

Technical Report

Evaluation Of Camet Resistively Heated
Metal Monolith Catalytic Converters
On An M100 Neat Methanol-Fueled Vehicle

Part III

by

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July 1991

NOTICE

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.

U. S. Environmental Protection Agency
Office of Air and Radiation
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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

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JUL 30 1991

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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 Camet Resistively Heated Metal Monolith Catalytic Converters On An M100 Neat Methanol-Fueled Vehicle - Part III" (EPA/AA/CTAB/91-03) describes the evaluation of the most current generation of quick light-off catalytic converters now being furnished by the Camet Co. to automobile manufacturers. This evaluation was conducted on a methanol-fueled (M100) vehicle.

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: 7-30-91
Charles L. Gray, Jr., Dir., ECTD

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

cc: E. Burger, ECTD

Table of Contents

	<u>Page Number</u>
I. Summary	1
II. Introduction.	2
III. Description of Catalytic Converters	3
IV. Description of Test Vehicle	5
V. Test Facilities and Analytical Methods.	5
VI. Test Procedures	7
VII. Discussion of Test Results.	8
A. QLOC Only, Without Air Assist.	8
B. QLOC Only, With Air Assist	12
C. QLOC + Main Catalyst, With/Without Air Assist. . .	19
VIII. Evaluation Highlights	26
IX. Future Efforts.	27
X. Acknowledgments	27
XI. References.	29

I. Summary

A low mileage resistively heated catalytic converter of a type currently furnished by the Camet Co. to automakers was evaluated on a methanol fueled vehicle. This converter was smaller in volume than typical three-way catalytic converters used on current model year vehicles of comparable engine displacement, and is designed specifically as a quick light-off catalyst (QLOC) by Camet.

The QLOC was evaluated in three separate modes. First, the QLOC was placed in the exhaust stream of the test vehicle and evaluated without the benefit of catalyst air assist (simulated oxidation catalyst) or a larger main catalyst (MC) also present downstream. Next, the QLOC was tested with resistive heating and simulated air assist, but without a MC in the exhaust. Finally, a low mileage nonresistively heated MC was added immediately downstream of the QLOC. This two-catalyst system was then evaluated with resistive heating applied to the QLOC and catalyst air assist. Because the additional air was added in front of the QLOC, this air assist also affected the operation of the larger MC positioned downstream.

With the QLOC alone and resistive heating applied for 15-seconds prior to and 40 seconds following cold start (15/40 resistive heating), Bag 1 emissions from the Federal Test Procedure (FTP) cycle were reduced 50 percent from unheated catalyst levels. Only a slight reduction in formaldehyde, and no change in carbon monoxide (CO) Bag 1 emission levels were noted when this catalyst was resistively heated.

Air was added in front of the catalyst at an average rate of 5 SCFM for short intervals following start in Bag 1. The addition of air for 30 seconds to the 15/40 resistively heated catalyst decreased Bag 1 methanol emissions a further 54 percent from heated catalyst only levels, to 1.83 grams. Bag 1 formaldehyde levels were reduced 30 percent when air assist was provided for 30 seconds to the resistively heated catalyst. CO levels decreased as the time period of air addition was increased. CO was reduced to 12.7 grams over Bag 1 with air addition for 30 seconds to the heated catalyst, a 33 percent decrease from heated-catalyst-only levels. CO emissions continued to decrease, to 4.5 grams in Bag 1 as the air assist period was extended to 120 seconds following start in Bag 1.

The addition of the MC behind the QLOC had the effect of reducing Bag 1 emissions of methanol, CO and formaldehyde to very low levels, while contributing to only a slight reduction in NOx emission levels. The most efficient configuration of the two-catalyst system modes evaluated utilized the 15/40 resistive heating schedule mentioned above and air addition for 100 seconds following cold start in Bag 1. The simultaneous use of these two assists decreased Bag 1 methanol emissions to 0.37 grams. This was down from 7.95 grams measured with no resistive heat or air assist provided to the two-catalyst system. Formaldehyde emissions were

also reduced, to 34 milligrams over Bag 1 with QLOC resistive heat/air addition. This was an 85 percent improvement from the 227 milligrams in Bag 1 measured when the two-catalyst system received no resistive heating or air assist.

The largest increase in catalyst efficiency when resistive heating/air assist was provided to the two-catalyst system occurred for CO control, however. Almost 16 grams of CO were measured over Bag 1 with the two-catalyst system, when the QLOC was not supplied with resistive heating or additional air. CO was reduced to less than two grams over Bag 1 with 15/40 resistive heating and 100 second air addition, a 90 percent reduction.

Improvements in Bag 1 emission levels generally caused average FTP emissions to decrease almost proportionally to the decrease in Bag 1 levels. With the resistively heated and air assisted two-catalyst system, OMHCE were reduced to a low 0.07 grams per mile. Formaldehyde emissions were also very low at only four milligrams per mile. The greatest percentage increase in efficiency from unassisted catalyst operation, however, was in the category of CO emissions. The heated/air assisted two-catalyst system gave average FTP CO emissions of only 0.2 grams per mile, an increase in efficiency of 80 percent over unassisted catalyst operation. Although Bag 1 NOx levels appeared to increase slightly with increasing air addition times, the level of FTP NOx emissions was 0.7 grams per mile with the two-catalyst system either unassisted or assisted with both resistive heating/air addition.

II. Introduction

The largest portion of methanol, carbon monoxide (CO), and formaldehyde exhaust emissions from a catalyst-equipped M100-fueled vehicle tested over the Federal Test Procedure (FTP) occur during the cold start and catalyst warm-up phase in Bag 1.[1] The same is generally true for hydrocarbon exhaust emissions from a catalyst-equipped gasoline-fueled vehicle emission tested over the FTP.[2] Emissions of oxides of nitrogen (NOx) at cold start are generally not as significant as levels of NOx emissions generated later in the cycle as they are produced at higher concentrations under greater load after the engine has warmed. Cold start is defined here as following a vehicle soak of 12-36 hours at 72-86°F.[3]

A catalytic converter is generally ineffective for oxidizing emissions of methanol and formaldehyde from an M100-fueled vehicle until the converter has reached catalytically active, or light-off temperature. Though this temperature varies for the catalyst considered, light-off temperatures for typical three-way converters of 350°C have been recently mentioned in the literature[4] when referring to the performance of an electrically heated catalyst (EHC). Resistively heating the substrate and thereby the catalyst to light-off temperature at cold start reduces the time during which the catalyst remains ineffective because of insufficient

warming by the relatively cold exhaust gas. This accelerated warmup would also have the advantage of occurring when the engine is cold and producing higher levels of unburned fuel and CO because of operation under relatively richer conditions.

EPA has been interested in catalyst preheating for some time and has conducted evaluations of resistively heated catalyst technologies supplied by Camet Co.[1,5,6,7,8,9] This work has involved both methanol and gasoline-fueled vehicle applications. Other sources, both government and industry, have conducted evaluations of this technology and published test results.[4,10,11,12,13] These other efforts have involved primarily gasoline-fueled test vehicles.

The Camet catalysts previously evaluated by EPA were a prototype design, consisting of a resistively heated segment and a slightly larger nonresistively heated main catalyst. These two segments were placed in close proximity to each other in the same converter shell. The end of the shell containing the resistively heated segment was placed upstream in the exhaust during the previous EPA evaluations. A complete description of these prototype converters was provided in an earlier report published by Camet; details are also given here below in the section providing a description of the catalysts evaluated.

The current generation of EHC now furnished by Camet to automakers for evaluation consists of a single resistively heated segment. This unit is designed specifically as a quick light-off catalyst, to oxidize excess emissions of unburned fuel and CO following cold start.[14] Camet suggests that a standard underfloor catalytic converter system may also be necessary to reduce unburned fuel and CO emissions from most vehicles to very low levels. Camet supplied EPA with a current-generation EHC for evaluation on an M100-fueled vehicle. This catalyst was evaluated by EPA as part of an effort to identify and determine the effectiveness of novel emission control technologies. The details of the technology evaluated and the test procedures are given below. All of the testing referred to here consists of an evaluation of fresh, unaged catalysts.

III. Description Of Catalytic Converters

The catalytic converter of primary interest in this evaluation is referred to hereafter as the quick light-off catalyst (QLOC). The QLOC uses a single-segment, resistively heated stainless steel foil substrate, configured into a honeycomb (Figure 1). The total volume of the honeycomb was approximately 200 cm³, and the energy for heating was supplied from a dedicated 12-volt, 115 amp-hour, deep cycle battery. The QLOC evaluated here was a fresh, unaged catalyst. A solid-state power controller, normally supplied by Camet to regulate the high current involved, was not used in this evaluation. Instead, a switch and engine starter motor relay were used to supply energy from the dedicated battery when desired. A typical three-way catalyst formulation was used; Table 1 contains more detailed specifications of the QLOC.

Figure 1

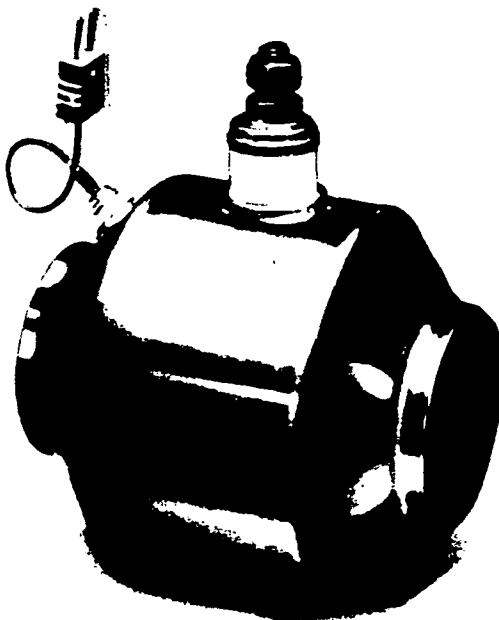
Camet Resistively Heated Catalyst

Table 1

Detailed Specifications Of Quick
Light-Off Catalyst Evaluated

	<u>Specification</u>
Camet Model Number	10-15
Catalyst Volume	216 cm ³
Rated Power Usage (Camet Data)	2,800 watts
Approx. Heating Time To 650°F	14 seconds
Substrate Material	Stainless steel foil
Back Pressure At 55 mph	230 mm of H ₂ O
Length Between Edges Of End Pipes	107 mm
Catalyst	5:1 Pt:Rh, 1.41 g/liter
Battery Used To Supply Resistive Heating	Action Pack, 12V Deep Cycle/Marine Battery, 115 Amp-Hr

The Camet QLOC tested here may not be a substitute for a larger volume main catalyst (MC). A MC was added in series with the QLOC in order to reduce emission levels over the remainder of the FTP to the low levels experienced with a conventional three-way catalyst. The simulated MC was a two-segment Camet EHC prototype previously evaluated by EPA.

This simulated MC (Figure 2) consisted of resistively heated and nonresistively heated segments canned in very close proximity to each other in a common shell. No resistive heating was applied to the EHC portion of this simulated main catalyst during any of the testing conducted as part of the current evaluation. Table 2 contains detailed specifications of this catalyst.

IV. Vehicle Description

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.[9]

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.[15,16] 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.[17]

Figure 2

Main Catalyst Used in Program

Table 2

Detailed Specifications Of Simulated
Main Catalyst*

<u>Camet Model</u>	<u>Specifications</u>
	Prototype Model 513
<u>Dimensions:</u>	
Frontal Area	54 cm ² heated brick, 57 cm ² unheated brick
Length	8.9 cm heated brick, 8.9 cm unheated brick
Cells/cm ²	20, heated segment 50, unheated segment
Weight	240 g, heated segment 345 g, unheated segment
Catalyst Type/Loading	Heated segment 3:1 Pt:Pd, 1.06 g/liter Unheated segment, 6.7:1 Pt:Rh, 1.41 g/liter
Designed Power Rating	3,000 watts

* From Reference 4, no heat applied to resistively heated segment during current testing.

Most of the emission results in this report are computed using the methods outlined in the "Final Rule For Methanol Fueled Motor Vehicles And Motor Vehicle Engines," which was published in the Federal Register on Tuesday, April 11, 1989. Because these specialized procedures and calculation methods are not in widespread use, we have also included a hydrocarbon result which is what would be obtained if the exhaust was treated as if the fuel were gasoline. This is done as a convenience for the readers and users of the report who may be more familiar with hydrocarbon results obtained this way.

VI. Test Procedures

This program had as its goal the evaluation of a QLOC provided by Camet Co. for the reduction of unburned fuel, CO and formaldehyde emissions from a methanol-fueled vehicle.

The evaluation consisted of three distinct phases which are discussed separately in the following section. The first phase consisted of a preliminary evaluation of the QLOC on the test vehicle. All emissions testing was conducted over the FTP cycle, and resistive heating was limited to different schemes during the cold start portion of Bag 1. All of the testing in this evaluation was conducted at 72-73°F conditions.

The next phase of the evaluation involved the addition of air during resistive heating to assist the oxidation of unburned fuel, CO and formaldehyde. This air addition allowed the catalyst to function as an oxidation catalyst; the catalyst formula, however, was a typical three-way variety. The QLOC alone was evaluated during this phase. Testing was conducted over the FTP cycle and resistive heating/air addition was again limited to the cold-start portion of Bag 1.

The final phase of the evaluation had the QLOC employed as a true warm-up catalyst. A main catalyst was added underfloor in series behind the QLOC. The purpose of the main converter was to provide sufficient catalyst volume and activity to reduce emissions to very low levels over a wide variety of engine speed and load conditions following catalyst warm-up.

Air addition in front of the QLOC, as well as resistive heating, were utilized in Bag 1 during this phase of the evaluation. Because the QLOC was located upstream from the main catalyst, any excess air added in front of it would also affect the operation of the main catalyst. The air assist was utilized for only limited periods following key-on, however; it was thought that limiting the addition of air to these brief periods would limit the effect on any possible increase in oxides of nitrogen due to the converter.

VII. Discussion Of Test Results

A. QLOC Only, Without Air Assist

This evaluation consisted of three separate phases. The first phase, commented on in this section, consisted of a brief evaluation of the QLOC without the benefit of air assist or a larger main catalyst.

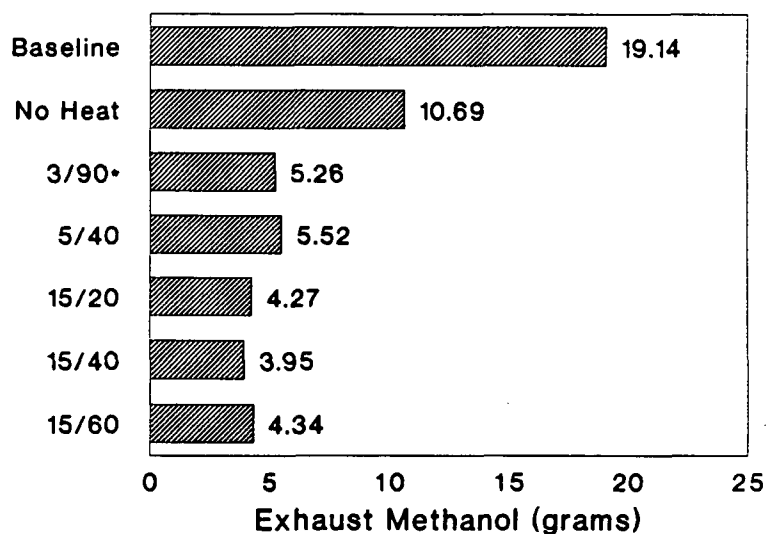
During all phases of this evaluation, resistive heating and air assist were restricted to the cold-start portion of Bag 1 of the FTP. The first 505 seconds of the FTP is commonly referred to as Bag 1; the cold-start portion consists of the initial minutes of Bag 1 during which the engine and exhaust system heat to a relatively steady-state temperature. The following discussion comments on differences in exhaust emission levels which may be related to oxidation catalyst operation, catalyst resistive heating or both. Bag 1 emission levels are given in grams of emissions over the test segment (Bag 1) except for formaldehyde, which are presented in milligrams over Bag 1. Composite FTP emissions are given in tabular form in grams per mile except for formaldehyde, which are presented in milligrams per mile.

Figure 3 presents Bag 1 methanol emission levels during the first phase of the evaluation. Several catalyst heating conventions were tried to gauge the effectiveness of changes in heating strategy. The notation used in Figure 3 and thereafter to denote the heating convention utilizes two numbers separated by a slash. The first number refers to the number of seconds of catalyst resistive heating applied prior to key-on (start) in Bag 1; the second number refers to the number of seconds of resistive heating applied immediately following cold start. All heating conventions involved 3-15 seconds of heating prior to start. Fifteen seconds of heating prior to key-on may be impractical in order to accommodate the driver's desire for a quick start/drive sequence, as well as for possible catalyst durability concerns. A 15-second heating period prior to start, however, ensured a warmed substrate and surroundings for these laboratory experiments.

Bag 1 emissions of methanol were reduced almost 50 percent from baseline levels by the small QLOC, without the aid of resistive heating. Resistive heating, even in the absence of additional air to promote oxidation, increased the efficiency of the catalyst significantly. Heating the catalyst for 90 seconds following start reduced methanol emissions from unheated catalyst levels almost 50 percent. It is less clear, however, how changes in the catalyst heating convention affected emissions when compared to levels from 3/90 catalyst heating. Increasing the time interval of resistive heating prior to key-on appeared to increase the heated catalyst's effectiveness. The three conventions which had 15-second heat periods prior to key-on had Bag 1 emission levels of methanol roughly 20 percent lower than the 3/90 heating configuration. Extending catalyst heating after key-on for modes utilizing 15-second heating periods prior to start gave mixed

Figure 3
QLOC Only, No Air Assist
Methanol Emissions, Bag 1 Of FTP

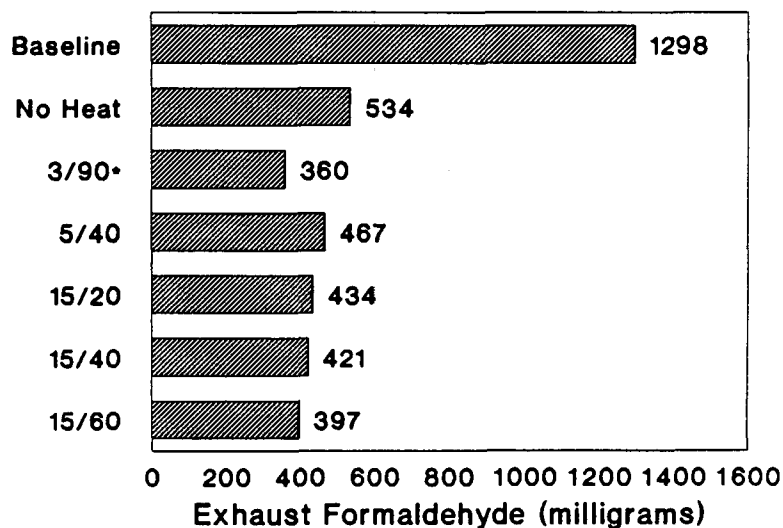
EHC Resistive Heating



* Heat 3 Seconds Prior To Start,
90 Seconds Following Start

Figure 4
QLOC Only, No Air Assist
Formaldehyde Emissions, Bag 1 of FTP

EHC Resistive Heating



* Heat 3 Seconds Prior To Start,
90 Seconds Following Start

results. The methanol emissions from the 60-second post-start heating period, 4.34 grams over Bag 1, were slightly higher than levels obtained with 20- and 40-second post-start heating periods. Although three tests were conducted in each mode, it may be necessary to conduct more tests, using modal analysis, to correlate average Bag 1 emissions with catalyst resistive heating time intervals.

Figure 4 presents Bag 1 formaldehyde emissions when the catalyst heating conventions referred to in Figure 3 were used. Resistive heating in the absence of any excess air assist to the catalyst appeared to increase catalyst efficiency, though not to the extent noted with unburned fuel (methanol) emissions. The most efficient scheme was 3/90 heating, which provided an approximately 30 percent decrease in formaldehyde emissions from unheated catalyst levels. Catalyst efficiency improved very slightly over the modes using 15-second prestart heating, when post-start heating times were increased. The decrease in formaldehyde emissions was only 8 percent as post-start heating was increased from 20 seconds to 60 seconds.

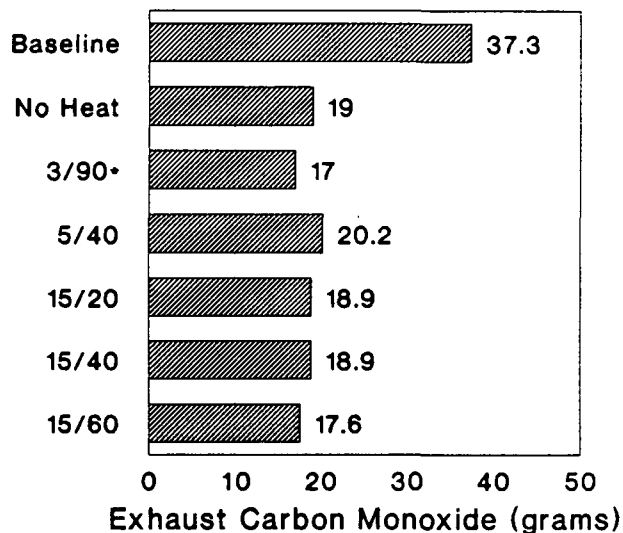
Figure 5 contains Bag 1 data from the FTP on CO levels with the QLOC over the same resistive heating modes. Generally no change in emissions of CO of the magnitude experienced with unburned fuel was noted when the catalyst was resistively heated. CO emissions from the 15/20 and 15/40 heating schemes were similar to levels obtained without catalyst heating. CO was measured at a higher level when the catalyst was tested using the 5/40 heating sequence than without any catalyst resistive heating. Although slightly lower CO emissions were noted with the 3/90 heating convention, other heating modes which involved significant amounts of resistive heating did not substantially reduce CO from unheated catalyst levels, in the absence of air assist.

Table 3 is a summary of Bag 1 levels for other emission categories as well as the three previously discussed here. NOx emissions did not appear to be significantly affected by catalyst resistive heating possibly because the heating occurred during the period of engine warmup to hotter, near steady-state temperature conditions.

Because Bag 1 emissions of unburned fuel, CO, and formaldehyde are comparatively greater than those from other segments of the FTP for a typical three-way catalyst equipped M100 vehicle, improvements in Bag 1 emissions due to catalyst resistive heating should also be seen in FTP composite emission averages. Table 4 is a summary of FTP weighted average emissions over the first phase of this evaluation. Generally, the weighted average emissions reflect Bag 1 emissions trends noted above. For example, FTP average methanol emissions were approximately 21 percent lower with the 15/40 catalyst heating convention than the 3/90 mode; the difference in Bag 1 emissions between tests with the same two resistive heating modes was 25 percent.

Figure 5
QLOC Only, No Air Assist
Carbon Monoxide Emissions, Bag 1 of FTP

EHC Resistive Heat Configuration



* Heat 3 Seconds Prior To Start,
90 Seconds Following Start

Table 3

Testing Limited To Current-Generation Catalyst
Bag 1 Of FTP Cycle
No Air Assist To Catalyst

Category	NMHC g	HC* g	CH ₃ OH g	HCHO mg	OMHCE g	CO g	NOx g
Baseline	1.55	7.33	19.14	1298	10.00	37.3	6.9
No Heat/No Air	0.56	4.10	10.69	534	5.50	19.0	3.7
3/90 Heat	0.27	2.03	5.26	360	2.77	17.0	3.5
5/40 Heat	0.35	2.21	5.52	467	3.02	20.2	3.5
15/20 Heat	0.17	1.62	4.27	434	2.28	18.9	3.6
15/40 Heat	0.17	1.51	3.95	421	2.13	18.9	3.7
15/60 Heat	0.19	1.66	4.34	397	2.34	17.6	3.7

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

Table 4

Testing Limited To Current-Generation Catalyst
 FTP Composite Emission Levels
No Air Assist To Catalyst

Category	NMHC g/mi	HC* g/mi	CH ₃ OH g/mi	HCHO mg/mi	OMHCE g/mi	CO g/mi	NOx g/mi
Baseline	0.28	1.17	2.93	323	1.63	7.3	1.6
No Heat/No Air	0.04	0.31	0.80	61	0.42	1.7	0.8
3/90 Heat	0.03	0.18	0.46	47	0.26	1.4	0.7
5/40 Heat	0.04	0.21	0.49	59	0.29	1.7	0.8
15/20 Heat	0.02	0.17	0.43	57	0.24	1.6	0.8
15/40 Heat	0.03	0.16	0.36	51	0.22	1.6	0.8
15/60 Heat	0.01	0.18	0.51	66	0.27	1.5	0.8

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

In summary, even without air assist to the QLOC, resistive heating significantly decreased emission levels of methanol over the FTP. Only marginal improvement in average FTP formaldehyde emissions was noted with resistive heating, and no substantial lowering of CO levels was noted with resistive heating alone. NOx emissions over the FTP were relatively unaffected by resistive heating.

B. QLOC Only, With Air Assist

Even if a catalyst is resistively heated during cold start, its effectiveness may be lessened by the absence of sufficient oxygen in the exhaust to bring the desired oxidation reactions to completion. In some cases, a lack of oxygen may promote partial combustion to undesired intermediate products. Air addition before the catalyst may supply sufficient oxygen to the relatively rich exhaust to promote the desired oxidation of unburned fuel and intermediate products (formaldehyde and CO). Alternatively, a flow of ambient air through an EHC may have the undesirable effect of hindering NOx reduction activity and cooling the resistively heated substrate.

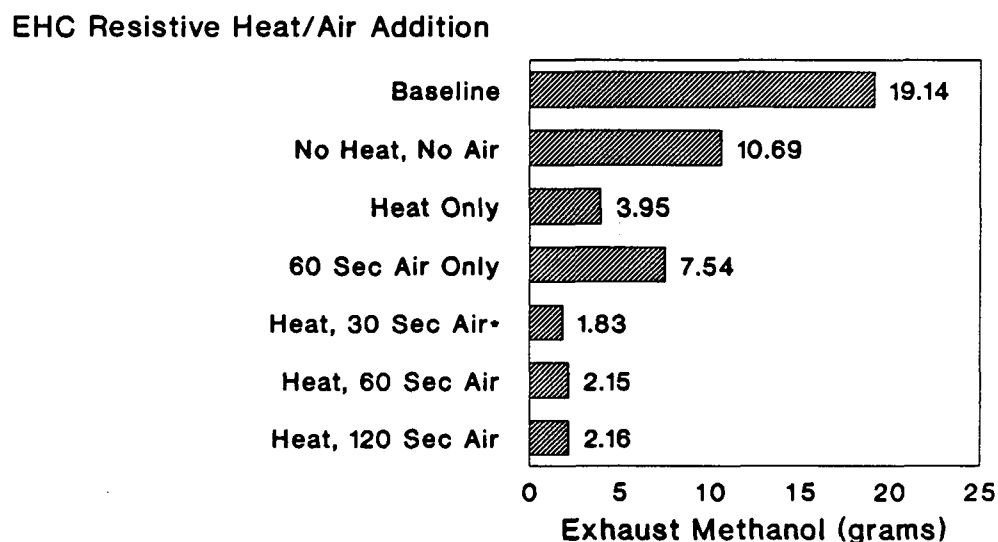
Catalyst air assist was used in a previous effort by EPA to reduce CO levels from a gasoline-fueled vehicle at lower ambient temperatures with an EHC.[7] In this case, additional air proved useful as an assist for EHC performance. Other EPA work with methanol-fueled vehicles has indicated, however, that air assist to contemporary platinum:rhodium catalysts caused a significant increase in Bag 1 emissions of formaldehyde.[18]

Air assist before the EHC was tried here as a strategy to improve catalyst efficiency. The air was added only during the initial portions of Bag 1 following key-on, in order to minimize any production of formaldehyde or increases in oxides of nitrogen.

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 ft³/minute. An airflow meter was also added to determine the effect of changes in exhaust flowrate on the flowrate of air in to the exhaust. The air addition began with key-on, and continued for intervals of 30 to 120 seconds.

Figure 6 contains unburned fuel emissions data in grams over Bag 1, when air assist is provided to the electrically heated catalyst. Baseline (no catalyst) and no-heat/no-air emissions data are also given in Figure 6 for comparison. All catalyst heating conducted during this phase of the evaluation utilized the 15/40 heating strategy.

Figure 6
QLOC Only, With Air Assist
Methanol Emissions, Bag 1 Of FTP



* Heat 15 Seconds Prior To/40 Seconds
Following Start, 30 Seconds Air
Addition Following Start

As previously shown in Figure 3, resistive heating alone over the 15/40 heating convention provided better than a 60 percent reduction in unburned fuel emissions from unheated catalyst levels. The addition of air for 60 seconds following start in Bag 1 also reduced methanol emissions, yet these levels were almost twice as high as those noted when the catalyst was resistively heated. Air flowrate over the catalyst did not vary much because of changes in the flowrate of exhaust; fluctuations of only 0.1-0.2 ft³/minute of air were noted.

The combination of air addition and resistive heating appeared to improve the efficiency of the EHC substantially with respect to methanol emissions. This improvement did not continue as the length of time the air addition occurred was lengthened, however. A roughly 50 percent improvement in efficiency was noted when air was added for 30 seconds to the heated catalyst (15/40 heating). The level of methanol emissions rose slightly when air addition time was increased to 60 seconds; a similar increase in the level of methanol emissions was noted at 120 seconds of air addition. Additional testing would have to be conducted to determine the statistical significance of the rise in methanol emissions noted when the length of air addition was increased to 60 seconds.

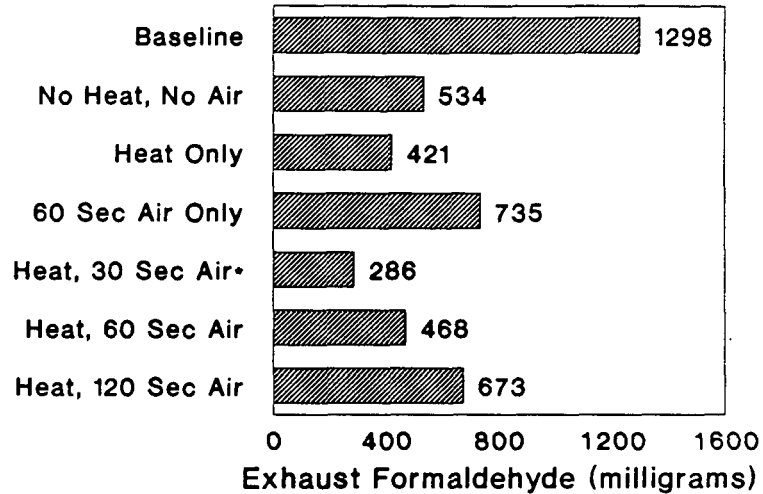
Figure 7 presents the levels of formaldehyde emissions noted when air assist was used. The addition of air, in the absence of catalyst heating, caused formaldehyde levels to increase above nonresistively-heated catalyst levels. In this first case, air was added for 60 seconds following start in Bag 1. When the catalyst was resistively heated, and air was added for only 30 seconds following start, Bag 1 formaldehyde emissions were reduced to 286 milligrams. As the air flow was extended over longer time periods, up to 120 seconds following start, formaldehyde levels increased. At the level of 2 minutes of air addition, in spite of 15/40 catalyst heating, formaldehyde levels increased to exceed levels from no heat/no air catalyst testing.

It is interesting to note that the single heat/air scheme at which formaldehyde levels were lower than heated catalyst only levels involved air addition for only 30 seconds following start. The heating scheme used here, 15/40 involved resistive heating for 40 seconds following start. The other two heat/air configurations had air addition times that exceeded the period of catalyst heating (40 seconds). It is not known how significant the period of air addition in the absence of catalyst heat is to the production of aldehydes during Bag 1. Given the 15/40 heating scheme, more testing, preferably using modal analysis, would have to be conducted to determine a more optimum air flowrate and addition period.

In previous testing on a gasoline-fueled vehicle at lower temperatures, a significant decrease in CO emissions was noted when air addition was used with a resistively heated catalyst.[7] Other researchers have noted an improvement in CO efficiency from a

Figure 7
QLOC Only, With Air Assist
Formaldehyde Emissions, Bag 1 Of FTP

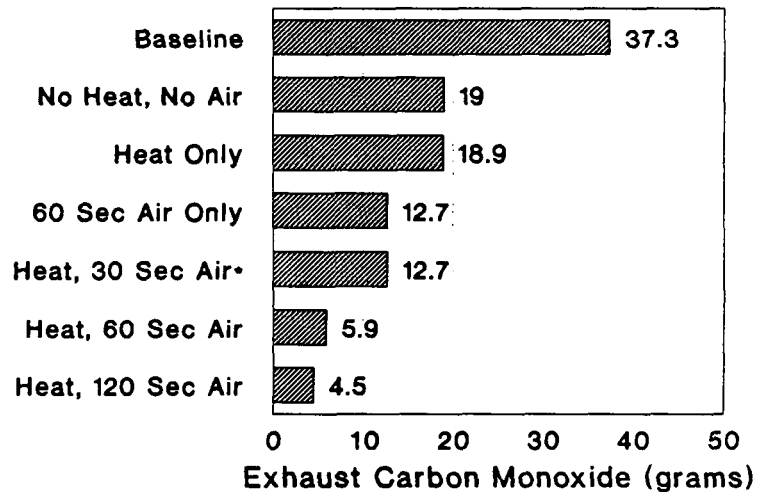
EHC Resistive Heat/Air Addition



* Heat 15 Seconds Prior To/40 Seconds
Following Start, 30 Seconds Air
Addition Following Start

Figure 8
QLOC Only, With Air Assist
Carbon Monoxide Emissions, Bag 1 Of FTP

EHC Resistive Heat/Air Addition



* Heat 15 Seconds Prior To/40 Seconds
Following Start, 30 Seconds Air
Addition Following Start

gasoline-fueled EHC-equipped vehicle when air addition is used.[2] The addition of air in front of the catalyst evaluated here provided a very significant enhancement of EHC activity for CO removal.

Figure 8 provides Bag 1 CO emissions data for the EHC with air addition. As mentioned above, catalyst heating alone provided virtually no benefit for CO beyond unheated catalyst emission levels. Sixty seconds of air addition following start reduced CO to approximately 12.7 grams, a 33 percent decrease from no-heat/no-air catalyst operation.

Catalyst heating with increasing lengths of air addition time provided significant increases in CO conversion efficiency. The 15/40 heating scheme, with 30 seconds of air addition following start, gave the same level of Bag 1 CO, 12.7 grams, as the addition of air only for 60 seconds. Increasing the time of air addition to a full 60 seconds with catalyst heating decreased CO by roughly 50 percent to 5.9 grams. (This convention involved air addition for approximately 20 seconds following the end of catalyst heating.) When the period of air addition was increased to 120 seconds, a further substantial decrease in CO emissions resulted. While it appears from these tests that catalyst resistive heating may provide a useful assist to an oxidation catalyst for CO control, more tests would have to be conducted to quantify the contribution of the heating. Different heating conventions could also be tried to determine a scheme that would more effectively complement the air addition strategy selected.

Bag 1 emissions data is summarized in Table 5. OMHCE trend in the same general direction as the heaviest organic component by total weight actually measured (methanol). A slight increase in NOx emissions was noted as air addition over the three-way catalyst was increased to 120 seconds. This increase was minimized by the limitation of catalyst air assist to relatively short periods of time of excess CO/unburned fuel emissions following cold start.

Table 6 presents the average FTP results for each emissions category. Because the Bag 1 emissions of the pollutants of interest here are such a significant component of average FTP emissions of these pollutants, it was expected that any improvement in Bag 1 emissions would be manifest in FTP emissions. This indeed was noted in most cases.

Though it is not possible to select an optimum catalyst operating strategy based upon the limited testing commented on here, the 15/40 heating/30 second air addition strategy appears to be relatively effective. Air addition time is kept to a minimum, reducing any cooling effect on the heated substrate. Excess

Table 5

Testing Limited To Current-Generation Catalyst
 Bag 1 Of FTP Cycle
Air Assist To Catalyst

Category	NMHC g	HC* g	CH ₃ OH g	HCHO mg	OMHCE g	CO g	NOx g
Baseline	1.55	7.33	19.14	1298	10.00	37.3	6.9
15/40 Heat/ No Air	0.17	1.51	3.95	421	2.13	18.9	3.7
30 Sec Air/No Heat	0.13	3.01	8.71	634	4.25	17.8	4.0
60 Sec Air/No Heat	0.05	2.70	7.54	735	3.67	12.7	3.9
120 Sec Air/No Heat	0.14	2.44	6.94	853	3.59	12.2	4.2
15/40 Heat/ 30 Sec Air	0.10	0.74	1.83	286	1.07	12.7	3.6
15/40 Heat/ 60 Sec Air	0.01	0.72	2.15	468	1.18	5.9	4.0
15/40 Heat/ 120 Sec Air	0.01	0.75	2.16	673	1.29	4.5	4.3

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

Table 6

Testing Limited To Current-Generation Catalyst
 FTP Composite Emission Levels
Air Assist To Catalyst

Category	NMHC g/mi	HC* g/mi	CH ₃ OH g/mi	HCHO mg/mi	OMHCE g/mi	CO g/mi	NOx g/mi
Baseline	0.28	1.17	2.93	323	1.63	7.3	1.6
15/40 Heat/ No Air	0.03	0.16	0.36	51	0.22	1.6	0.8
30 Sec Air/No Heat	0.01	0.26	0.76	84	0.38	1.8	0.9
No Heat/60 Sec Air	0.00	0.23	0.69	91	0.35	1.4	0.8
No Heat/120 Sec Air	0.01	0.23	0.66	98	0.35	1.3	0.8
15/40 Heat/ 30 Sec Air	0.02	0.13	0.30	50	0.18	1.3	0.8
15/40 Heat/ 60 Sec Air	0.01	0.13	0.37	67	0.20	1.0	0.8
15/40 Heat/ 120 Sec Air	0.00	0.14	0.38	83	0.21	0.8	0.9

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

formaldehyde and NO_x formation are also minimized by reducing the air addition time, and the lowest rates of methanol and formaldehyde emissions were noted with this catalyst operating procedure. It should be recalled, however, that this QLOC has a small volume and it requires the assistance of a larger main catalyst, according to the manufacturer, Camet Inc. Therefore, although the small QLOC was generally more efficient when resistively heated and operated in the oxidation catalyst mode, it would still be necessary to use a larger main catalyst to ensure better performance. The lowest formaldehyde emission level noted here, 50 milligrams/mile far exceeded the California standard of 15 milligrams/mile over the FTP, even at low mileage.

C. QLOC + Main Catalyst, With/Without Air Assist

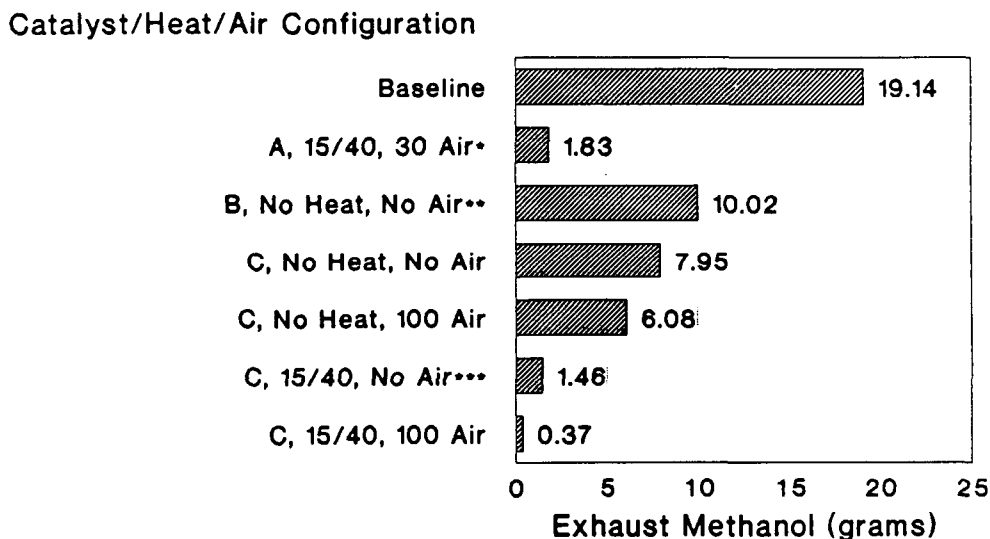
The QLOC evaluated here used a small substrate in order to minimize the power requirements for catalyst heating. The smaller volume also ensures ease of location, wherever desired, in the exhaust system. According to Camet, it is necessary to equip vehicles with a larger, nonresistively heated catalyst in order to reduce pollutant emissions to very low levels over the entire FTP.

A metal monolith catalyst, described earlier in Section III, was installed immediately following the QLOC underfloor to simulate a QLOC assisted by a main catalyst. The larger main catalyst also had the capability of being resistively heated, however, at no time during the testing commented upon here was any resistive heating applied to the main catalyst. Catalyst heating of the QLOC was limited to the 15/40 convention, and air addition occurred over 100-second intervals.

Three separate catalyst configurations are referred to in the remaining Figures. Configuration "A" refers to the electrically heated catalyst only, without benefit of a main catalyst in the exhaust. This data is from the catalyst testing with 15/40 heating and air addition for 30 seconds. Configuration "B" refers to testing conducted with the main catalyst only present in the exhaust stream. No resistive heating or air addition was used during this testing. Configuration "C" is the QLOC with the main catalyst close coupled downstream. Resistive heating here was limited to 15/40, and air addition occurred in front of the QLOC. This additional air was added for intervals of 100 seconds following start in Bag 1. Because the MC was coupled immediately downstream of the QLOC, the activity of the MC would also be affected by the supplemental air.

Figure 9 presents emissions data from the QLOC + MC testing, compared with other selected test results of single converter systems. The catalyst system denoted "A" is a mode of QLOC operation discussed previously that appeared more efficient with respect to other QLOC operating conventions evaluated. Catalyst system "B" refers to the evaluation of the MC without the QLOC in the exhaust.

Figure 9
QLOC & MC, W/WO Air Assist
Methanol Emissions, Bag 1 Of FTP



*A (EHC Only), 15/40 Heat, 30 Sec Air

**B (MC Only), No Heat, No Air

***C (EHC+MC), 15/40 Heat, No Air

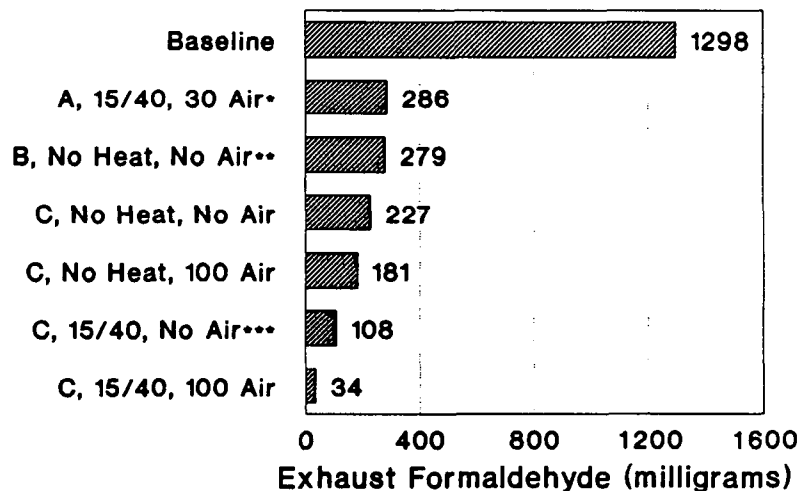
The QLOC alone, in Configuration "A," provided good methanol conversion efficiency in spite of its limited size. The simulated MC alone, however, was not nearly as efficient for methanol conversion. The Bag 1 emission level of 10.02 grams of methanol was comparable to the smaller QLOC's performance (10.69 grams, Figure 3) in the unheated, no air assist mode. Adding the QLOC in front of the MC did not improve methanol emissions to much below 8 grams/Bag 1. Even with the addition of air for 100 seconds, the decrease in emissions to 6.08 grams was only a small improvement from the 7.54 grams noted with the addition of air for 60 seconds over the QLOC only (Figure 6).

Heating the QLOC + MC configuration, in the absence of excess air, significantly lowered methanol emissions from levels obtained with the heated QLOC only. 1.46 grams of methanol in Bag 1 were noted with the two-catalyst system and the QLOC heated 15/40 in Bag 1. This is a 63 percent decrease from the 3.95 grams measured with QLOC alone heated over the 15/40 convention (Figure 3). With 100 seconds of excess air added in front of the two-catalyst configuration, methanol emissions were reduced again very significantly to 0.37 grams/Bag 1.

The use of a MC also significantly assisted the conversion of formaldehyde emissions. Roughly similar levels of formaldehyde emissions from Bag 1 were measured from the heated/air assisted QLOC only (Configuration A) and the unassisted MC, Configuration B; this data is presented in Figure 10. Substantial successive decreases in aldehyde emissions were noted with the two-catalyst configuration (C) when air only, then heat only, and finally resistive heat/air assist were utilized. While the final two-catalyst configuration tested yielded a very efficient 34 milligrams of formaldehyde in Bag 1, more additional testing would have to be conducted to determine a more optimum resistive heating/air addition strategy.

Figure 10
QLOC & MC, W/WO Air Assist
Formaldehyde Emissions, Bag 1 Of FTP

Catalyst/Heat/Air Configuration



*A (EHC Only), 15/40 Heat, 30 Sec Air

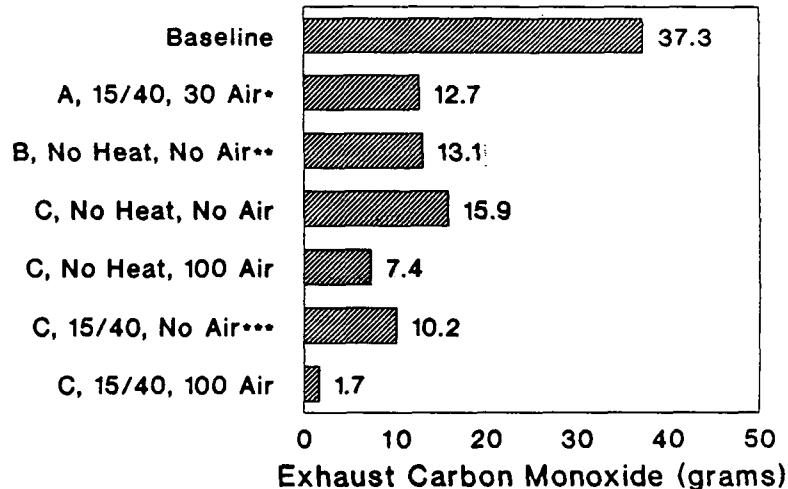
**B (MC Only), No Heat, No Air

***C (EHC+MC), 15/40 Heat, No Air

Figure 11 presents CO emissions over Bag 1 for Configuration C. Though not shown there, it should be recalled that the QLOC alone, with 120 seconds air assist, gave very low Bag 1 CO emissions of only 4.5 grams (Figure 8).

Figure 11
QLOC & MC, W/WO Air Assist
Carbon Monoxide Emissions, Bag 1 Of FTP

Catalyst/Heat/Air Configuration



*A (EHC Only), 15/40 Heat, 30 Sec Air

**B (MC Only), No Heat, No Air

***C (EHC+MC), 15/40 Heat, No Air

CO emissions rose slightly above MC only levels, when the QLOC was placed in front of it in the exhaust stream (no resistive heat or air assist utilized). No reason for this unexpected occurrence is given here. No unusual driving conditions or engine problems were noted during this testing that might have contributed substantially to this unexpected result.

The addition of air and the use of QLOC resistive heating separately had a beneficial effect on catalyst performance. The use of 100 seconds of air addition alone reduced Bag 1 CO emissions by 50 percent to 7.4 grams, over no heat/no air emission levels with the two-catalyst system. QLOC heating in the absence of additional air also reduced CO, to approximately 10 grams/Bag 1. This was a 35 percent improvement from the two-catalyst configuration which did not rely on QLOC resistive heating. This improvement was not noted when the QLOC was heated in the absence of a MC (Figure 5).

A very big assist for CO control to Configuration C was provided by combined QLOC resistive heating and the addition of excess air. Bag 1 emissions of CO were reduced to 1.7 grams, a very significant decrease from levels measured when either resistive heating or excess air was employed alone. Again, more testing would have to be conducted, however, to obtain an optimum resistive heating/air addition strategy for CO.

A summary of Bag 1 emissions from the two-catalyst system testing is given below in Table 7. Although much of the data there has been discussed above, one new observation which may be made is that the addition of the main catalyst did not cause a significant decrease in NOx emissions in Bag 1. The MC by itself was effective as a NOx removal catalyst, yet its additional catalyzed surface area did not substantially lower Bag 1 NOx emissions when added behind the QLOC. Slight trends toward increased NOx efficiency with catalyst heating and decreased NOx efficiency with air addition were noted with the QLOC + MC configuration. Reduced levels of other emissions, caused by the increased conversion efficiency of the heated/air assisted QLOC, may play a significant role in the ability of the MC to reduce NOx emissions. More detailed work would have to be conducted to quantify the effects of the reduction of other emission levels caused by catalyst heating/air assist on NOx conversion efficiency, however.

Table 8 presents FTP average emissions from the QLOC + MC evaluation. The very low Bag 1 CO levels from the two-catalyst system using both resistive heating and air addition significantly lowered CO over the FTP. The configuration utilizing 15/40 resistive heating and 100 seconds of air addition was the most effective configuration tested overall. While the CO levels of 0.2 grams per mile were very low, emissions of formaldehyde were also measured at only four milligrams per mile with this configuration, well under the level of California standard of 15 milligrams per mile. It must be pointed out that these 4 mg/mi emission levels were achieved at low mileage.

In the configuration suggested by Camet (QLOC assisting a larger main catalyst) the addition of air and the use of resistive heating appeared to be successful strategies to improve the overall efficiency of the catalysts. When the no-heat/no-air assist configuration is compared with the heated/air assisted configuration, every FTP emission level except NOx is substantially lower with the assisted catalysts. OMHCE, formaldehyde, and CO were lowered by approximately 75 percent. NOx emissions over the FTP were essentially unchanged, in spite of the addition of air. Further lowering of emission levels could depend upon a refinement and better integration of resistive heat/air addition strategies, as well as a more appropriate selection of active catalysts for the application.

Table 7
Quick Light-Off And Main Catalyst Testing
Bag 1 Of FTP Cycle

Category	NMHC g	HC* g	CH ₃ OH g	HCHO mg	OMHCE g	CO g	NOx g
Baseline	1.55	7.33	19.14	1298	10.00	37.3	6.9
15/40 Heat/No Air/No Main Catalyst	0.17	1.51	3.95	421	2.13	18.9	3.7
No Heat/60 Sec Air/No Main Catalyst	0.05	2.70	7.54	735	3.67	12.7	3.9
15/40 Heat/30 Sec Air/No Main Catalyst	0.10	0.74	1.83	286	1.07	12.7	3.6
Main Catalyst Only/No Heat/No Air	0.21	3.51	10.02	279	4.72	13.1	3.7
QLC + Main No Heat/No Air	0.19	2.83	7.95	227	3.79	15.9	3.3
QLC + Main No Heat/100 Sec Air	0.07	2.09	6.08	181	2.83	7.4	3.4
QLC + Main 15/40 Heat/No Air	0.04	0.57	1.46	108	0.78	10.2	3.1
QLC + Main 15/40 Heat/100 Sec Air	0.02	0.17	0.37	34	0.22	1.7	3.4

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

Table 8

Quick Light-Off And Main Catalyst Testing
FTP Composite Emission Levels

Category	NMHC g/mi	HC* g/mi	CH ₃ OH g/mi	HCHO mg/mi	OMHCE g/mi	CO g/mi	NOx g/mi
Baseline	0.28	1.17	2.93	323	1.63	7.3	1.6
15/40 Heat/No Air/No Main Catalyst	0.03	0.16	0.36	51	0.22	1.6	0.8
No Heat/60 Sec Air/No Main Catalyst	0.00	0.23	0.69	91	0.35	1.4	0.8
15/40 Heat/30 Sec Air/No Main Catalyst	0.02	0.13	0.30	50	0.18	1.3	0.8
Main Catalyst Only/No Heat/No Air	0.01	0.26	0.73	22	0.35	0.8	0.8
QLC + Main No Heat/No Air	0.02	0.21	0.57	16	0.28	1.0	0.7
QLC + Main No Heat/100 Sec Air	0.01	0.17	0.47	13	0.23	0.5	0.6
QLC + Main 15/40 Heat/No Air	0.01	0.08	0.19	9	0.10	0.7	0.6
QLC + Main 15/40 Heat/100 Sec Air	0.00	0.06	0.14	4	0.07	0.2	0.7

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

VIII. Evaluation Highlights

1. Catalyst resistive heating alone reduced Bag 1 methanol emissions by 50 percent from unheated catalyst levels with the QLOC only in the exhaust. (Several heating conventions were evaluated; the most efficient convention was 15/40 heating. This convention was only slightly more efficient than the others evaluated, however.)

Only a slight reduction in Bag 1 formaldehyde levels was gained by resistively heating the QLOC in the absence of additional air. Bag 1 CO was unaffected by catalyst resistive heating without air assist.

2. Adding air in front of the resistively heated QLOC significantly improved its efficiency of methanol conversion. Air was added at an average rate of 5.0 SCFM; Bag 1 methanol emissions were reduced approximately 50 percent to two grams when air was added for 30 seconds after start. Formaldehyde emissions were reduced approximately 30 percent from heated catalyst levels when air was added for only 30 seconds in front of the heated catalyst. Extending the time of air addition past 30 seconds caused substantial increases in formaldehyde emissions. Formaldehyde more than doubled to 673 milligrams when air addition was increased to 120 seconds from the 286 milligrams in Bag 1 with air addition for only 30 seconds.

Bag 1 CO emissions steadily decreased as the time of air addition was increased at a constant rate of catalyst resistive heating. At 60 seconds of air addition following start, without catalyst heating, CO was measured at almost 13 milligrams in Bag 1. This emission level was reduced by more than half, to 5.9 milligrams when 15/40 catalyst resistive heating and 60 seconds of air assist were used. CO emissions appeared to decrease at a slower rate as the time of air addition was extended beyond 60 seconds.

3. Very low Bag 1 emissions of methanol, formaldehyde and CO were measured when a main catalyst was added to the exhaust system immediately following the QLOC. Overall, the lowest emissions of all three pollutants were obtained when resistive heating and air assist to the QLOC were used simultaneously. The main catalyst was not resistively heated.

The QLOC resistive heating/air addition convention used during the two-catalyst system evaluation was 15/40 heating and air assist for 100 seconds following start in Bag 1. The simultaneous use of these two assists decreased Bag 1 methanol emissions to 0.37 grams. This was down from 7.95 grams measured with no resistive heat or air assist provided to the two-catalyst system. Formaldehyde emissions were likewise affected; formaldehyde emissions were reduced to 34 milligrams over Bag 1 with QLOC resistive heat/air

addition. This was an 85 percent improvement from the 227 milligrams in Bag 1 measured when the two-catalyst system received no resistive heating or air assist.

The largest increase in catalyst efficiency when resistive heating/air assist was provided to the two-catalyst system occurred for CO control, however. Almost 16 grams of CO were measured over Bag 1 with the two-catalyst system, when the QLOC was not supplied with resistive heating or additional air. CO was reduced to less than two grams over Bag 1 with 15/40 resistive heating and 100 second air addition, a 90 percent reduction.

Improvements in Bag 1 emission levels generally caused average FTP emissions to decrease roughly proportionally to the decrease in Bag 1 levels. With the resistively heated and air assisted two-catalyst system, OMHCE were reduced to a low 0.07 grams per mile. Formaldehyde emissions were also very low at only four milligrams per mile. The greatest percentage increase in efficiency from unassisted catalyst operation, however, was in the category of CO emissions. The heated/air assisted two-catalyst system gave average FTP CO emissions of only 0.2 grams per mile, an increase in efficiency of 80 percent over unassisted catalyst operation. Although Bag 1 NOx levels appeared to increase slightly with increasing air addition times, the level of FTP NOx emissions was 0.7 grams per mile with the two-catalyst system either unassisted or assisted with both resistive heating and air addition.

IX. Future Efforts

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 Emissions 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

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