3.5	7.0	8.2	8.3	6.3	5.5	3.2	3.5	1.2	1.3	0.3	0.7	0.2	0.2	0.3
20		3.1	5.4	7.1	7.5	4.3	5.0	1.6	3.0	0.3	1.2	0.2	0.5	0.2	0.2	0.2
25		3.0	5.1	7.1	6.3	2.9	2.8	0.5	0.6	0.2	0.2	0.2	0.3	0.3	0.3	0.4

*Loaded and unloaded are dynamometer simulation for 5% inclined road and for free horizontal road.

TAB. 2 - AVERAGE VALUES OF CARBON MONOXIDE (CO), IN PERCENT (%), OBTAINED WITH AN OPALA AT IDLE AND SEVERAL SPEEDS ON UNLOADED* AND LOADED* MODE IN DYNAMOMETER

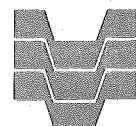
Km/h % Alcohol	IDLE	20		30		40		50		60		70		80		
		UN- LOADED	LOADED	UN- LOADED	LOADED	UN- LOADED	LOADED	UN- LOADED	LOADED	UN- LOADED	LOADED	UN- LOADED	LOADED	UN- LOADED	LOADED	
0	3.4	3.3	3.8	3.0	2.9	2.9	2.4	2.4	2.4	1.3	3.4	0.3	1.5	0.2	1.0	0.3
5	3.3	3.1	2.9	2.4	2.2	1.7	1.9	1.9	0.7	1.7	0.4	0.9	0.3	0.3	0.4	0.3
10	3.2	3.1	2.0	2.2	1.6	2.0	1.0	1.0	2.0	2.0	0.2	0.2	0.3	0.2	0.2	0.2
15	2.9	2.5	1.9	1.7	1.3	1.7	0.5	0.5	0.2	0.9	0.2	0.2	0.5	0.1	0.3	0.2
20	2.7	2.3	2.1	1.7	0.6	1.5	0.3	0.3	0.1	0.5	0.2	0.2	0.2	0.2	0.2	0.2
25	2.3	2.1	1.2	0.9	0.5	0.8	0.2	0.2	0.7	0.1	0.3	0.1	0.2	0.1	0.2	0.2

* Loaded and unloaded are dynamometer simulation for 5% inclined road and for free horizontal road.

TAB. 3 - AVERAGE VALUES OF CARBON MONOXIDE (CO), IN PERCENT (%), OBTAINED WITH A C-14 AT IDLE AND SEVERAL SPEEDS ON UNLOADED* AND LOADED* MODE IN DYNAMOMETER

Km/h % Alcohol	IDLE	20		30		40		50		60		70		80	
		UN- LOADED	LOADED	UN- LOADED	LOADED	UN- LOADED	LOADED	UN- LOADED	LOADED	UN- LOADED	LOADED	UN- LOADED	LOADED	UN- LOADED	LOADED
0	3.1	1.8	3.1	0.5	2.1	2.9	2.1	2.0	1.9	2.0	1.9	2.3	1.7	2.4	1.5
5	3.9	4.0	2.7	3.1	1.5	2.5	1.5	1.8	1.5	1.1	1.7	1.3	1.4	1.3	1.5
10	3.7	1.0	0.6	0.7	0.2	0.2	0.2	0.1	0.2	0.2	0.2	0.2	0.3	0.3	0.3
15	2.9	2.7	2.5	0.6	1.4	0.2	1.4	0.1	1.3	0.1	1.5	0.1	1.3	0.2	0.9
20	2.5	1.8	1.8	0.3	1.1	2.1	0.9	1.7	0.8	1.3	0.8	1.1	0.6	1.0	0.4
25	1.7	1.9	1.6	0.4	0.8	1.4	0.7	1.0	0.7	0.7	0.7	0.7	0.6	0.7	0.5

* Loaded and unloaded are dynamometer simulation for 5% inclined road and for free horizontal road.



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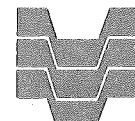
TAB. 4 - AVERAGE VALUES OF ALDEHYDE EMISSION IN PARTS PER MILLION (ppm), OBTAINED WITH VEHICLE CHEVETTE AT IDLE AND SEVERAL SPEEDS ON UNLOADED* MODE IN DYNAMOMETER

$\frac{\%}{\text{Alcohol}}$ \ km/h	IDLE	50	60	80
0	40	92	114	227
5	59	104	125	290
10	55	106	147	341
15	55	120	118	156
20	55	96	148	160
25	61	112	115	166

TAB. 5 - AVERAGE VALUES OF ALDEHYDE EMISSION IN PARTS PER MILLION (ppm), OBTAINED WITH VEHICLE OPALA AT IDLE AND SEVERAL SPEEDS ON UNLOADED*MODE IN DYNAMOMETER

$\frac{\%}{\text{Alcohol}}$ \ km/h	IDLE	40	50	60	70	80
0	38	50	61	61	86	104
5	41	52	64	67	102	106
10	42	54	67	69	105	137
15	47	59	67	71	118	141
20	50	62	81	89	142	211
25	53	68	85	91	149	228

* Unloaded mode is dynamometer simulation for free horizontal road



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TAB. 6 - AVERAGE VALUES OF ALDEHYDE EMISSION IN PARTS PER MILLION (ppm), OBTAINED WITH VEHICLE C-14 AT IDLE AND SEVERAL SPEEDS ON UNLOADED*MODE IN DYNAMOMETER

% Alcohol \ km/h	IDLE	40	50	60	70	80
0	41	50	57	67	74	94
5	52	51	58	67	83	125
10	54	52	54	81	94	114
15	59	58	66	84	96	119
20	68	64	67	98	106	122
25	69	72	108	126	139	141

* Unloaded mode is dynamometer simulation for free horizontal road.

4. USE OF NEAT ETHANOL IN OTTO CYCLE ENGINES

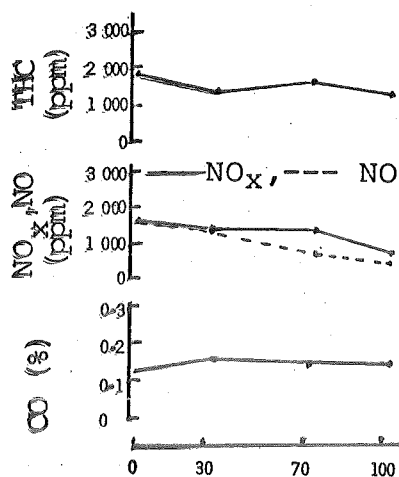
The Otto cycle engines can burn ethanol very well if in their designs it has been taken the advantages of its high knocking resistance quality to increase engine efficiency and specific fuel economy, thus compensating the lower heat of combustion.

Theoretically, a well designed Otto ethanol engine can produce 18% more power, consuming 17% more fuel, when compared to an equivalent gasoline engine of the same size. (1)

The first step on that way is to adapt some vehicles to burn neat ethanol, by reworking their heads to increase the compression ratio. Modifications in intake manifold and new calibration for carburetor and distributor advance curve have to be done to achieve the best advantages. The best compromise with power, driveability and fuel consumption was achieved with compression ratio around 12:1 and equivalence ratio near 1.3. In addition the cold start and fuel system corrosion problems have to be solved to complete those engine's development.

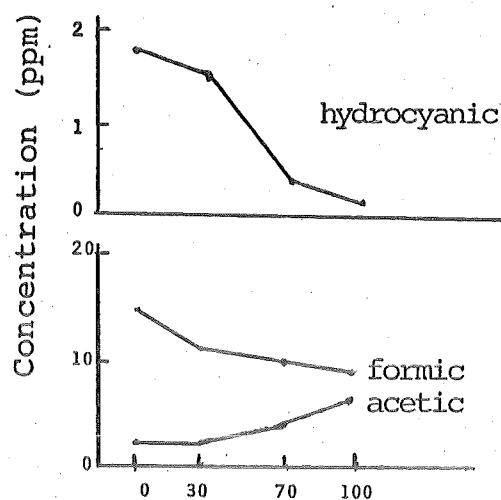
In an experiment developed with an one cylinder engine, with 8:1 compression ratio, 1.2 equivalence ratio, at 1.800 rpm, MBT, using gasoline and ethanol-gasoline blends, it was concluded that total hydrocarbon and oxides of nitrogen have decreased while carbon monoxide remained constant as expected due 1.2 equivalence ratio, with the increase in the percentage of ethanol, in the fuel (see figure 3).

It might be noted that even so the total hydrocarbon remained around 1.600 ppmC with neat ethanol, a gas chromatograph analysis identified the major constituents of these pollutants as 1.100 ppmC of ethanol (unburned fuel) and 400 ppmC ethylene (practically the only hydrocarbon generated in combustion chamber). These results show that



Alcohol content (vol.%)

FIG.3- Relations between the alcohol content of fuels and the NO_x , CO and THC concentrations in the exhaust gas



Alcohol content (vol.%)

FIG.4- Relations between the alcohol content of fuels and the acids concentrations in the exhaust gas

ethanol engines emit much more alcohol than true hydrocarbons, which suggests the development of further researches to determine the ethanol influence on atmospheric chemistry and new ethanol analysis methods have to be improved for auto emissions testing.

It has to be cited a decrease in formic acid, an increase in acetic acid and a decrease in the hydrocyanic acid emissions, observed with the increase of the percentage of alcohol in the fuel (see figure 4).

Another experience was conducted by Ford (2) on a 1.4 l engine and a 2.3 l light duty truck engine, both recalibrated for ethanol use but, unfortunately, the compression ratio was maintained at 8.0:1 not profiting all the advantages of ethanol octane number. This test showed an increase of acetaldehyde and ethanol emissions, a decrease of carbon monoxide and hydrocarbons, and the

TABLE 7 - CARBON MONOXIDE EMISSION (%) FOR ETHANOL VEHICLE AND GASOLINE VEHICLE, ON LOADED* AND UNLOADED* DYNAMOMETER

SPEED	LOADED		UNLOADED	
	Gasoline Vehicle	Ethanol Vehicle	Gasoline Vehicle	Ethanol Vehicle
30	2.6	1.1	2.5	2.7
40	2.5	0.5	2.3	1.4
50	1.9	1.0	2.1	1.0
60	1.1	1.2	1.6	0.6
70	2.0	0.7	1.3	1.4
80	1.0	0.5	0.9	1.1
90	1.1	0.5	0.6	0.5
100	1.2	0.7	0.4	0.3

TABLE 8 - TOTAL ALDEHYDE EMISSION (ppm) FOR ETHANOL AND GASOLINE VEHICLE, ON UNLOADED* DYNAMOMETER.

SPEED	Gasoline Vehicle	Ethanol Vehicle
50	80	111
60	89	127
70	109	164
80	1011	203

*Loaded and unloaded are dynamometer simulation for 5% inclined road and for free horizontal road.

nitrogen oxides remained practically unchanged

Tests performed at CETESB Emissions Laboratory on 1.3 l engines adapted to run on ethanol, according to modifications described at the beginning of this item including compression ratio, showed the results presented in tables 7 and 8. As shown in those tables, one may compare ethanol to gasoline engines and conclude:

- a) carbon monoxide decreased significantly, due to the leaner mixture;
- b) the aldehyde emission is higher due to leaner mixture, higher quantity of aldehydes in the fuel and to a thicker quenching layer in the combustion chamber;
- c) the hydrocarbon emissions are lower, because these pollutants come only from generation in the combustion chamber. However, ethanol is a new pollutant emitted due to unburned fuel;
- d) the nitrogen oxides emission was not measured. Since the heat of combustion of the ethanol is lower, NO_x emissions will be lower too. Inversely, the higher compression ratio will cause this emission to increase. However, the Brazilian ethanol engines were developed to have the same power as they have with gasoline. For this reason the same temperatures are achieved in the combustion chamber and we may expect the same NO_x emission too, this fact might not occur when higher power/displacement ratios were obtained.

5. THE USE OF ETHANOL IN DIESEL ENGINES

The use of ethanol in Diesel engines is not so recommendable as it is in Otto cycle engines. This is due to following properties:

- a) the cetane number for alcohol is too low, which

implies in the use of some techniques to improve the fuel auto-ignition capability;

- b) the lower heat of combustion of ethanol will decrease engine power or will increase its fuel consumption to achieve the same power, since the compression ratio change advantages are not reliable in this case.

Many attempts have been done to solve the auto-ignition in Diesel engines running on ethanol, but each one presented some problems as described below:

- a) Injected Diesel oil/carburetted ethanol (7):

The experience was carried by reducing the amount of Diesel oil injection and ethanol is supplied through a carburetor until the same torque obtained at 100% Diesel injection. It was observed a significant reduction in smoke emission, which was the only pollutant measured in this test (see fig.5).

- b) Injected Diesel/Ethanol emulsion:

Some additive stabilized Diesel/Ethanol emulsions were tried, as well as it was tried to emulsionate both fuels mechanically. Unfortunately these experiences didn't show good results yet, mainly the second case which presented emulsion separation in fuel lines.

- c) Dual injection system:

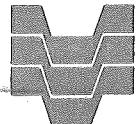
In this design a constant small amount of Diesel oil is injected to provide idle fuel requirement.

A separated fuel system injects ethanol in the combustion chamber to supply the necessary fuel to achieve the desired torque.

The main problems in this concept is ethanol injection pump wear and engine cost due to fuel system duplication.

- d) Diesel completely substituted by ethanol:

Some engineers tried to use a spark plug (9) or even a hot spot plug in the combustion chamber to promote



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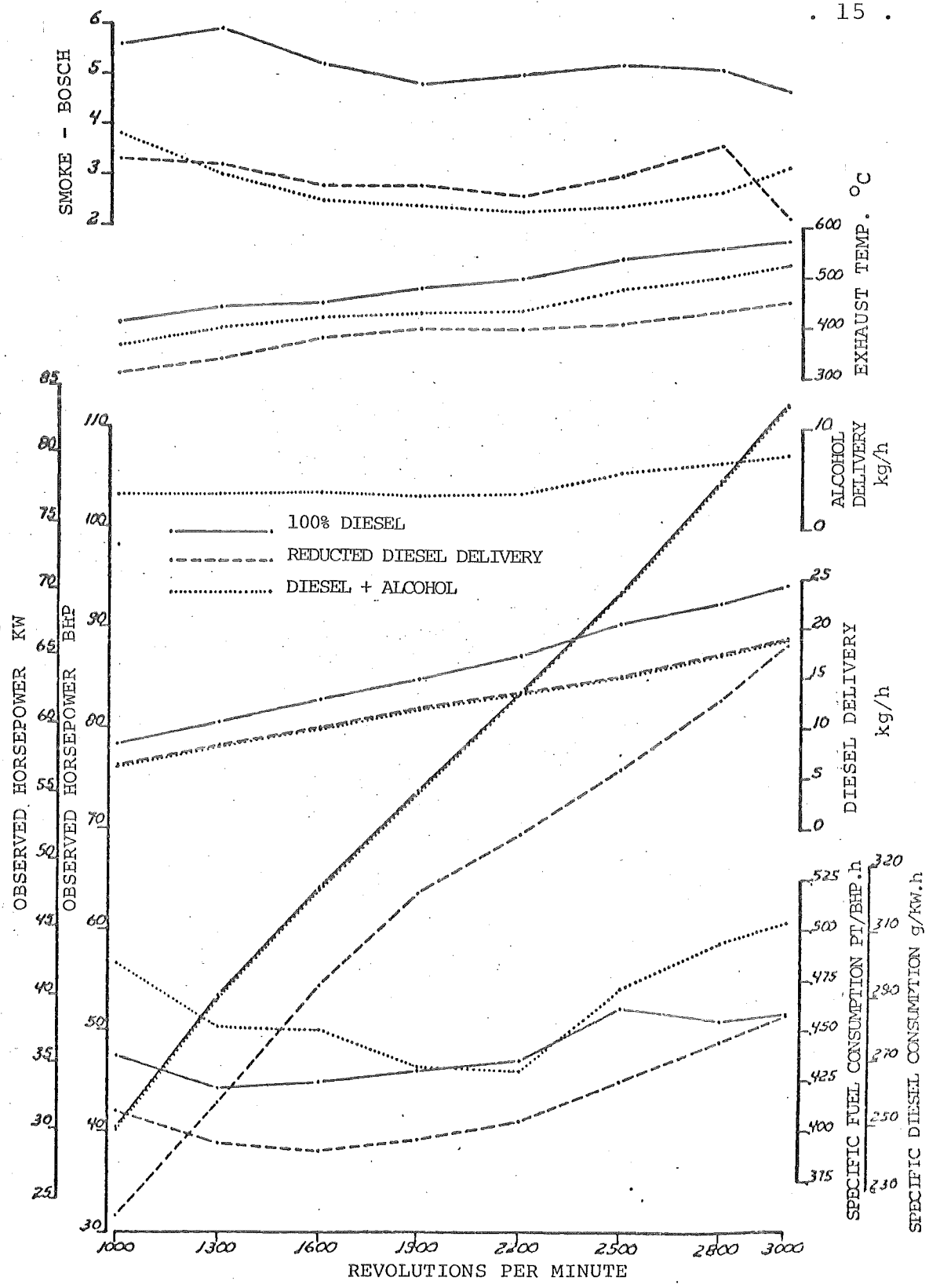


FIG. 5 - Performance curves for injected Diesel oil/carburetted alcohol engine.

charge ignition. However, in Brazil, the use of nitrated additives to improve ethanol auto-ignition properties seems to be the industries tendency.

Experiments were run with the addition of 20% amyl nitrate or 6% diethyl glycol dinitrate, but it is expected this practice should alter the present emissions of aldehydes, nitrogen oxides, etc. and cause some pollutants to appear like hydrocyanic acid and others.

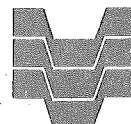
Since this subject is very recent, there is not enough data to define the problem associated to these engines.

As described in next item, determination of important pollutants emitted by these engines is necessary and, possibly, new analytical methods will be developed later.

6. ANALYTICAL METHODS

The current methods for measurement of exhaust gas emissions were developed for gasoline and Diesel powered engines. The use of gasoline-alcohol blends or neat alcohol as fuel arises some problems of interferences that must be eliminated by further improvements in the actual methods.

For example, the flame ionization detector (FID) method for total hydrocarbon emissions have interferences concerned to compounds in which carbon is bonded directly to oxygen (carbonyls), nitrogen (cyanides) and halogenes (halides). The quantity of compounds with these bonds is generally small when compared to that of hydrocarbon on pure gasoline engine emissions and cause little error in the measurements of total organics as ppmC. However the use of a fuel that will provide an appreciable quantity of partially oxygenated compounds resulting from combustion or even in the form of unburned fuel will potentiate the interferences to a degree that they could not be ignored anymore.



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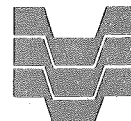
In terms of overall detector response to total organics will happen a decrease and in terms of "pure HC" the response will be higher since the FID responds, even though not in a direct proportion to the number of carbon atoms per molecule, to the carbon-hydrogen bonds of the partially oxidated compounds. To solve this problem, extensive experiments using chromatographic systems directly associated with FID monitors must be carried on for the most abundantly partially oxigenated compounds searching for FID relative responses to them and thus optimal FID correction calibration coefficients.

Another existing problem in the case of fuel change is that unfortunately no instrumental methods are available for aldehyde analysis, and wet chemical methods employing measurement of light absorbance after reation with a suitable reagent must be used. This circunstance is not feasible to use simultaneously with constant volume sampler techniques. Similar problems are to be showed for ammonia, hydrocyanic acid and some expected organic acids emissions.

Finally, the research and identification of new chemical species on exhaust emissions as the development of new continous monitoring methods, developed under corrosion prevention engineering, seems to be a large gap in relation to the current CVS mass emissions systems for gasoline powered engines, however it is a defiance that technology will certainly overcame as soon as fuel changes will become as mandatory as environment preservation.

7. CONCLUSIONS:

- The addition of ethanol to gasoline decreases HC and CO emissions, increase aldehydes emissions and permits the reduction of lead emissions if one decrease the tetra ethyl lead percentage in the gasoline.
- The partial substitution of diesel oil by ethanol



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decreases black smoke.

- The use of neat ethanol as engine fuel decreases CO emission, increases aldehyde emission and reduces the true hydrocarbon emissions but creating a new pollutant: the unburned ethanol.
- The use of additive improved cetane number ethanol as Diesel engines fuel may produce different pollutants, which might be studied.
- It is recommended more studies should be made to determine and quantify the ethanol engine's pollutants, as well as researches on atmospheric reactivity and toxicological effects of these pollutants are necessary.
- Other emission measurements through a driving cycle with variations in speed, that represents the actual driving habits and traffic conditions, well correlated with air quality and having its results in g/km and not in concentration.
- Studies have to be made to determine new methods to analyse and quantify new pollutants.
- Engine development should be made to minimize costs and increase efficiency of control devices for alcohol engines.

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