EPA/AA/CTAB/91-04

Technical Report

Evaluation Of A Kemira Oy Resistively Heated Catalyst On A Methanol-Fueled Vehicle

by

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September 1991

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Technical Reports do not necessarily represent final EPA decisions or positions. They are intended to present technical analysis of issues using data which are currently available. The purpose in the release of such reports is to facilitate the exchange of technical information and to inform the public of technical developments which may form the basis for a final EPA decision, position or regulatory action.

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

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SEP 25 1991

OFFICE OF
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MEMORANDUM

SUBJECT: Exemption From Peer and Administrative Review

FROM: Karl H. Hellman, Chief KH
Control Technology and Applications Branch

TO: Charles L. Gray, Jr., Director
Emission Control Technology Division

The attached report entitled "Evaluation Of A Kemira Oy Resistively Heated Catalyst On A Methanol-Fueled Vehicle" (EPA/AA/CTAB/91-04) describes the evaluation of resistively heated catalyst system on a methanol-fueled vehicle. A compact resistively heated metal monolith converter was used to reduce emission levels of unburned fuel, carbon monoxide, and formaldehyde over the Bag 1 portion of the Federal test procedure driving cycle. This catalyst system was evaluated with and without secondary air assistance.

Since this report is concerned only with the presentation of data and its analysis and does not involve matters of policy or regulation, your concurrence is requested to waive administrative review according to the policy outlined in your directive of April 22, 1982.

Concurrence: Charles L. Gray Jr. Date: 9-22
Charles L. Gray, Jr., Dir., ECTD

Nonconcurrence: _____ Date: _____
Charles L. Gray, Jr., Dir., ECTD

cc: E. Burger, ECTD

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I. Summary

A fresh resistively heated catalytic converter was furnished by Kemira Oy to the U.S. Environmental Protection Agency (EPA) for evaluation on a methanol-fueled vehicle. This converter substrate was constructed from metallic foil and was considerably smaller in volume than three-way catalysts found on most late model U.S. automobiles. The Kemira Oy converter is referred to hereafter as an electrically heated catalyst (EHC).

The EHC was evaluated in four separate modes. First, this catalyst was placed on an M100 (neat methanol) fueled vehicle and emission tested without resistive heating or catalyst air assist. The EHC was then tested using resistive heating, but with no air assist provided during the period of heating. A catalyst operating mode utilizing both resistive heating and air assist was evaluated next. Finally, a larger catalyzed ceramic monolith was added behind the EHC as a main catalyst. This two-catalyst system was then evaluated, with resistive heating and catalyst air assist applied to the upstream EHC.

The testing described here utilized M100 neat methanol fuel and was conducted over the Federal test procedure (FTP) CVS-75 test cycle. Catalyst resistive heating and air assist were limited to portions of the initial cold start Bag 1 phase (first 505 seconds) of the FTP. The emissions of primary interest during this evaluation were methanol (unburned fuel), formaldehyde, and carbon monoxide (CO). Details of the test procedure are discussed later in a separate section of this report.

Resistively heating the EHC in the absence of catalyst air assist provided a very limited reduction in emission levels. The only substantial reduction occurred when the Bag 1 emissions of methanol were reduced to 3.06 grams, from 6.22 grams with the unassisted (no resistive heat/no air addition applied) catalyst. A combination of EHC resistive heating and air assist however, provided substantial reductions in emission levels of unburned fuel and CO. Bag 1 emissions of methanol were reduced to 1.81 grams, a reduction of over 70 percent from unassisted catalyst levels. CO emissions were also reduced over 60 percent from unassisted catalyst levels through this combination of EHC heating/air assist.

The two-catalyst system mentioned above, using resistive heating/air assist of the EHC, provided the lowest emissions of all catalyst configurations tested. Methanol and formaldehyde emissions were reduced to 0.09 grams and 11 milligrams respectively over Bag 1 with the two-catalyst system. These low Bag 1 emission levels contributed substantially to the calculated emission rate of 0.02 grams per mile of organic material hydrocarbon equivalents (OMHCE) over the FTP. Weighted average formaldehyde emissions over the FTP were less than 2 milligrams per mile, well below the State of California standard of 15 milligrams per mile. The very low Bag

1 levels of methanol and formaldehyde, with the two-catalyst system here, represent conversion efficiencies of greater than 99 percent from baseline (no catalyst) levels from the test vehicle.

CO emissions over Bag 1 were reduced more than 96 percent from no catalyst levels using the two-catalyst system. This efficiency was reflected in FTP weighted average CO emissions, where the two-catalyst system also provided 96 percent conversion efficiency from no catalyst levels. NOx emissions, however, were relatively unaffected by changes in catalyst configuration here. Even the use of catalyst air assist (restricted to 100 seconds following cold start in Bag 1) did not greatly affect NOx levels. A slight decrease in Bag 1 emissions of NOx was noted with the two-catalyst system, compared with the other catalyst configurations evaluated.

II. Introduction

HC and CO emissions from the cold start portion of Bag 1 represent the greatest portion of these emissions over the Federal Test Procedure (FTP) from today's catalyst-equipped gasoline vehicles.[1] The same is true for emissions of unburned fuel (methanol), CO and formaldehyde for vehicles fueled on M100 neat methanol.[2,3] Recent enactment of new clean air legislation in the United States has also refocused attention on regional problems of excess CO emissions from motor vehicles operated at low ambient temperature conditions.[4]

One strategy to decrease cold start emissions utilizes a resistively heated catalyst to shorten the time to light-off, or the time at which the converter becomes catalytically active. Excess emissions of unburned fuel and CO occur during engine warmup, when the engine is operated slightly rich of normal operating conditions to improve driveability. It is during this period of excess emissions that conventional three-way exhaust catalysts are not yet active, because of insufficient warming from the relatively cool exhaust gases. Resistive heating can bring the catalyst to active temperature (approximately 350°C for conventional catalysts) quickly, seconds after the engine is started during FTP testing at 75°F. The decrease in catalyst light-off time, coupled with secondary air addition to assist oxidation, can provide a flexible solution to this problem.

EPA has evaluated several resistively heated metal monolith converters in efforts to reduce Bag 1 emissions of unburned fuel and CO.[5,6,7,8,9] These efforts have involved the use of converter substrates of different volumes and several different active catalyst formulations. These catalysts were all low mileage and relatively efficient at low mileage. All of the resistively heated metal monolith converters evaluated and reported on to date by EPA were supplied by Camet Co., a subsidiary of W. R. Grace.

One of the reasons that EPA conducts and publishes the results from emission control technology evaluations is to spur further interest in new technologies by automakers and industry hardware suppliers. Interest in resistively heated catalyst technology for mobile sources has continued to grow, and several industry sources have agreed to provide EPA with samples of their catalysts for evaluation. One of these catalyst suppliers, Kemira Oy, recently furnished EPA with a heated catalyst for evaluation on a methanol-fueled vehicle. A preliminary evaluation of this low-mileage converter was conducted; results from this testing are presented below. More testing, however, will be necessary in order to refine the catalyst heating and air addition strategies.

III. Description Of Catalytic Converter Technology

The resistively heated catalytic converter consists of a folded metal foil which has been washcoated and catalyzed with a 5:1 platinum/rhodium mixture. The converter is described below; a more complete description was provided by the manufacturer, Kemira Oy, in an earlier paper of the Society of Automotive Engineers.[10]

The foil used for the substrate consisted of Aluchrom ISE with a thickness of 0.044 mm. While the foil can be folded and rolled to cell densities of 200-800 cells/square inch (cpsi), an intermediate density of 500 cpsi was utilized here. A round, rather than oval, substrate shape was utilized. Unlike the catalysts described in the earlier paper by Kemira Oy,[10] a wool insulation was added between the shell and the rolled foil for the catalyst described here.

A 12-volt DC automotive battery was used to supply the energy for resistively heating the converter. Resistance across the can electrical connection posts was measured at 0.2 ohms. The application of 12 volts from the fully charged battery caused a current of approximately 350 amps at start in the circuit (the other circuit components were #6 gauge copper cables six feet in length and #00 gauge copper cables nine feet in length). This measured current decreased to approximately 230 amps after 40 seconds of resistive heating.

Table 1 below presents specifications of the resistively heated catalytic converter evaluated here. A picture of the converter is presented here as Figure 1.

A catalyzed ceramic monolithic substrate provided by Engelhard Industries was installed in back of the EHC during the latter part of this evaluation. This ceramic monolith functioned as a main catalyst in the two-catalyst system referred to later. This substrate was cylindrical in shape, 4.0 inches in diameter and 6.0 inches in length. The monolith contained 400 cells per square inch and was catalyzed with platinum only, at a loading of 50 grams per cubic feet.

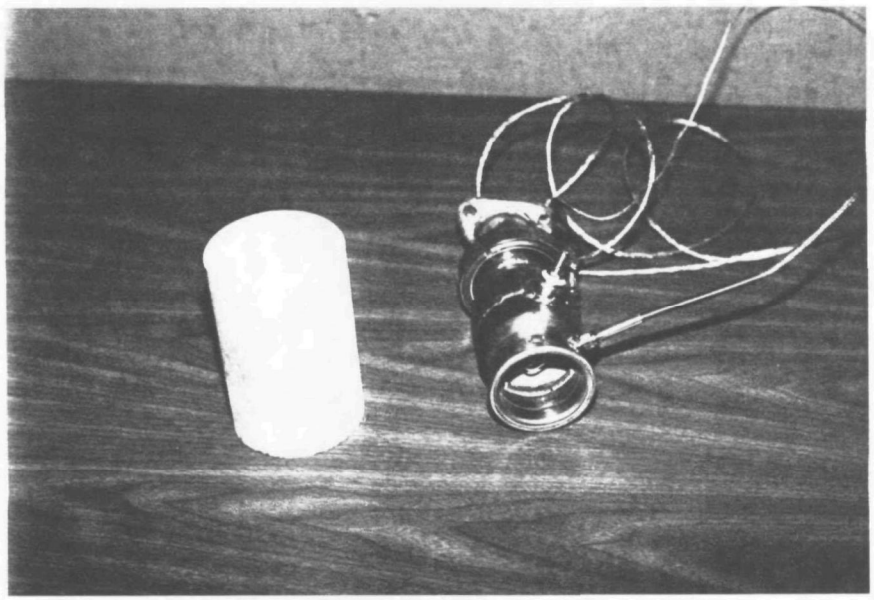
Table 1

Specifications Of Kemira Oy Resistively Heated Catalyst

Specification	Dimension
Substrate Diameter	68.5 mm
Length	50 mm
Volume	0.184 dm^3
Cells Per Square Inch	500
Geometric Surface Area	0.6 m^2
Cross Section	36.9 cm^2
Active Catalyst	0.26 grams total 1.41 g/dm^3 (40 g/ft^3) 5:1 Platinum/Rhodium
Weight of Substrate (Average)	235 grams
Total Weight (Average)	1065 grams
Shell Material	Thermax (AISI 409)

Figure 1

Main Catalyst Left, EHC Right



IV. Description Of Test Vehicle

The test vehicle was a 1981 Volkswagen Rabbit 4-door sedan, equipped with automatic transmission, air conditioning, and radial tires. The 1.6-liter engine had a rated maximum power output of 88 horsepower at 5,600 rpm, when using neat methanol fuel. The vehicle was tested at 2,500 lbs inertia weight and 7.7 actual dynamometer horsepower. This vehicle was loaned to the U.S. EPA by Volkswagen of America.

A detailed description of the vehicle and special methanol modifications were provided in an earlier report.[5]

V. Test Facilities And Analytical Methods

Emissions testing at EPA was conducted on a Clayton Model ECE-50 double-roll chassis dynamometer, using a direct-drive variable inertia flywheel unit and road load power control unit. The Philco Ford constant volume sampler has a nominal capacity of 350 CFM. Exhaust HC emissions were measured with a Beckman Model 400 flame ionization detector (FID). CO was measured using a Bendix Model 8501-5CA infrared CO analyzer. NOx emissions were determined by a Beckman Model 951A chemiluminescent NOx analyzer.

Exhaust formaldehyde was measured using a dinitrophenylhydrazine (DNPH) technique.[11,12] Exhaust carbonyls including formaldehyde are reacted with DNPH solution forming hydrazine derivatives; these derivatives are separated from the DNPH solution by means of high performance liquid chromatography (HPLC), and quantization is accomplished by spectrophotometric analysis of the LC effluent stream.

The procedure developed for methanol sampling and presently in-use employs water-filled impingers through which are pumped a sample of the dilute exhaust or evaporative emissions. The methanol in the sample gas dissolves in water. After the sampling period is complete, the solution in the impingers is analyzed using gas chromatographic (GC) analysis.[13]

VI. Test Procedures

The goal of this test program was a brief evaluation of the Kemira Oy resistively heated catalyst on a methanol-fueled vehicle. The test procedures were similar to those used in the evaluation of a resistively heated Camet compact EHC in June 1991. These procedures were used for two reasons. First, the Kemira Oy and Camet converters had total displacements that were similar in volume, and both made use of typical three-way (platinum:rhodium) catalyst formulations. Second, a comparison of the performance of the two heated catalyst systems was facilitated because the same test vehicle/procedures were used. Further testing of the Kemira Oy catalyst will be conducted to determine the most efficient

resistive heating/air addition convention for the reduction of Bag 1 emissions of unburned fuel, CO, and formaldehyde.

The testing commented on here was conducted in several phases. Each succeeding phase used an additional assist which was intended to further lower pollutant emission levels. The Bag 1 emissions of particular interest were unburned fuel (methanol), CO, and formaldehyde.

Several baseline emission tests were first conducted. Baseline here refers to emission tests over the FTP cycle with a straight pipe inserted in place of the underfloor catalyst. After these tests, the straight pipe was removed and the fresh Kemira Oy EHC was placed in exhaust underfloor, approximately 2½ feet downstream of the ends of the exhaust manifold runners.

Several emission tests were conducted over the FTP without catalyst heating or air assist. This testing provided a reference for determining the improvement in emission level reduction provided by catalyst resistive heating and/or air assist.

Resistive heating over selected initial portions of Bag 1 of the FTP was then used to shorten catalyst light-off time. The first scheme, 0/20, denotes a 20-second period of heating following cold start in Bag 1. The first number, or numerator in these fractions, refers to the time of resistive catalyst preheating before start in Bag 1. Several tests were also conducted using a 0/40 convention. In both of these cases, catalyst heating commenced upon cold start; no preheating was involved.

CTAB asked the catalyst manufacturer (Kemira Oy) to permit a short period of catalyst preheating prior to cold start in Bag 1. This was to enable the catalyst to reach light-off temperature prior to start. One possible drawback to this technique may be heightened durability concerns, however. Kemira Oy responded by stating that a short 10-20 second resistive heating period prior to start would probably give better emission test results.[14]

The catalyst was then tested several times over the FTP using a 15/40 second heating scheme. The 15-second preheat period was the same length as that used during a recent evaluation of a similarly sized resistively heated Camet catalyst. A limited performance comparison between these two catalysts was enhanced by this choice of heating schedule here. This schedule, however, is probably not optimized for the Kemira Oy catalyst. More testing will be necessary to determine an optimized resistive heating scheme. Kemira Oy has used 120 seconds of resistive heating following start in Bag 1 during some of their developmental work.[14]

Following this heated catalyst-only testing, air was added in front of the catalyst to assist the oxidation reactions. The air

was added from a shop air line during the period of resistive heating following start in Bag 1. The air assist was used for a limited period of time only, however. It was assumed that limiting air addition to this period would minimize any undesired effect on the ability of the three-way catalyst to convert NOx emissions.

A gas rotameter was inserted in the shop air line to the vehicle to measure excess air flowrate to the catalyst. This meter also provided an indication of the effect of exhaust backpressure on air flowrate. A bypass valve in the air line controlled excess air flow to an average 5.0 ft^3/minute over the period of air addition.

The converter was tested over a 15/40 second heating cycle with air addition occurring during a 100 second period following cold start. Following this testing, the EHC was replaced by the main catalyst, and several emission tests were conducted using this ceramic monolith and catalyst air assist. The EHC was then placed into the exhaust again, upstream of the main catalyst (MC). This two-catalyst system was emission tested with resistive heating and catalyst air assist applied to the upstream EHC.

VII. Discussion Of Test Results

A. EHC Without Resistive Heat/Air Assist

This evaluation was divided into four separate phases. First, the EHC was emission tested over the FTP to determine its efficiency without resistive heating or air assist. This testing is described here, in Section A of the Discussion Of Test Results. The next section describes the performance of the catalyst when it was resistively heated. The final sections of the Discussion describe the emissions performance when air assist was provided to the resistively heated catalyst alone, and with the MC.

The first 505 seconds of Bag 1 of the FTP cycle includes the initial minutes of the test during which the engine and catalytic converter warm to relatively steady-state temperatures. This warm-up period is important to the emissions process for two reasons. First, current automotive engines operate over relatively richer air/fuel ranges during cold start and warm-up. This is done to ensure that sufficient fuel is vaporized for starting and smooth performance after start. This richer operation causes excess emissions of unburned fuel and CO over levels occurring after the warmed engine begins operating at a leaner setting. Second, the catalyst is ineffective until its surface temperature has reached light-off, or catalytically active temperature. The resistively heated catalyst is designed to minimize this time period.

The emissions of primary interest here are those related to the warm-up period after start. Emissions of unburned fuel (methanol) are related to the larger quantities of fuel inducted,

poorer vaporization and mixing, and colder combustion chamber conditions at cold start. CO and formaldehyde emissions are important as products of partial combustion or intermediates, production of which are enhanced at the relatively richer conditions.

Bag 1 emission levels are presented in grams over the Bag 1 test segment, except for formaldehyde, which is given in milligrams over Bag 1. Composite FTP emissions are given in grams per mile except for formaldehyde levels, which are presented in milligrams per mile.

Table 2 presents the results from emissions testing with the catalyst in the unheated mode, and no air assist provided. The category referred to as baseline describes testing with a straight pipe, rather than a catalytic converter present in the exhaust. The catalyst was reasonably effective in the no-heat/no-air mode, in spite of its smaller volume. Emissions of unburned fuel were reduced by more than 50 percent from baseline levels, as were CO emissions. Bag 1 NOx emissions were also substantially reduced, as were aldehyde emissions. This approximately 75 percent reduction in aldehyde emissions, however, is not sufficient to bring aldehyde levels under the 15 mg/mile limit mandated in the State of California.

Table 2

No Resistive Heat, No Air Assist
Bag 1 Of FTP Cycle

Category	NMHC g	HC* g	CH_3OH g	HCHO mg	OMHCE g	CO g	NOx g
Baseline	0.13	5.16	15.28	1983	7.71	35.9	6.1
No Heat/No Air	0.13	2.20	6.22	521	3.11	16.5	3.6

* Gasoline-fueled vehicle measurement procedure with a propane-calibrated FID.

The roughly 50 percent improvement in most Bag 1 emissions is complimented by increases in efficiency in the other portions of the test cycle. These improvements are evident in the composite FTP results given in Table 3. For example, emissions of unburned fuel decreased almost 80 percent over the entire FTP through the use of the unheated catalyst. Emissions of formaldehyde over the FTP were very high though, at an average 85 mg/mile. This level of emissions far exceeds the California standard; the active catalyst would have to be altered or supplemented by another converter to be a practical methanol vehicle emission control technology.

Table 3

No Resistive Heat, No Air Assist
FTP Composite Emission Levels

Category	NMHC g/mi	HC* g/mi	CH_3OH g/mi	HCHO mg/mi	OMHCE g/mi	CO g/mi	NOx g/mi
Baseline	0.02	0.91	2.71	480	1.43	8.1	1.3
No Heat/No Air	0.03	0.22	0.57	85	0.33	1.8	0.8

* Gasoline-fueled vehicle measurement procedure with a propane-calibrated FID.

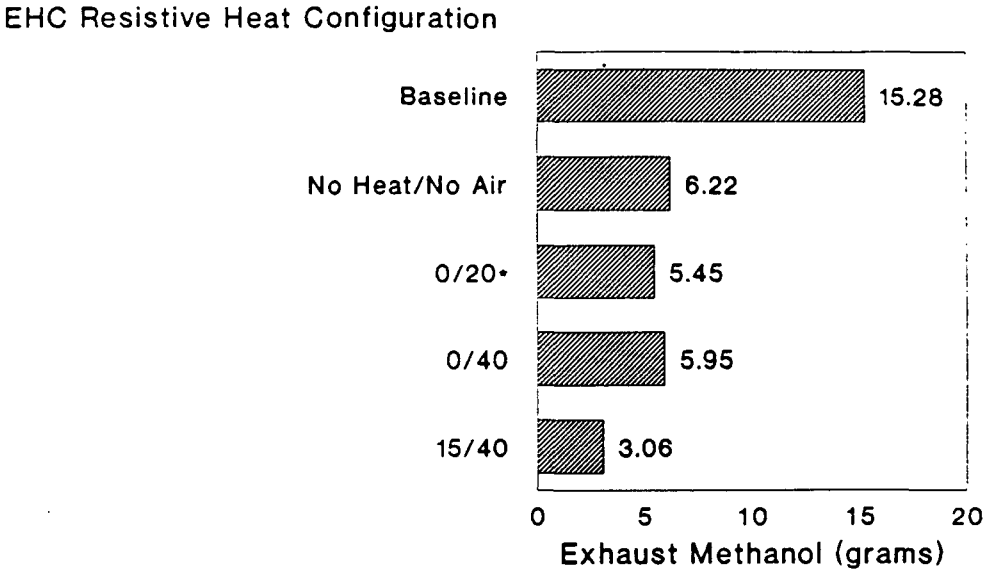
B. EHC With Resistive Heating Only

The EHC was next tested using three separate resistive heating schemes. No air assist was provided to the catalyst during this testing.

The three heating schemes evaluated here utilized resistive heating only during the Bag 1 phase of the FTP. Heating was limited to Bag 1 primarily because of the influence of cold start emissions on the weighted FTP, but also to limit deep drains on the storage battery power source. Limiting the number of deep discharge episodes in practice could significantly extend the useful life of the power source.

Figure 2 presents the results from methanol sampling over the Bag 1 phase of the FTP. Emissions are given in grams/Bag 1. The numerator in the description of the catalyst heating refers to the number of seconds of resistive heating applied to the catalyst before start in Bag 1. The denominator refers to the number of seconds of resistive heating applied following the Bag 1 cold start.

Figure 2
Resistive Heat/No Air Assist, EHC Only
Methanol Emissions, Bag 1 Of FTP



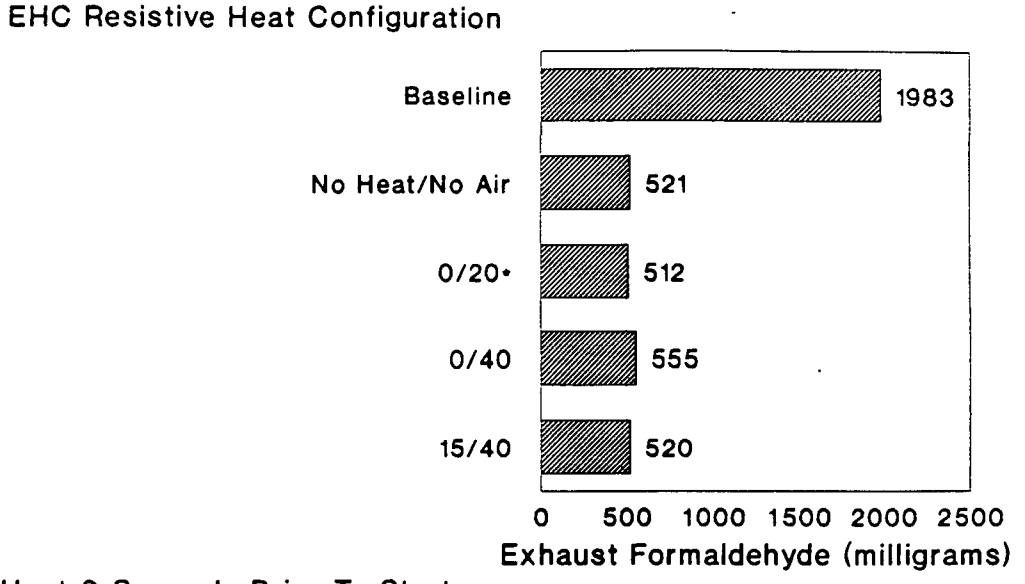
* Heat 0 Seconds Prior To Start,
20 Seconds Following Start

Methanol emissions decreased slightly with the application of resistive heating after start in Bag 1. The usefulness of this heating may be questioned, however, as the extension of heating time to 40 seconds did not result in lower emissions of unburned fuel. A significant decrease in emissions occurred when a short period of resistive heating preceded Bag 1 cold start. The 3.06 grams of methanol measured with the 15/40 heating convention represents a 50 percent reduction in emissions from unheated catalyst levels.

Emissions of formaldehyde over Bag 1 are presented in Figure 3. Resistive heating appeared ineffective as an emissions reduction strategy. Extending the time of resistive heating following cold start did not decrease formaldehyde emissions, and preheating the catalyst for 15 seconds prior to start appeared to have no effect on emissions. Another three-way resistively heated catalyst recently evaluated [9] reduced Bag 1 formaldehyde approximately 20 percent from unheated catalyst levels, on this methanol-fueled vehicle. No noticeable decrease in formaldehyde levels occurred with resistive heating of the catalyst evaluated here, however.

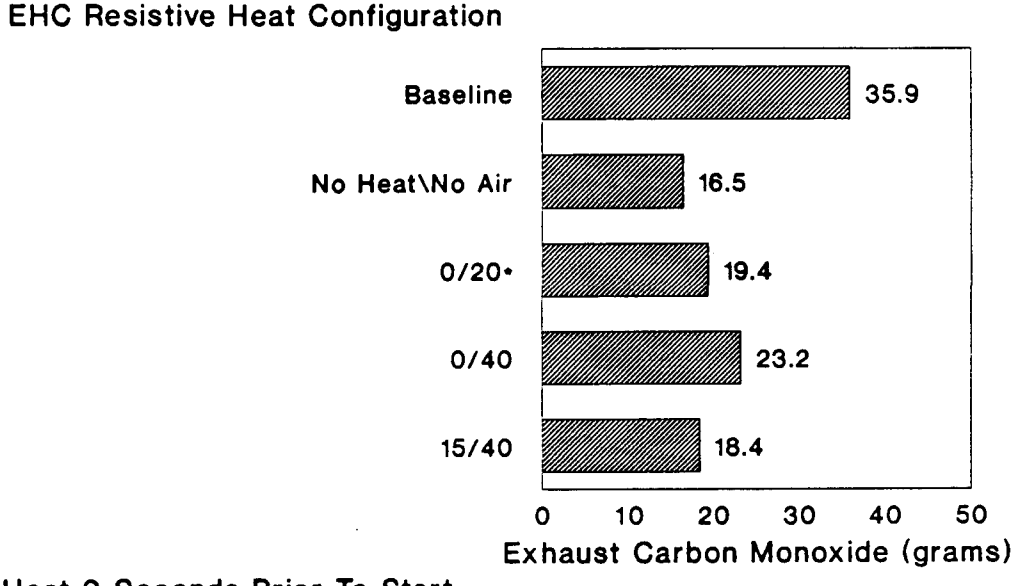
Figure 4 presents CO emission levels over Bag 1. As in the case of formaldehyde, CO emissions did not decrease with resistive heating. CO indeed substantially increased, as the length of resistive heating time following cold start was increased to 40

Figure 3
Resistive Heat/No Air Assist, EHC Only
Formaldehyde Emissions, Bag 1 of FTP



* Heat 0 Seconds Prior To Start,
20 Seconds Following Start

Figure 4
Resistive Heat/No Air Assist, EHC Only
Carbon Monoxide Emissions, Bag 1 of FTP



* Heat 0 Seconds Prior To Start,
20 Seconds Following Start

seconds. Resistively heating the catalyst prior to cold start gave the lowest CO emissions of the heated configurations evaluated, 18.4 grams CO over Bag 1. Even this lower level of emissions, however, exceeded the rate of CO emissions with the unheated catalyst.

These higher levels of CO may have resulted from catalyst temperatures still too low to promote the oxidation reaction or comparatively rich conditions in the converter. Additional testing with catalyst air assist, described later in this report, was conducted to improve the converter efficiency with respect to CO conversion.

A summary of emissions over the Bag 1 phase with the heated catalyst is provided in Table 4. Calculated OMHCE emissions, closely related to measured unburned fuel emissions, significantly decreased as catalyst heating was increased to the 15/40 configuration. NOx emissions were not significantly impacted by the various catalyst heating schemes.

Table 4

Resistive Heating Applied, No Air Assist
Bag 1 Of FTP Cycle

Category	NMHC g	HC* g	CH_3OH g	HCHO mg	OMHCE g	CO g	NOx g
Baseline	0.13	5.16	15.28	1983	7.71	35.9	6.1
No Heat/No Air	0.13	2.20	6.22	521	3.11	16.5	3.6
0/20 Heat	0.10	1.94	5.45	512	2.76	19.4	3.6
0/40 Heat	0.09	2.10	5.95	555	3.00	23.2	3.5
15/40 Heat	0.03	1.05	3.06	520	1.62	18.4	3.4

* Gasoline-fueled vehicle measurement procedure with a propane-calibrated FID.

Table 5 presents weighted emission levels over the FTP cycle. Generally, the changes in Bag 1 emissions brought about by catalyst heating are reflected in the weighted FTP levels. For example, the insignificant changes in Bag 1 formaldehyde levels contributed to very similar weighted cycle averages for all of the heating conventions evaluated. Average weighted CO for the 0/40 heated catalyst testing was substantially increased above emission rates from no resistive heat/no air assist mode catalyst testing.

Table 5

Resistive Heating Applied, No Air Assist
FTP Composite Emission Levels

Category	NMHC g/mi	HC* g/mi	CH_3OH g/mi	HCHO mg/mi	OMHCE g/mi	CO g/mi	NOx g/mi
Baseline	0.02	0.91	2.71	480	1.43	8.1	1.3
No Heat/No Air	0.03	0.22	0.57	85	0.33	1.8	0.8
0/20 Heat	0.02	0.21	0.57	88	0.31	1.9	0.8
0/40 Heat	0.02	0.23	0.61	98	0.34	2.5	0.8
15/40 Heat	0.01	0.15	0.43	92	0.24	1.7	0.8

* Gasoline-fueled vehicle measurement procedure with a propane-calibrated FID.

While this catalyst-equipped vehicle appears to meet current Federal emission standards for light-duty vehicles at low mileage, the high formaldehyde emission rates are a serious concern. The EHC in its tested configuration would have to be supplemented with additional formaldehyde emission control technologies for the entire system to be considered practical.

C. EHC With Resistive Heat/Air Assist

Catalyst efficiency with respect to oxidation reactions may be severely limited at cold start due to the lack of sufficient oxygen in the exhaust to bring the desired reactions to completion. The testing described in this section made use of catalyst air assist to promote the desired oxidation reactions.

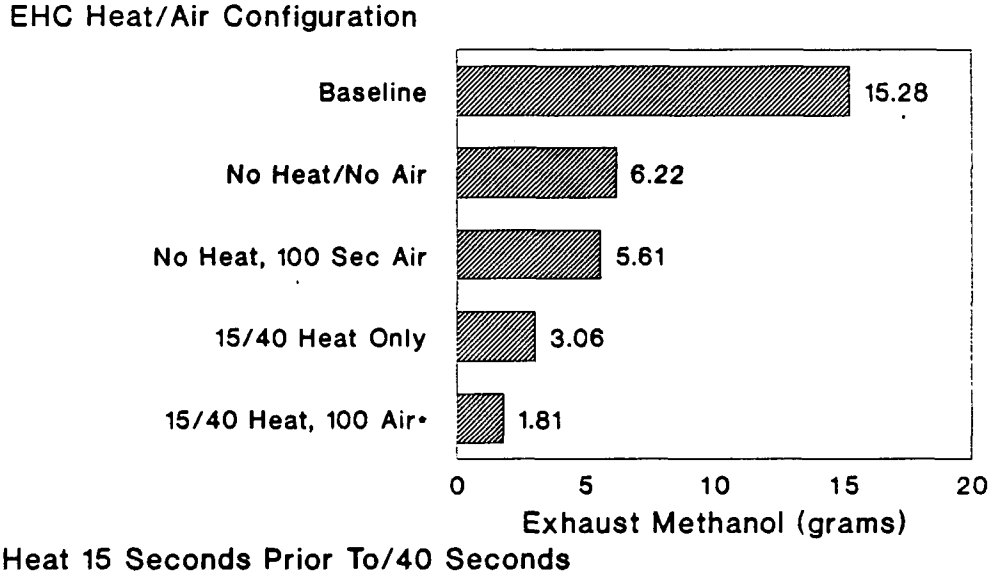
Other EPA work with methanol-fueled vehicles has indicated that air assist to conventional three-way catalysts can cause a significant increase in the production of NOx and formaldehyde emissions.[9,15] In order to minimize the formation of these pollutants and also limit the cooling effect of the added air on the resistively heated substrate, air assist only occurred during the initial portion of Bag 1. The period of air addition was restricted to the first 100 seconds of vehicle operation following

cold start for the testing described here. Restricting the period of air assist in this manner has been shown to substantially limit the production of excess NOx emissions from methanol vehicles.[9]

Air was added from a shop air hose, rather than from a belt or electrically driven air pump. A regulator was placed in the air line to decrease the air flowrate to approximately 5.0 cubic feet per minute. An airflow meter was also added to determine the effect of changes in exhaust flowrate on the flow of air assist to the catalyst. The air addition began at key-on and continued for a period of 100 seconds.

Figure 5 presents the results of this testing for methanol emissions over Bag 1. Some previously presented data is also included for comparison. Baseline methanol emissions of 15.28 grams over Bag 1 were reduced to 6.22 grams with the Kemira Oy catalyst unassisted by resistive heating/air addition. The use of 15/40 resistive heating resulted in a roughly 50 percent decrease in emissions from unassisted catalyst levels, to 3.06 grams. The use of air assist for 100 seconds after cold start increased methanol conversion efficiency by only 10 percent, however, from unassisted catalyst levels.

Figure 5
Resistive Heat/Air Assist, EHC Only
Methanol Emissions, Bag 1 Of FTP

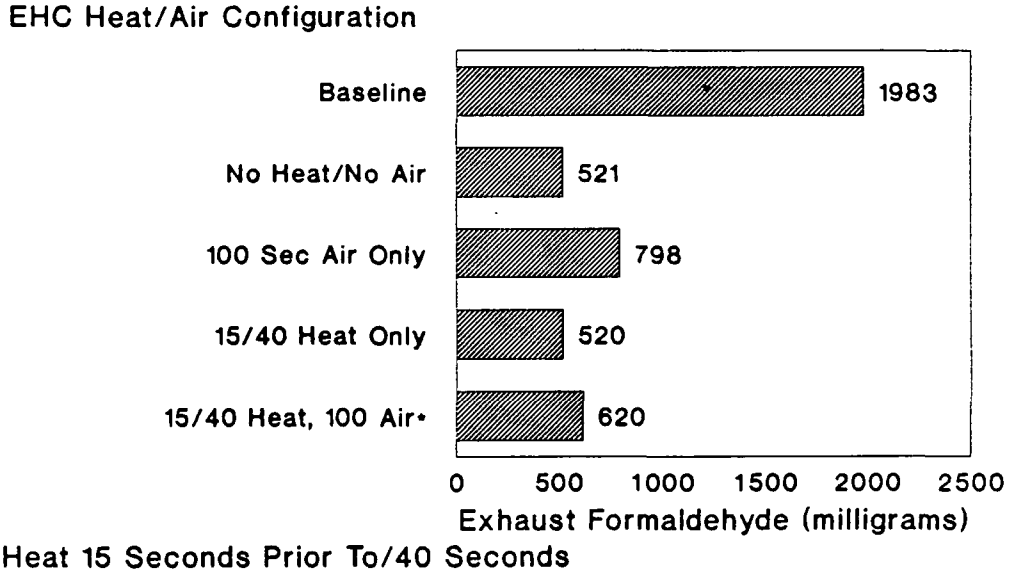


* Heat 15 Seconds Prior To/40 Seconds Following Start, 100 Seconds Air Addition Following Start

A combination of catalyst resistive heating and air assist provided a greater reduction in Bag 1 emissions of methanol than either assist by itself. 15/40 catalyst heating was combined with air addition for 100 seconds following cold start to reduce methanol emissions to 1.81 grams. This level of emissions represented a substantial decrease, greater than 70 percent, from unassisted catalyst levels.

An improvement in formaldehyde emissions over Bag 1 was not noted when catalyst air addition was utilized (Figure 6). In the absence of resistive heating, the use of air addition under the previously described convention increased the emissions of formaldehyde substantially, more than 50 percent above unassisted catalyst levels. Adding resistive heating decreased the formaldehyde emissions rate, though it still exceeded formaldehyde emissions from unassisted catalyst operation. The 620 milligrams of formaldehyde emitted with the heated/air assisted catalyst represented an increase of almost 20 percent over levels from the unassisted catalyst.

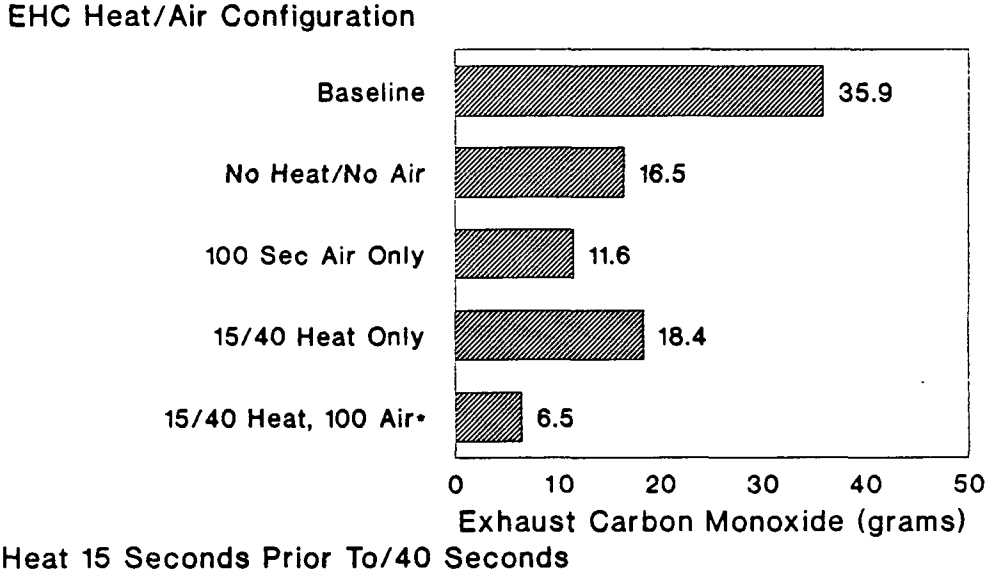
Figure 6
Resistive Heat/Air Assist, EHC Only
Formaldehyde Emissions, Bag 1 Of FTP



* Heat 15 Seconds Prior To/40 Seconds Following Start, 100 Seconds Air Addition Following Start

Figure 7 presents Bag 1 CO emissions results. As previously noted, resistive heating alone did not reduce CO emissions below levels with the unassisted catalyst. The use of air assist alone, however, decreased CO emissions almost 30 percent from unassisted catalyst levels. Adding 15/40 resistive heating to the air assist strategy further decreased Bag 1 CO emissions to 6.5 grams. This lower level represents an increase in efficiency greater than 60 percent from unassisted catalyst levels. This degree of improvement in CO efficiency with catalyst resistive heating/air assist has been noted in previous EPA catalyst technology evaluations.[7,9]

Figure 7
Resistive Heat/Air Assist, EHC Only
Carbon Monoxide Emissions, Bag 1 Of FTP



* Heat 15 Seconds Prior To/40 Seconds Following Start, 100 Seconds Air Addition Following Start

Table 6 is a summary of Bag 1 emissions from air assisted catalyst testing. Most of the emission levels there have been discussed above; it should be noted that OMHCE decreased approximately 30 percent from heated catalyst levels when catalyst air assist was also used. The 40 percent decrease in methanol emissions noted when air assist was provided to the heated catalyst was partially offset by the increase in formaldehyde emissions. NOx emissions did not change with resistive heating/air assist restricted to the cold start portion of Bag 1.

Table 6

Catalyst Resistive Heating/Air Assist
Bag 1 Of FTP Cycle

Category	NMHC g	HC* g	CH_3OH g	HCHO mg	OMHCE g	CO g	NOx g
Baseline	0.13	5.16	15.28	1983	7.71	35.9	6.1
No Heat/No Air	0.13	2.20	6.22	521	3.11	16.5	3.6
100 Sec Air Only	0.16	2.04	5.61	798	3.01	11.6	3.7
15/40 Heat Only	0.03	1.05	3.06	520	1.62	18.4	3.4
15/40 Heat, 100 Sec Air	0.02	0.65	1.81	620	1.14	6.5	3.5

* Gasoline-fueled vehicle measurement procedure with a propane-calibrated FID.

Table 7 details the impact of changes in Bag 1 emission levels on weighted FTP emissions. Though the FTP averages generally follow the direction of changes in Bag 1 emissions caused by the different catalyst conventions, the changes may not be directly translated in magnitude. For example, the decrease in Bag 1 CO levels when the resistively heated catalyst was assisted with air addition was substantial, approximately 65 percent below heated catalyst only levels. The difference in CO emission rates over the FTP between these two catalyst configurations is only 12 percent, however. A difference between these incremental changes should be expected because of the weighting of Bag 2 and 3 emissions (no catalyst assists) in the FTP averages. However, Bag 2 and 3 CO emissions from the heated/air assisted catalyst testing were actually substantially higher than Bag 2 and 3 emissions from the heated catalyst only testing. This was an unexpected result; the cause of these differences later in the test were not investigated at this time, as they were outside the area of immediate concern of this testing (Bag 1 cold start emissions).

D. EHC With Main Catalyst Testing

One obvious method of improving the performance of this compact EHC is to supplement it with a larger, non-resistively heated main catalyst. The smaller EHC may be more easily located close to the engine, near the exhaust manifold. A larger main catalyst might be mounted in a more accessible underfloor location

Table 7

Catalyst Resistive Heating/Air Assist
FTP Composite Emission Levels

Category	NMHC g/mi	HC* g/mi	CH_3OH g/mi	HCHO mg/mi	OMHCE g/mi	CO g/mi	NOx g/mi
Baseline	0.02	0.91	2.71	480	1.43	8.1	1.3
No Heat/No Air	0.03	0.22	0.57	85	0.33	1.8	0.8
100 Sec Air Only	0.02	0.24	0.63	125	0.36	2.3	0.8
15/40 Heat Only	0.01	0.15	0.43	92	0.24	1.7	0.8
15/40 Heat, 100 Sec Air	0.01	0.15	0.39	104	0.24	1.5	0.8

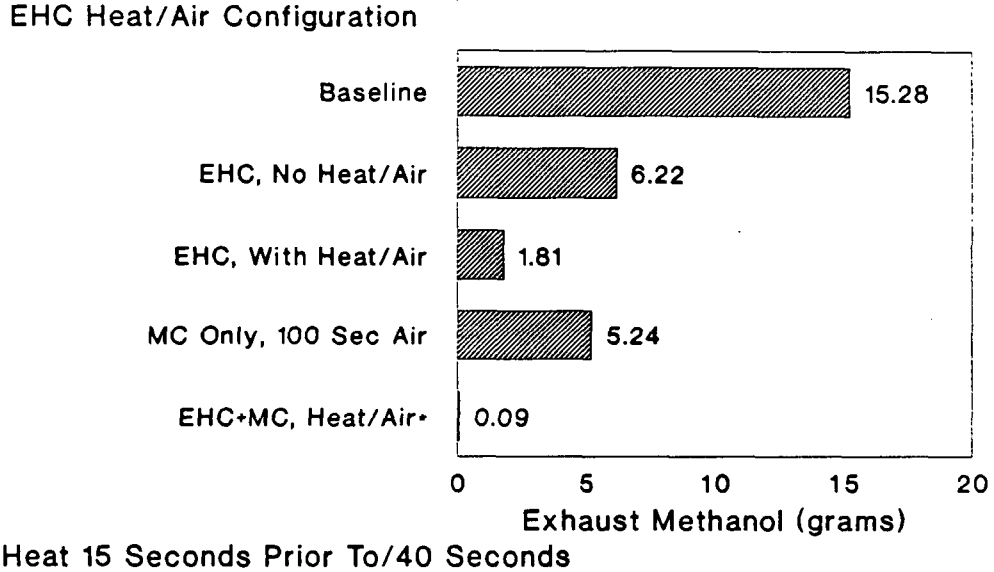
* Gasoline-fueled vehicle measurement procedure with a propane-calibrated FID.

downstream of the EHC. Here, a catalyzed ceramic monolith, described earlier in Section III, was installed immediately behind the Kemira Oy EHC, underfloor. This ceramic monolith is referred to hereafter as the main catalyst (MC). Because of its location downstream, but close to the EHC, the MC may have received a light-off assist due to the catalytic activity/resistive heating of the EHC. Also, the use of air assist to the EHC will affect the performance of the downstream MC.

Figure 8 summarizes Bag 1 methanol emissions testing of this two-catalyst system. Air was added in front of the EHC for 100 seconds after cold start. The platinum main catalyst, with air assist, had Bag 1 unburned fuel emissions nearly three times higher than the most efficient EHC configuration separately tested. When used as part of a two-catalyst emission control system with the EHC, however, extremely low Bag 1 emissions of methanol were noted. Bag 3 methanol emissions, an average of 0.25 grams, were even higher than Bag 1 emissions (the EHC was not resistively heated nor was catalyst air assist used during Bag 3). The 0.09 grams of methanol measured with the two-catalyst system represents a greater than 99 percent methanol conversion efficiency from baseline (no catalyst) levels.

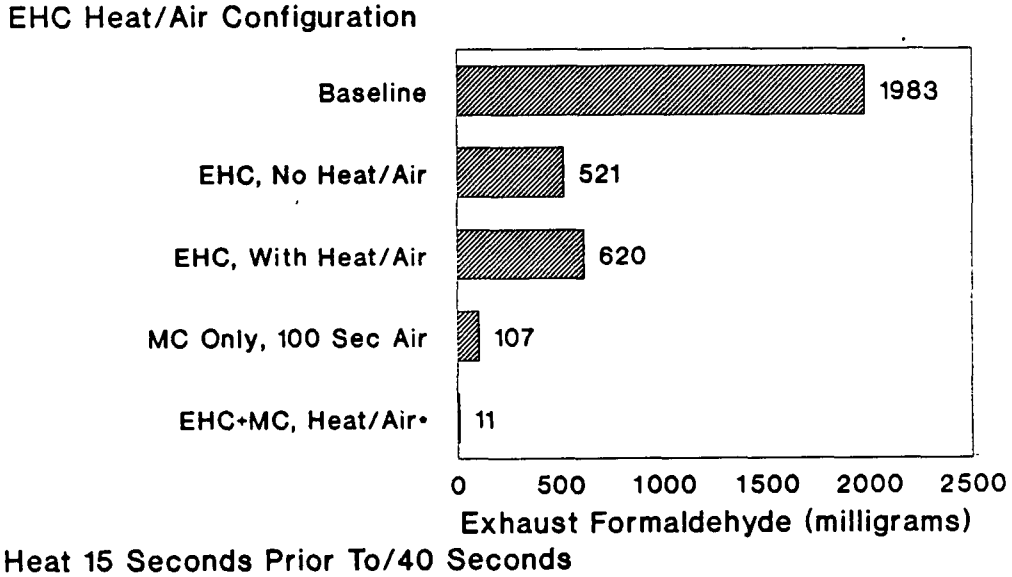
A summary of Bag 1 formaldehyde emissions results is given in Figure 9. The air assisted main catalyst substantially decreased formaldehyde below levels from the most efficient EHC configuration. As in the case of the conversion of methanol, the heated/air assisted two-catalyst system reduced formaldehyde

Figure 8
EHC And Main Catalyst Testing
Methanol Emissions, Bag 1 Of FTP



* Heat 15 Seconds Prior To/40 Seconds Following Start, 100 Seconds Air Addition Following Start

Figure 9
EHC And Main Catalyst Testing
Formaldehyde Emissions, Bag 1 Of FTP

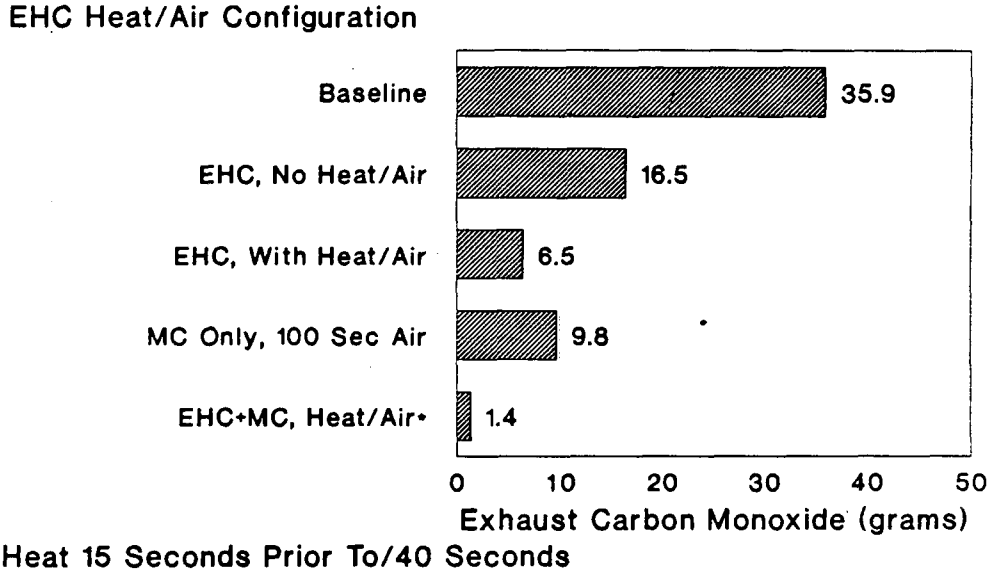


* Heat 15 Seconds Prior To/40 Seconds Following Start, 100 Seconds Air Addition Following Start

emissions to levels far below the lowest noted with the EHC alone. An average of only 11 milligrams of formaldehyde was noted over Bag 1 with the two-catalyst system, an efficiency in excess of 99 percent from no catalyst levels.

The compact EHC alone, with catalyst heat/air assist, was substantially more efficient for the conversion of CO than the MC with air assist (Figure 10). However, the use of the MC in conjunction with the assisted EHC provided the lowest CO levels of any catalyst configuration tested. The two-catalyst system reduced CO emissions almost 80 percent from levels with the most efficient EHC configuration. The low 1.4 grams of CO over Bag 1 obtained with the two-catalyst system represents an efficiency of 96 percent from no catalyst levels.

Figure 10
EHC And Main Catalyst Testing
Carbon Monoxide Emissions, Bag 1 Of FTP



* Heat 15 Seconds Prior To/40 Seconds Following Start, 100 Seconds Air Addition Following Start

Table 8 contains a summary of Bag 1 emissions from testing the two-catalyst system. The substantial decrease in measured emissions of methanol and formaldehyde is evident in the very low calculated OMHCE emissions. NOx emissions were relatively unaffected by either catalyst assist or the use of the MC behind the resistively heated EHC.

Table 8

EHC and Main Catalyst Testing
Bag 1 of FTP Cycle

Category	NMHC g	HC* g	CH_3OH g	HCHO mg	OMHCE g	CO g	NOx g
Baseline	0.13	5.16	15.28	1983	7.71	35.9	6.1
QLOC Only, No Heat/No Air	0.13	2.20	6.22	521	3.11	16.5	3.6
QLOC Only, 15/40 Heat, 100 Sec Air	0.02	0.65	1.81	620	1.14	6.5	3.5
Main Cat Only, 100 Sec Air	0.08	1.84	5.24	107	2.45	9.8	3.5
QLOC and Main Cat, 15/40 Heat, 100 Sec Air	0.01	0.05	0.09	11	0.07	1.4	3.2

* Gasoline-fueled vehicle measurement procedure with a propane-calibrated FID.

Very low emissions over the weighted FTP resulted from the use of the two-catalyst system (and the EHC provided with resistive heating/air assist). Bag 2 and 3 emission levels are not commented upon here, as the purpose of this testing was to evaluate the improvement in Bag 1 emissions of unburned fuel, formaldehyde, and CO with the heated/air assisted EHC. It should be noted, however, that the two-catalyst system was extremely efficient at converting emissions of methanol, formaldehyde, and CO over Bags 2 and 3, even without catalyst resistive heating/air assist applied to the EHC in Bag 3. These emission level improvements, though not as great in magnitude as the improvements noted above in Bag 1, are also reflected in the FTP composite averages (Table 9).

Table 9

EHC and Main Catalyst Testing
FTP Composite Emission Levels

Category	NMHC g/mi	HC* g/mi	CH_3OH g/mi	HCHO mg/mi	OMHCE g/mi	CO g/mi	NOx g/mi
Baseline	0.12	0.91	2.71	480	1.43	8.1	1.3
QLOC Only, No Heat/No Air	0.03	0.22	0.57	85	0.33	1.8	0.8
QLOC Only, 15/40 Heat, 100 Sec Air	0.01	0.15	0.39	104	0.24	1.5	0.8
Main Cat Only, 100 Sec Air	**	0.11	0.31	7	0.15	0.6	0.8
QLOC and Main Cat, 15/40 Heat, 100 Sec Air	**	0.02	0.04	2	0.02	0.3	0.7

* Gasoline-fueled vehicle measurement procedure with a propane-calibrated FID.

** Less than 0.005 measured.

Non-methane HC emissions with the two-catalyst system were low enough to be considered negligible over the weighted FTP. OMHCE emissions at low mileage were below Ultra Low Emission Vehicle standards, as considered by the State of California. Very little CO was produced (0.3 grams per mile) over the FTP with the two-catalyst system. Methanol emissions over the FTP were reduced more than 98 percent when the two-catalyst system was used. NOx emissions were not adversely impacted by the use of the additional MC; a very small improvement in Bag 1 NOx emissions is manifest in a slightly lower weighted FTP value.

VIII. Evaluation Highlights

1. Resistive heating, in the absence of catalyst air assist, provided little reduction in most Bag 1 emission levels when the EHC was tested without a main catalyst in the exhaust. Bag 1 emissions of methanol were reduced to 3.06 grams when the EHC was resistively heated, from 6.22 grams with no catalyst resistive heating.

2. Catalyst air assist was provided for 100 seconds following start in Bag 1, and the catalyst was resistively heated using the 15/40 convention described earlier. This combination of catalyst heating/air assist decreased methanol emissions over Bag 1 to 1.81 grams, down from 6.22 grams with the no heat/no air EHC configuration. CO emissions over Bag 1 also decreased substantially, below air assisted catalyst levels, when a combination of catalyst resistive heating/air assist was used. Formaldehyde emissions, however, increased almost 20 percent above unassisted catalyst levels when the EHC was provided with 15/40 resistive heating and catalyst air assist.

3. A two-catalyst system, incorporating the EHC and a catalyzed ceramic monolith main catalyst, was evaluated. Resistive heating, using the 15/40 convention, and 100 seconds of air assist following cold start in Bag 1 were used with the EHC during this testing. The two-catalyst system produced the lowest Bag 1 emissions of unburned fuel, formaldehyde, and CO of the catalyst configurations tested. The platinum-catalyzed main catalyst, with air addition, was more efficient than the compact EHC without heat/air assist. When combined into a two-catalyst system located underfloor, these catalysts provided extremely low Bag 1 emissions of all measured pollutants with the exception of NOx.

Methanol and formaldehyde emissions were reduced to 0.09 grams and 11 milligrams respectively over Bag 1 with the two-catalyst system. The low Bag 1 emissions contributed substantially to the calculated emission rate of 0.02 grams per mile of OMHCE over the FTP. Weighted average formaldehyde emissions over the FTP were less than 2 milligrams per mile, well below the California standard of 15 milligrams per mile for alcohol-fueled vehicles. The very low Bag 1 levels of methanol and formaldehyde, with the two-catalyst system here, represent conversion efficiencies of greater than 99 percent from baseline (no catalyst) levels from the test vehicle.

CO emissions over Bag 1 were reduced greater than 96 percent from no catalyst levels using the two-catalyst system. This efficiency was reflected in FTP weighted average CO emissions, where the two-catalyst system also provided a 96 percent conversion efficiency from no catalyst levels. NOx emissions, however, were relatively unaffected by changes in catalyst configuration here. Even the use of catalyst air assist (restricted to 100 seconds

following cold start in Bag 1) did not greatly affect NOx levels. A slight decrease in Bag 1 emissions of NOx was noted with the two-catalyst system, compared with the other catalyst configurations tested.

IX. Future Efforts

The evaluation of the EHC discussed here did not determine an optimized resistive heating/air assist strategy. In addition, some EHC operating strategies, such as no resistive heat/air assist in the two-catalyst configuration mentioned previously, were not evaluated. To ensure a more accurate accounting of the contribution of the components of resistive heating and air assist to catalyst efficiency, it is necessary to supplement the testing discussed here. Additional testing will be conducted to better determine the EHC's ability to reduce emission levels of unburned fuel, CO, and formaldehyde.

Future efforts will be made to quantify the relationship between catalyst heating/air addition and real time emission rates of individual pollutants. These efforts will be concerned only with the period of time during which resistive heating and/or air addition is occurring.

A Horiba modal analysis system has been installed at the EPA Motor Vehicle Emission Laboratory; this analyzer will be used to map the effects of changes in catalyst resistive heating/air addition on emissions. While it is not possible to obtain methanol or formaldehyde analysis, CO, NOx, and FID-measured hydrocarbons emission levels will be determined.

X. Acknowledgments

The resistively heated catalyst evaluated in this test program was supplied by Kemira Oy, located in Finland. The platinum-coated ceramic monolith used here as a main catalyst was supplied by the Specialty Chemicals Division of the Engelhard Corporation. The methanol-fueled test vehicle was supplied by Volkswagen of America.

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