Emissions From the Methanol Fueled Stanford University Gremlim

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# Background

The methanol-fueled AMC Gremlin built by Stanford University students was named winner in the Liquid Fuel Division of the 1970 Clean Air Car Race. For this reason the car was evaluated by the Test and Evaluation Branch, as a prototype vehicle under the Federal Clean Car Incentive Program, between March 1 and March 19, 1971.

### Control Technique

The use of methanol as a fuel is the basic technique used in the Stanford Gremlin for control of pollutant emissions. Carburetor jets were changed to furnish air-fuel ratios slightly on the lean side of stoichiometric. The intake manifold was modified to supply additional heat to the mixture. An Engelhard catalyst was placed about six inches downstream of the exhaust manifold. An exhaust gas recirculation system was installed, but not used during the course of our tests.

#### Test Program

The test car was an American Motors Gremlin with a 232 cubicinch six-cylinder engine and standard three-speed transmission. Methanol fuel was obtained from a local chemical supply company.

Test procedures included the 1972 Federal Test Procedure (per the November 10, 1970, Federal Register), the 1970 FTP, and the 9 x 7 procedure, all with hot starts as well as cold starts.

At the start of the program lead-free gasoline was used as the fuel for one 1972 FTP and one 9  $\times$  7 test, to provide baseline emission data.

After testing at Ypsilanti was completed, the car was delivered to the Division of Chemistry and Physics, Fairfax Facility, Cincinnati, Ohio, for a thorough characterization of hydrocarbons and determination of aldehyde emissions.

### Results

Results of the emissions tests are presented in Tables 1 and 2. Table 1 is from the 1972 FTP, while 7-mode cycle results are in Table 2. In the 1972 FTP and the 9 x 7 procedures, HC data are determined by FID, and  $\mathrm{NO}_{\mathrm{X}}$  emissions by two techniques: chemiluminescence (C.L.) and Saltzman. In the 1970 FTP all data are determined by NDIR. All  $\mathrm{NO}_{\mathrm{X}}$  emissions data presented in Tables 1 and 2 are reported as  $\mathrm{NO}_{2}$ , corrected to 75 grains humidity.

The 1972 FTP mass emissions data show good control of emissions, as the car comes very close to meeting the 1975-76 Federal standards of .41 gm/mi HC, 3.4 gm/mi CO, and .4 gm/mi  $NO_x$ .

Results from the testing at DCP Cincinnati are summarized in this report as Appendix A. Appreciation is extended to John Sigsby for these data.

#### Conclusion

The results of these tests indicate that the use of methyl alcohol as fuel can result in very low emissions. The most noticeable change on this car was in the reduction of  $\mathrm{NO}_X$  when changing from gasoline to methanol. This may be due chiefly to the higher heat of vaporization of methanol, leading to a lower flame temperature.

Table 1
Stanford Methanol Gremlin
Mass Emissions
1972 Federal Test Procedure

Test No.	HC gm/mi	CO gm/mi	NO <sub>X</sub> C.L. gm/mi	NO <sub>X</sub> Saltzman gm/mi	Comments
12-1350	.33	1.30	.20	.31	Standard Test
12-1361	.50	13.13	no data	.29	Standard Test
12-1368	.58	4.57	.22	.24	Standard Test
12-1376	.43	5.77	no data	5.23*	Standard Test
12-1378	.64	12.61	.22	.25	Standard Test
12-1408	.24	3.55	. 30	.30	Standard Test
1353	.09	.20	.17	.37	Hot Start
12-1370	.06	.92	.20	.23	Hot Start
12-1377	.04	.50	.09	2.22*	Hot Start
12-1409	.04	.49	. 26	.27	Hot Start
					·
12-1331	. 34	5.44	4.74	4.27	Cold, Gasoline

<sup>\*</sup> Saltzman data believed not correct.

Table 2
Stanford Methanol Gremlin
Mass Emissions
7-Mode Driving Cycle

Test No.	HC gm/mi	CO gm/mi	NO <sub>X</sub> C.L. gm/mi	NO <sub>X</sub> Saltzman gm/mi	Comments
12-1391	. 32	3.87	. 39	. 32	9 x 7
12-1400	1.58	9.46	.20	. 36	9 x 7
12-1367	.05	1.37	.04	.41	$9 \times 7 \text{ Hot}$
12-1401	.10	.23	.55	.46	9 x 7 Hot
12-1333	.28	7.25	2.80	2.41	9 x 7 Cold, Gasoline
					dasoline
6-0618	.32	1.59	.09 by N	IDIR	70 FTP
6-0622	.47	2.17	.15 by N	IDI R	70 FTP
			•		
6-0615	.19	. 34	·· no data		70 FTP Hot
6-0623	.20	.16	.10 by N	IDIR .	70 FTP Hot

# Appendix A

- 1. Tests were performed using the proposed 1972-3 Federal cycle from both a cold and a hot start. A 3500 lb. fly-wheel was used. The hot start consisted of insuring that the car was thoroughly warmed up; turning it off, and within ten minutes re-running the Federal cycle. The cold starts were run after an overnight soak on the dynamometer. After these runs were made, the catalyst was removed and one run each was made from both a cold and a hot start. One false start, i.e., the engine died at the beginning of the cycle, occurred on each of the cold starts except C7. The vehicle was restarted and the test begun over. The effluent was defined by the constant volume sampler. The summary of these results is shown in the attached tables.
- 2. As expected, few aldehydes other than formaldehyde, were present in appreciable quantities. DNPH derivatives were made and gas chromatographed to determine the distribution of the aldehydes formed. This confirmed the wet chemical tests which are shown in the tables. Formaldehyde was the only specific aldehyde that could be quantitatively measured, traces of higher aldehydes were also seen with acetaldehyde being the most abundant.
- 3. A remarkable number of other hydrocarbons were seen over background. Concurrent background samples were collected and analyzed for each run. The values are confirmed by the runs which were made with the catalyst removed. As might be expected, the primary hydrocarbons produced were olefinic in nature. Any reactivity consideration must be based on the reactivity of methanol which overrides any other compound in concentration.
- 4. The largest effect of the catalyst was to reduce the methanol 90% for cold starts and 96% for hot. The catalyst also reduced CO by about 70% while having no effect on the oxides of nitrogen. Aldehydes were reduced 75 to 80%.
- 5. Methane was not measureable above background in the hot start tests. It was very low in the cold starts accounting for 4% of the total. Methanol accounted for 95% and 97% of the hydrocarbons seen from cold and hot starts respectively.
- 6. The largest difference between cold and hot starts were in hydrocarbons and CO which decreased between 80 and 90%. Aldehydes were only reduced 30% and  $\rm CO_2$  and  $\rm NO_x$  about 10%.
- 7. The  $NO_X$  emissions were predominately NO with little  $NO_X$  or reduced nitrogen present.

Appendix A

Stanford Methanol Gremlin
With Catalyst
Cold Start Tests

<i>•</i>					
Run #	C <sub>4</sub>	C5	c <sub>7</sub>	Average	
Compound	ppmc	ppmc	ppmc		
Methanol	137	220	127	161	
Methane	5.6	9.1	5.2	6.6	
Ethylene	0.47	1.0	0.47	0.6	
Butene-1/2 Methyl Propen	0.44 ne	0.62	0.01	0.4	
Propylene	-	2.2	0.71		
Ethane	0.31	0.44			
obutane	0.31	trace	0.37		
Acetylene		0.08			
N-Pentane			0.07		
TOTAL	144	233	134	170	٠
			missions s/mile		
Hydrocarbon	0.17	0.22	0.14	0.18	
СО	2.88	<b>3.</b> 51	3.35	3.3	
co <sub>2</sub>	545	541	548	545	
$NO_\mathbf{X}$	0.54	0.57	0.54	0.55	٠
Total Aldehydes	0.077	0.099	0.093	0.090	
rmaldehyde	0.075	0.089	0.086	0.083	

Appendix A

Stanford Methanol Gremlin With Catalyst Hot Start Tests

Run #	C <sub>3</sub>	c <sub>6</sub>	C8	Average
Compound	ppmc	ppmc	ppmc	
Methano1	27	26	33	29
Methane				•
Ethylene	0.47	0.18	0.47	0.37
Butene-1/2 methy1 Propene	0.03		· ·	
Isobutane		1.0	.06	
N-Pentane		0.76	Service .	
Tso pentane		1.0	70.	
. opylene	••	0.01		
Ethane		trace		
TOTAL	27.5	28.8	33.6	30
•			. •	
		Mass Emissions grams/mile		
Hydrocarbon	0.02	0.02	Not Measured	0.02
СО	0.61	0.46	0.75	0.61
CO <sub>2</sub>	490	506	486	494
$\mathtt{NO}_{\mathbf{X}}$	0.506	0.48	0.45	0.48
Total Aldehyde	0.033	0.076	0.085	0.065
Formaldehyde	0.019	0.072	0.079	0.057

Appendix A
Stanford Methanol Gremlin
Catalyst Removed

Run #	COLD START	•	HOT START	
			c <sub>10</sub>	
Compound	ppmc		ppmc	
Methanol	1580.	•	810	
Methane	7.8		Not measured	
Ethylene	4.2		5.0	
Butene-1/2 Methy1 Propene	0.49		0.28	
Propylene	trace		0.21	
Ethane	trace		trace	
obutane	0.09		0.40	
Acetylene	1.72		1.16	
N-Pentane	0.10		0.03	
TOTAL HYDROCARBON	1600		820	
	Mass Emissi grams/mil			
Hydrocarbon	1.33		0.77	
СО	10.8		2.6	
co <sub>2</sub>	520		488	
$NO_\mathbf{x}$	0.45		0.43	
Total Aldehyde	0.36		0.33	
Formaldehyde	0.34		0.30	