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Technical Report

Evaluation Of An Emitec Resistively Heated Metal Monolith Catalytic Converter On Two M100 Neat Methanol-Fueled Vehicles

by

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

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MEMORANDUM

SUBJECT: Exemption From Peer and Administrative Review

FROM: Karl H. Hellman, Chief KH
Technology Development Group

TO: Charles L. Gray, Jr., Director
Regulatory Programs and Technology Division

The attached report entitled "Evaluation Of An EMITEC Resistively Heated Metal Monolith Catalytic Converter On Two M100 Neat Methanol-Fueled Vehicles" (EPA/AA/TDG/92-04) describes the evaluation of a resistively heated catalyst system on two different methanol-fueled vehicles. The EMITEC catalyst consisted of a compact resistively heated metal monolith in front of a larger conventional main converter. The goal of this project was the reduction of unburned fuel, carbon monoxide (CO), and formaldehyde emissions over the Federal Test Procedure driving cycle.

Resistive heat and air assist were provided during cold start in Bag 1; some tests also included catalyst heat/air assist during Bag 3. Modal analysis was also performed to further investigate the effect of the catalyst on unburned fuel and CO emissions.

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., Director, RPT

Date: [illegible]

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I. Summary

A fresh electrically heated catalytic converter (EHC) was furnished by EMITEC to the U.S. Environmental Protection Agency (EPA) for evaluation on two methanol-fueled vehicles. The EHC consisted of a compact resistively heated quick light-off catalyst followed by a larger conventional three-way main converter. The main catalyst was similar in volume to catalysts found on most late-model U.S. automobiles.

The EMITEC EHC was evaluated on two neat methanol-fueled vehicles, a 1981 Volkswagen Rabbit and a 1988 Toyota Corolla. Emission testing was conducted over the Federal Test Procedure (FTP) CVS-75 test cycle. The emissions of primary interest were cold start methanol (unburned fuel), CO and formaldehyde.

The EHC was evaluated in several modes. First, the EHC was emission tested without resistive heating or air assist. Different heating sequences with/without heat applied prior to starting the engine were then evaluated. Catalyst air assist with/without resistive heating was evaluated. Initially, resistive heating and air assist were limited to the cold start segment (Bag 1) of the FTP. However, as emission levels of unburned fuel over the Bag 1 portion with the Rabbit vehicle were reduced below Bag 3 levels, resistive heating and air assist were also used during the initial portion of Bag 3 on some tests.

Resistively heating the EHC without air assist provided mixed results on the VW vehicle. Bag 1 unburned fuel emissions were reduced 55 percent from levels obtained with the unassisted catalyst when a 15/40-second heat sequence (resistive heating 15 seconds prior to and 40 seconds following start) was used. Bag 1 CO emissions, however, increased above unassisted catalyst levels.

When secondary air injection was utilized with 15/40 heating, Bag 1 unburned fuel emissions were reduced to 0.20 grams, a 93 percent reduction from heated catalyst only levels. CO emissions over Bag 1 were 1.2 grams with this configuration, a 90 percent reduction from unassisted catalyst levels.

Formaldehyde emissions were also significantly reduced when the catalyst was assisted in Bag 1 by resistive heating and air addition. Bag 1 formaldehyde levels with the unassisted catalyst were approximately 96 milligrams. With catalyst resistive heating and air assist, Bag 1 formaldehyde levels were reduced to 17 milligrams, an 83 percent reduction.

Bag 1 unburned fuel emissions were lower than those from Bag 3 when catalyst heating/air addition were used. Tests were then conducted with catalyst heating/air assist provided during Bag 3 as well as during Bag 1. This additional catalyst assist reduced Bag 3 methanol, CO, and formaldehyde emissions and lowered composite FTP emission levels of unburned fuel and formaldehyde to 0.03 grams/mile and 1 milligram/mile respectively.

The EMITEC EHC was then installed underfloor on a lean-burn M100 Toyota Corolla vehicle and the test sequence was repeated. With catalyst resistive heating only, Bag 1 unburned fuel emissions were reduced 70 percent from unassisted catalyst levels. Resistive heating also significantly lowered Bag 1 formaldehyde levels. (With the 15/40 heat sequence, Bag 1 formaldehyde was measured at 69 milligrams, approximately 72 percent less than the 245 milligrams obtained with the unassisted catalyst.) Resistive heating without catalyst air assist did not significantly lower Bag 1 CO levels.

Catalyst efficiency improved when secondary air injection was used together with 15/40 heating. Unburned fuel emissions were reduced to 0.71 grams over Bag 1, almost 89 percent below unassisted catalyst levels and 96 percent below engine-out levels. Bag 1 CO was also reduced to 5.3 grams, approximately 65 percent lower than the 14.9 grams measured with the unassisted catalyst. Formaldehyde emissions over Bag 1 were reduced to 28 milligrams with this catalyst configuration, 97 percent below baseline levels.

Some testing was also conducted on the Corolla with heat/air assist supplied to the catalyst during the Bag 3 portion of the FTP as well as Bag 1. FTP composite emissions of unburned fuel here were measured at 0.05 grams/mile, CO at 0.3 grams/mile, and formaldehyde at 3 milligrams/mile. FTP NOx emissions remained relatively constant at 0.4 grams/mile.

II. Introduction

Cold start accounts for the most significant portion of unburned fuel, carbon monoxide, and formaldehyde emissions over the Federal Test Procedure (FTP) from catalyst-equipped, methanol-fueled vehicles.[1,2] Recent enactment of Federal and California clean air legislation has focused attention on reducing these cold start emissions.[3,4]

One strategy to reduce cold start emissions uses an electrically heated catalyst (EHC) to shorten the time to catalyst light-off (the time in which the converter becomes catalytically active). Excess emissions of unburned fuel and CO at cold start occur because the engine and catalytic converter have not warmed to relatively steady state conditions, and a period of fuel enrichment is necessary to ensure good starting and driveability. EPA has evaluated several electrically heated metal monolith catalytic converters to reduce Bag 1 emissions of unburned fuel, CO, and formaldehyde from methanol-fueled vehicles.[1,2,5,6,7,8] These evaluations involved the use of low mileage catalyst substrates with various volumes and active catalyst loadings.

EPA conducts and publishes the results from emission control technology evaluations to enhance interest in new technologies by automakers and industry hardware suppliers. Interest in resistively heated catalyst technologies for mobile sources has continued to grow, and several industry sources have provided EPA with samples of their catalysts for evaluation. One of these catalyst suppliers, EMITEC, recently furnished EPA with an electrically heated catalyst for evaluation on two methanol-fueled vehicles. A preliminary evaluation of this converter was conducted, and results of this evaluation are presented in this report.

III. Description of Catalytic Converter Technology

Figure 1 below is a cut-away diagram of the EMITEC heated catalyst system. The compact electrically heated substrate has a cell density of 200 cpsi, with a catalyst loading of 60 g/ft^3 of 5:1 platinum:rhodium. Downstream of the EHC is the main converter, which consists of two separate metal foil bricks. The first brick (Catalyst No. 1) is an oxidation catalyst, and the second brick (Catalyst No. 2) functions as a 3-way catalyst. A more detailed description of the EMITEC EHC system is provided in Appendix A.

Figure 1
EMITEC Electrically Heated Catalyst System

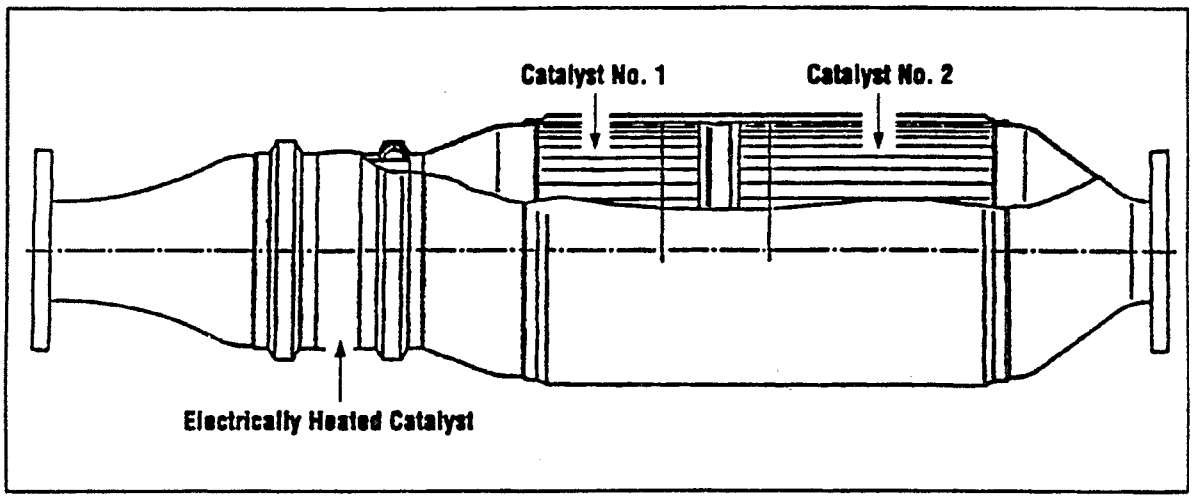
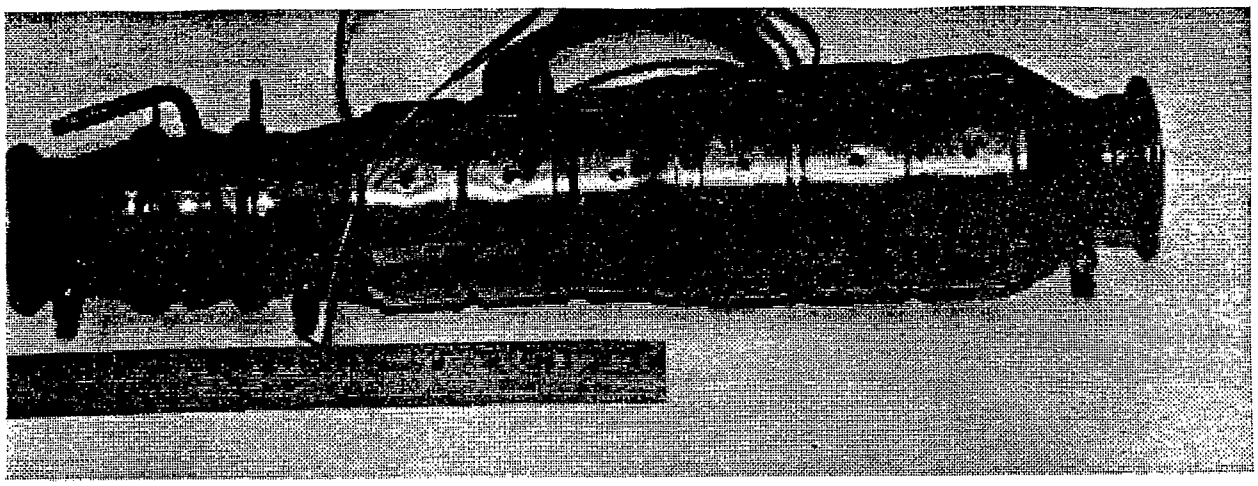


Figure 2 below is a photograph of the EMITEC electrically heated catalyst system. The small light-off converter on the left is resistively heated; the larger main converter is on the right. The overall length of the entire unit (EHC plus main catalyst) was 565 millimeters. This system is described in more detail by the manufacturer in an earlier paper. [9]

Figure 2
Photograph of EMITEC EHC System



A 12-volt DC automotive battery was used to supply the energy for resistively heating the EHC. Resistance across the can electrical connection posts was measured at 1.2 ohms. The application of 12 volts from the fully charged battery caused a current of approximately 300 amps at start in the circuit which decreased to about 260 amps after 50 seconds of resistive heating. The other circuit components consisted of #06 gauge copper cables six feet in length and #00 gauge copper cable 9 feet in length.

IV. Description of Test Vehicles

The first test vehicle (Figure 3) was a 1981 Volkswagen Rabbit 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 on neat methanol fuel. The vehicle was tested at an equivalent test weight of 2,500 lbs. and an actual dynamometer horsepower of 7.7. This vehicle was loaned to the U.S. EPA by Volkswagen of America; a detailed description of the vehicle and its modifications were provided in an earlier report.[5]

The second test vehicle was a 1988 4-door Toyota Corolla equipped with Toyota's second-generation methanol lean-burn system. The 1.6-liter engine is equipped with 4-valves/cylinder, compact combustion chamber technology, swirl control valve system, lean-mixture sensor, sequential fuel injection, and exhaust gas recirculation for NOx control. A detailed description was provided in previous papers.[2,10,11] The Corolla was tested at an equivalent test weight of 2,750 lbs. and an actual dynamometer horsepower of 8.9. This vehicle was loaned to the EPA by Toyota Motor Corporation; a picture of the car is given in Figure 4.

Figure 3
M100 Volkswagen Rabbit Test Vehicle

Figure 4
M100 Toyota Corolla Test Vehicle

V. Test Facilities and Analytical Techniques

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. A Philco Ford constant volume sampler with a nominal capacity of 600 cfm was used. Exhaust hydrocarbon 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 dinitrophenol-hydrazine (DNPH) technique.[12,13] Exhaust carbonyls including formaldehyde are reacted with DNPH solution forming hydrazone derivatives. These derivatives are separated from the DNPH solution by 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 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.[14]

VI. Test Procedures

The goal of this test program was an initial evaluation of an EMITEC resistively heated catalyst system on two methanol-fueled vehicles. The test procedures used here were similar to those used in two recent evaluations of resistively heated catalysts conducted by EPA.[7,8] These procedures were used because the EMITEC EHC has a total volume similar to the Kemira Oy and Camet EHCs evaluated previously, and all three EHC's had platinum:rhodium three-way catalyst formulations.

The testing was conducted in several phases, each succeeding phase using an additional catalyst assist in an attempt to further lower emission levels. Cold start emissions of particular interest were unburned fuel (methanol), CO, and formaldehyde.

Several baseline emission tests were first conducted. Baseline for the Rabbit refers to emission tests over the FTP driving cycle with a straight pipe inserted in place of the underfloor catalyst. A dummy substrate was inserted in place of the underfloor emissions catalyst with the Corolla vehicle. After these tests, the straight pipe/dummy catalyst was removed and the EMITEC catalyst system installed in its place. Several tests were then conducted over the FTP without catalyst heating or secondary air injection. This unassisted testing provided a reference for determining the improvement in catalyst conversion efficiency provided by catalyst heating and/or air assist.

The next phase of testing involved catalyst resistive heating without secondary air injection. Two heat sequences, 0/40 and 15/40 were evaluated on the Volkswagen vehicle. 15/40 refers to a 15-second period of heating prior to starting the engine followed by 40 seconds of resistive heating after cold start. The heated catalyst testing on the Corolla was limited to the 15/40 sequence.

Secondary air assist was then added in front of the EHC to assist the oxidation reactions. The air was added from a shop air line immediately following engine start in Bag 1. The air assist was limited to 100 seconds following cold start; it was assumed that limiting air addition 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 secondary air flow to an average 5.0 ft^3/minute over the period of air addition.

The EHC was tested on each vehicle with a 15/40 heating sequence and catalyst air addition for 100 seconds following Bag 1 cold start. Initially, resistive heating and air assist were limited to the Bag 1 portion of the FTP. Unburned fuel emission levels over Bag 1 with catalyst heat/air assist were lower than Bag 3 levels in some tests with the Rabbit vehicle. Therefore, the last phase of testing utilized the same Bag 1 resistive heating (15/40) and air assist (100 seconds after start) sequences as well as 5/30 heating and 30 seconds of air assist at the start of Bag 3. This configuration was expected to result in the lowest FTP composite emission levels of unburned fuel, CO, and formaldehyde for both vehicles.

VII. Discussion of Test Results

A. M100 Volkswagen Rabbit Vehicle

This section provides the results of emission testing utilizing the methanol-fueled Volkswagen Rabbit vehicle. The following section describes similar emissions testing on the lean-burn methanol-fueled Toyota Corolla vehicle.

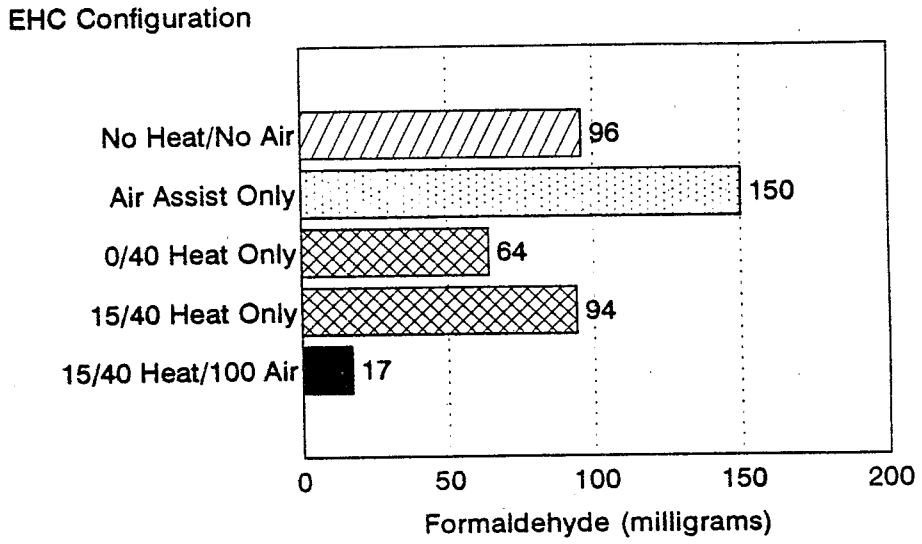
The emissions of primary interest here are unburned fuel, CO and formaldehyde emissions related to the cold start and warm-up period. Unburned fuel emissions are a result of the large quantities of fuel inducted during the cold enrichment period, poor vaporization and mixing, and cold cylinder walls and intake manifold runners. CO and formaldehyde emissions are related to incomplete combustion, and their formation is also enhanced by the fuel enrichment period.

All test results presented below were obtained over the FTP driving cycle. Bag 1 emissions are presented in grams over the test segment, except for formaldehyde, which is presented in milligrams. Composite FTP emission levels are presented in grams/mile, except for formaldehyde, which are presented in milligrams/mile.

Figure 5 below presents formaldehyde emissions obtained over the cold start portion of the FTP with the M100 Volkswagen vehicle. Resistive heating and air assist were limited to Bag 1. Following baseline testing, the vehicle was emissions tested with the catalyst in the unheated mode and without air assist. The vehicle was then tested without resistive heating but with 100 seconds of catalyst air assist provided immediately following cold start in Bag 1. The EHC system was then tested using two different resistive heating sequences. No air assist was provided to the catalyst during this testing. The final catalyst configuration evaluated combined Bag 1 resistive heating with air assist.

Figure 5

EMITEC EHC, M100 VW Vehicle
Formaldehyde Emissions, Bag 1



The two resistive heating sequences evaluated here involved catalyst heating during the cold start portion of the FTP. Heating was limited to Bag 1 because of the importance of cold start emissions to weighted FTP levels. The numerator in the heat scheme fraction represents the number of seconds of catalyst preheating prior to cold start; the denominator represents the number of seconds of catalyst heating following start. The last catalyst configuration combined the 15/40 resistive heating sequence with 100 seconds of air assist after start in Bag 1.

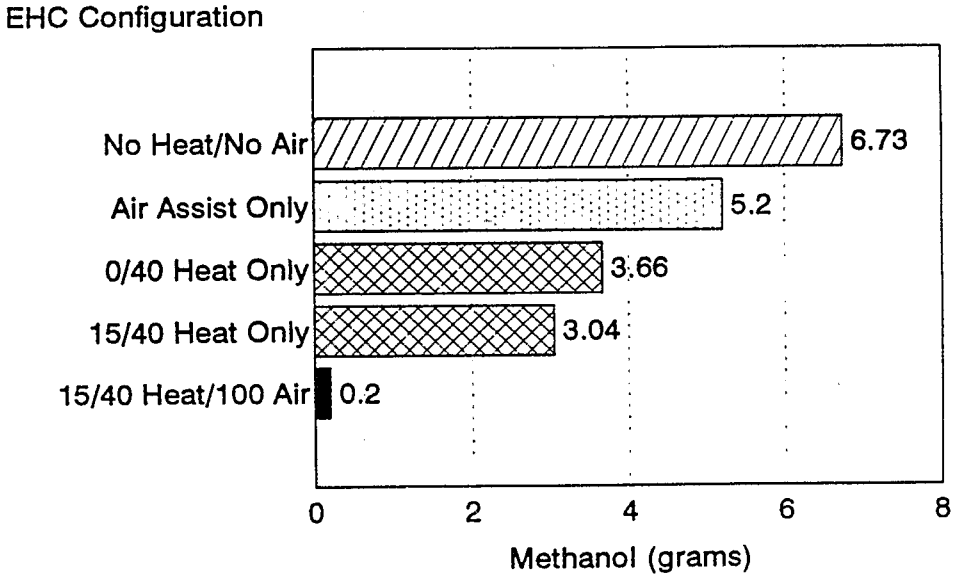
The unassisted catalyst (no heat/no air mode) reduced Bag 1 formaldehyde levels to 96 milligrams, a reduction from baseline of over 95 percent. Bag 1 formaldehyde levels increased above unassisted catalyst levels when 100 seconds of secondary air addition was used. Preheating the catalyst for 15 seconds had little effect on Bag 1 formaldehyde when compared to the unassisted catalyst. However, when 40 seconds of catalyst resistive heating were used after starting the engine, Bag 1 formaldehyde levels decreased to 64 milligrams. This represents a 33 percent reduction from levels obtained with the unassisted catalyst.

A significant reduction in formaldehyde was noted when both resistive heating and air assist were provided to the catalyst. Bag 1 formaldehyde was measured at 17 milligrams when the 15/40 resistive heating sequence and 100 seconds of secondary air assist were used. This represented an 83 percent reduction from unassisted catalyst levels and approached the Bag 3 emissions level.

Figure 6 presents the results from exhaust methanol sampling over the same test sequence in Figure 5. The fresh unassisted catalyst was very effective in converting unburned fuel. The methanol level measured without catalyst assist, 6.73 grams, represents a 58 percent reduction from the baseline level of 16.09 grams (not shown).

Figure 6

EMITEC EHC, M100 VW Vehicle
Methanol Emissions, Bag 1



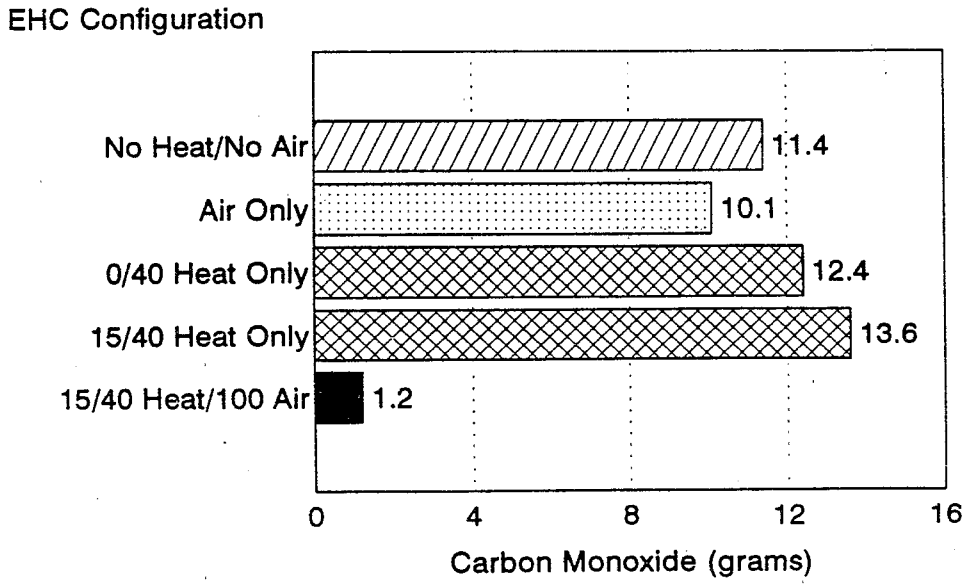
Secondary air injection during the initial portion of Bag 1 also reduced unburned fuel emissions below unassisted catalyst levels. Bag 1 methanol emissions were reduced to 5.20 grams when air was added before the catalyst for 100 seconds after key-on. Methanol emissions over Bag 1 decreased to 3.66 grams, approximately 46 percent from the unassisted catalyst level, when resistive heating was applied for 40 seconds in the absence of air assist. Preheating the catalyst for 15 seconds without air assist reduced Bag 1 unburned fuel levels further from no preheat levels, to 3.04 grams.

When resistive heating and air assist were combined, Bag 1 methanol emissions were reduced to very low levels. In this catalyst configuration, Bag 1 exhaust methanol was measured at 0.20 grams, a 97 percent reduction from levels obtained with the unassisted catalyst. Bag 1 unburned fuel measured here was lower than the exhaust methanol level measured over the Bag 3 segment (0.3 grams), when the engine was warm at start.

Figure 7 below presents CO levels measured during the same testing described above. Without resistive heat or air assist to the catalyst, Bag 1 CO was measured at 11.4 grams, a 67 percent reduction from the baseline level of 34.3 grams. When catalyst air assist was used exclusively, Bag 1 CO levels decreased slightly, to 10.1 grams.

Figure 7

EMITEC EHC, M100 VW Vehicle
Carbon Monoxide Emissions, Bag 1



Resistive heating without air assist caused higher Bag 1 CO emissions. During testing with resistive heating only, Bag 1 CO emissions rose above levels obtained with the unassisted catalyst. When a 15-second preheat period was used, Bag 1 CO rose above levels measured without preheat. However, when resistive heating and air assist were used together, Bag 1 CO decreased to very low levels. The level of Bag 1 CO measured then was 1.2 grams, a 90 percent reduction from the unassisted catalyst level. Bag 1 CO emissions approached levels measured over the Bag 3 segment with this configuration.

A summary of emission levels measured over Bag 1 from this testing is provided in Table 1. Organic material hydrocarbon equivalents (OMHCE), a method of expressing the combined effects of conventional hydrocarbons, unburned fuel and aldehyde emissions, are also calculated and presented here. Baseline refers to engine-out emission levels.

Table 1

EMITEC EHC Evaluation
Bag 1 Emission Levels, M100 VW Vehicle

Catalyst Configuration	NOx g	CO g	CH_3OH g	HCHO mg	OMHCE g	NMHC g
Baseline	7.2	34.3	16.09	2021	9.06	1.10
No heat/ no air	4.3	11.4	6.73	96	3.29	0.27
Air only*	4.7	10.1	5.20	150	2.31	**
0/40 heat only	3.8	12.4	3.66	64	1.85	0.16
15/40 heat only	4.3	13.6	3.04	94	1.55	0.14
15/40 heat and air	4.6	1.2	0.20	17	0.15	0.03

* Air assist for 100 seconds after key-on.
** Less than 0.005 grams measured.

Bag 1 OMHCE emission levels generally follow trends similar to those noted with unburned fuel, the most significant component of OMHCE. Without catalyst resistive heating/air assist, Bag 1 NOx decreased from baseline (7.2 grams) to 4.3 grams. When secondary air injection was used with/without resistive heating, Bag 1 NOx increased slightly above levels from no heat/no air assist testing. The lowest Bag 1 NOx levels, however, were recorded when 0/40 catalyst heating was utilized without air assist.

Table 2 below presents composite FTP emissions from this testing.

Table 2

EMITEC EHC Evaluation
FTP Test Results, M100 VW Vehicle

Catalyst Configuration	NOx g/mi	CO g/mi	CH_3OH g/mi	HCHO mg/mi	OMHCE g/mi	NMHC g/mi
Baseline	1.6	6.4	2.64	429	1.70	0.35
No heat/no air	1.0	0.7	0.40	7	0.21	0.02
Air only*	1.0	0.7	0.33	11	0.16	**
0/40 heat only	0.8	0.8	0.23	5	0.13	0.01
15/40 heat only	1.0	0.9	0.22	7	0.12	0.01
15/40 heat and air	1.0	0.2	0.04	2	0.03	0.01

* Air assist for 100 seconds after key-on.
** Less than 0.005 grams/mile measured.

Generally, the changes in Bag 1 emissions of methanol, CO, and formaldehyde are reflected in overall FTP emission levels. Air assist alone resulted in a reduction of exhaust methanol from 0.40 grams/mile to 0.33 grams/mile. Composite FTP formaldehyde levels increased to 11 milligrams/mile, however, when catalyst resistive heating was not used. FTP levels of CO were unaffected by the use of Bag 1 air assist only.

Mixed results occurred when catalyst resistive heating was used in the absence of air assist. A substantial reduction in unburned fuel emissions was noted with this catalyst configuration, from 0.4 grams/mile to 0.22 grams/mile. However, a slight increase in overall FTP CO also occurred, from 0.7 grams/mile to 0.9 grams/mile. Aldehyde levels were unchanged by catalyst heat assist.

Very low FTP composite emission levels were obtained when both 15/40 heat and secondary air assist were combined. FTP emissions of unburned methanol, CO, and formaldehyde were measured at 0.04 grams/mile, 0.2 grams/mile, and 2 milligrams/mile respectively. These levels represent over a 70 percent reduction in formaldehyde and CO, and a 90 percent reduction in methanol emissions from levels obtained with the unassisted catalyst. OMHCE emissions over the FTP were reduced to 0.03 grams/mile, below California ULEV standards.

The slight changes in Bag 1 NOx emissions were not reflected in composite FTP levels. FTP NOx levels remained constant at 1.0 grams/mile, except when 0/40 heating was used in the absence of air assist. FTP composite emissions of OMHCE, HC, and NMHC, however, followed trends similar to those noted with unburned fuel. For example, the 90 percent reduction in unburned fuel emissions obtained when both heat/air assist were provided to the catalyst contributed to an 86 percent reduction in OMHCE.

The combined use of catalyst resistive heating and air assist during cold start in Bag 1 caused unburned fuel emissions over Bag 3 to exceed Bag 1 levels on some tests. Additional tests were conducted with catalyst resistive heating/air assist at the start of both Bag 1 and 3 segments of the FTP in an attempt to further reduce composite emission levels. A 15/40-second heat sequence with 100 seconds of air assist was used at the beginning of Bag 1, and 5/30 heating with 30 seconds of air assist was used at the beginning of Bag 3. Table 3 below presents Bag 1 and 3 emission levels from this testing.

Table 3

EMITEC EHC Evaluation
Bag 1/3 Emission Levels, M100 VW Vehicle

Catalyst Configuration	NOx g	CO g	CH_3OH g	HCHO mg	OMHCE g	NMHC g
Baseline:						
Bag 1	7.2	34.3	16.09	2021	9.06	1.10
Bag 3	7.9	19.0	8.86	1239	5.54	1.10
No Heat/No Air:						
Bag 1	4.3	11.4	6.73	96	3.29	0.27
Bag 3	4.4	0.6	0.15	4	0.12	0.03
Bag 1 Heat and Air Assist:						
Bag 1	4.6	1.2	0.20	17	0.15	0.03
Bag 3	4.5	0.9	0.30	6	0.25	0.10
Bag 1 and 3 Heat and Air Assist:						
Bag 1	4.5	1.1	0.22	17	0.18	0.04
Bag 3	4.4	0.7	0.05	3	0.08	0.03

* Gasoline-fueled vehicle measurement with a propane-calibrated FID.
** Less than 0.005 grams measured.

Bag 3 CO and formaldehyde emissions were reduced slightly by the combined use of catalyst heating/air assist; Bag 3 methanol emissions were substantially reduced. The large decrease in methanol emissions caused Bag 3 OMHCE emissions to be reduced to 0.08 grams, a decrease of 66 percent from the unassisted catalyst testing conducted immediately prior to this testing.

Table 4 below presents an emissions summary from this testing.

Table 4

EMITEC EHC Evaluation
FTP Composite Emissions, M100 VW Vehicle

Catalyst Configuration	HC* g/mi	NOx g/mi	CO g/mi	CH_3OH g/mi	HCHO mg/mi	OMHCE g/mi	NMHC g/mi
Baseline	1.22	1.6	6.4	2.64	429	1.70	0.35
No heat/ no air	0.16	1.0	0.7	0.40	7	0.21	0.02
Bag 1 heat and air assist	0.03	1.0	0.2	0.04	2	0.03	0.01
Bag 1 and 3 heat and air assist	0.02	0.9	0.2	0.03	1	0.02	**

* Gasoline-fueled vehicle measurement with a propane-calibrated FID.
** Less than 0.005 grams/mile measured.

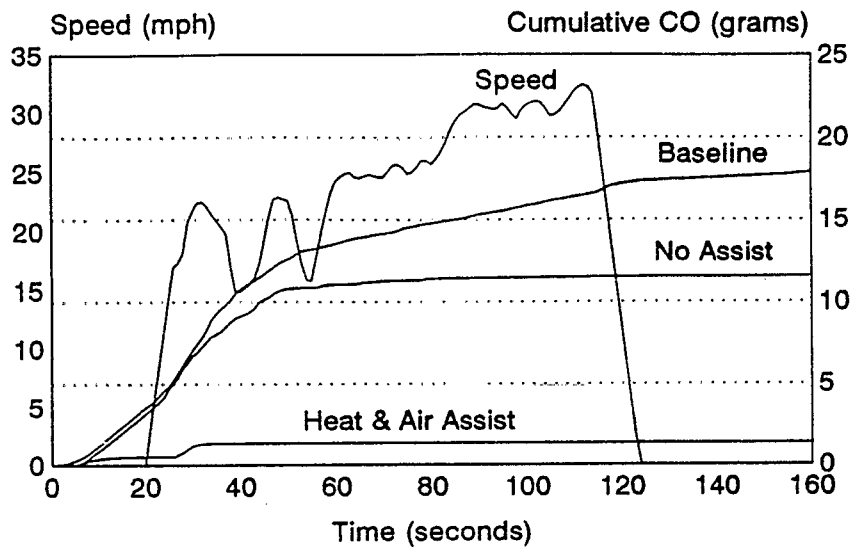
With catalyst resistive heating/air assist used during Bag 3, FTP composite emissions of methanol and formaldehyde were reduced to even lower levels, 0.03 grams/mile and 1 milligram/mile respectively. FTP composite CO emissions remained unchanged from levels obtained with catalyst heat/air assist used only during Bag 1. NOx levels over Bag 3 did not appear to increase when heat and air assist were provided during the Bag 3 segment. FTP composite NOx emission levels were relatively unchanged by the catalyst assist provided to both Bag segments. Calculated OMHCE decreased very slightly from already low levels with Bag 3 assist.

Modal testing (emissions versus time) over the FTP cycle was also performed as part of the catalyst evaluation. Emissions of total HC and CO were measured over the FTP for three catalyst configurations. The first configuration was engine-out emissions; the second used the EHC system without heat/air assist (No Assist). The final configuration utilized a 15/40 heat sequence with 100 seconds of secondary air injection (Bag 1 Heat/Air Assist).

Figure 8 below presents cumulative CO emissions over the first 160 seconds of the FTP for the catalyst configurations described above. Cumulative and instantaneous emissions can be related; as the cumulative emissions trends in the following plots approach horizontal, instantaneous emissions approach zero. Vehicle speed is also presented.

Figure 8

EMITEC EHC, First 160 Seconds Of FTP Cycle
Cumulative CO Emissions, M100 VW Vehicle

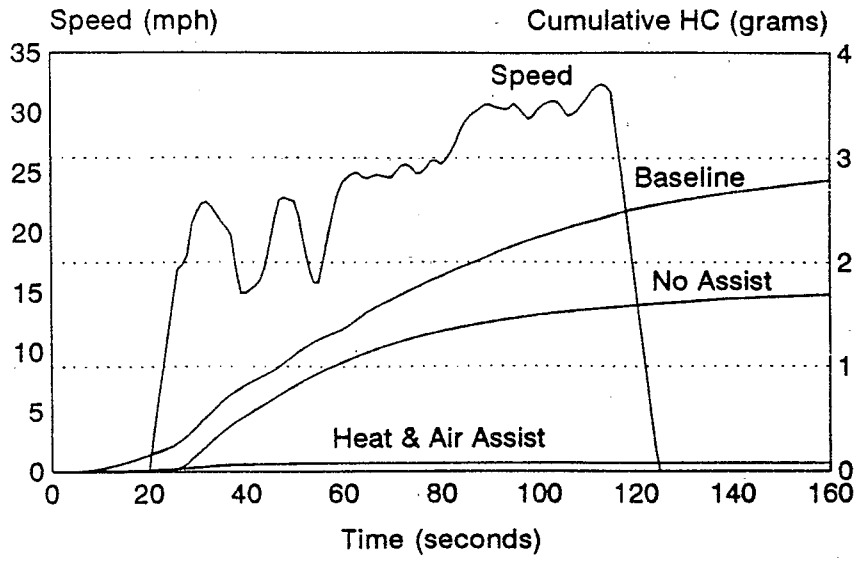


Cumulative CO levels are approximately equal for both baseline and no catalyst assist configurations over the first 30 seconds of the FTP cycle. This condition means that the catalyst has not yet achieved light-off temperature. Cumulative CO levels with the unassisted catalyst begin to stabilize after this period of catalyst inactivity. The cumulative CO trace for the unassisted catalyst becomes relatively horizontal (no instantaneous CO produced) approximately 90 seconds after start. This interval denotes light-off of the unassisted catalyst.

Cumulative CO emissions begin to diverge from unassisted catalyst levels approximately 8 seconds after start in the FTP when catalyst heat/air assist were used. After approximately 30 seconds of vehicle operation, the cumulative CO curve for the assisted configuration approaches a horizontal position, denoting near complete instantaneous catalyst conversion efficiency of CO.

Figure 9 below presents emissions measured as total HCs for the three catalyst configurations in Figure 8. HC levels are presented because modal analysis of methanol was not possible.

Figure 9
EMITEC EHC, First 160 Seconds Of FTP Cycle
Cumulative HC Emissions, M100 VW Vehicle



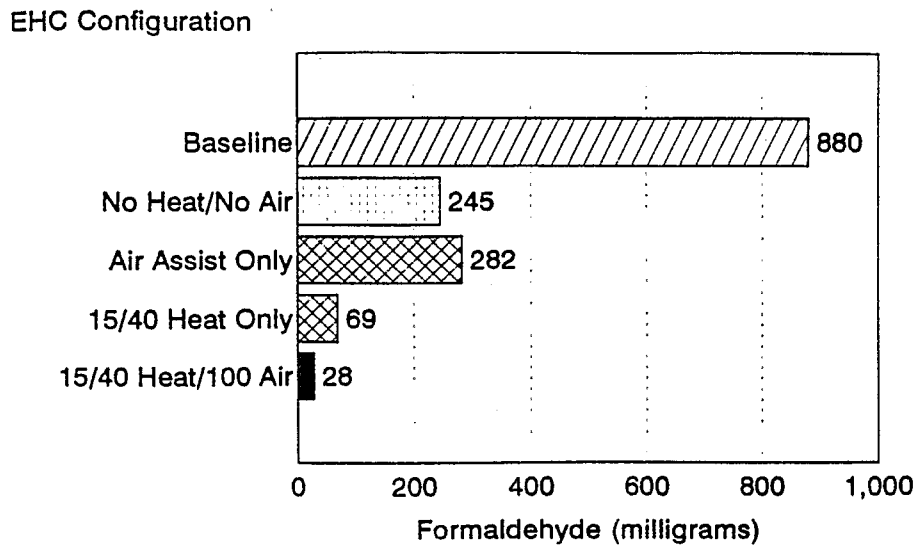
Baseline HC emissions were notably higher than unassisted catalyst levels beginning almost immediately after start. Cumulative HC levels begin to stabilize after approximately 70 seconds with the unassisted catalyst. When catalyst heat/air assist were provided, cumulative HC emissions diverged from unassisted catalyst levels approximately 25 seconds after start and stabilized shortly thereafter.

B. <u>Toyota Corolla Test Results</u>

Following completion of the testing with the Volkswagen vehicle, a similar test program was begun with an M100-fueled Toyota Corolla. This vehicle was equipped with a second-generation Toyota "Methanol Lean Combustion System". [10] Exhaust gas recirculation was also used to control NOx emissions.

Resistive heating/air assist during testing on the M100 Corolla were limited to Bag 1 only. Engine-out emissions for this vehicle were obtained with the use of a dummy catalyst in place of underfloor catalyst, rather than a straight pipe. The EHC system was then placed on the vehicle underfloor, and emissions tested without resistive heating or air assist. The vehicle was then emissions tested without catalyst resistive heating but with 100 seconds of secondary air assist after start in Bag 1. 15/40 catalyst heating without secondary air assist was the next configuration tested. The final configuration combined the 15/40 heat sequence in Bag 1 with 100 seconds of secondary air assist. Figure 10 presents Bag 1 aldehyde levels from this testing.

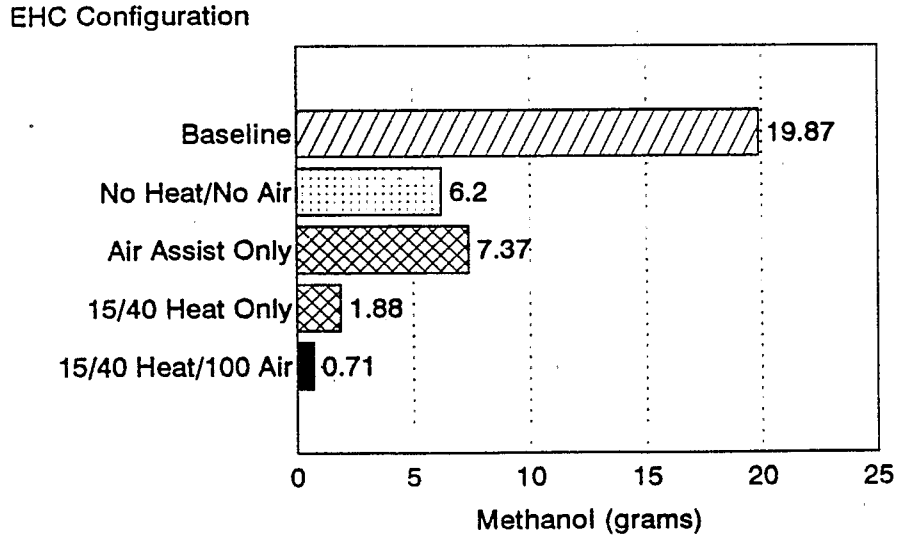
Figure 10
EMITEC EHC, M100 Toyota Corolla
Formaldehyde Emissions, Bag 1



The unassisted catalyst reduced Bag 1 formaldehyde 72 percent from baseline; formaldehyde increased, however, when catalyst air assist was used. Bag 1 formaldehyde decreased to 69 milligrams, (72 percent below unassisted catalyst levels) with catalyst heating (no air assist). Combined resistive heating/air assist reduced formaldehyde to 28 milligrams, 97 percent lower than baseline.

Figure 11 presents Bag 1 emissions of unburned fuel.

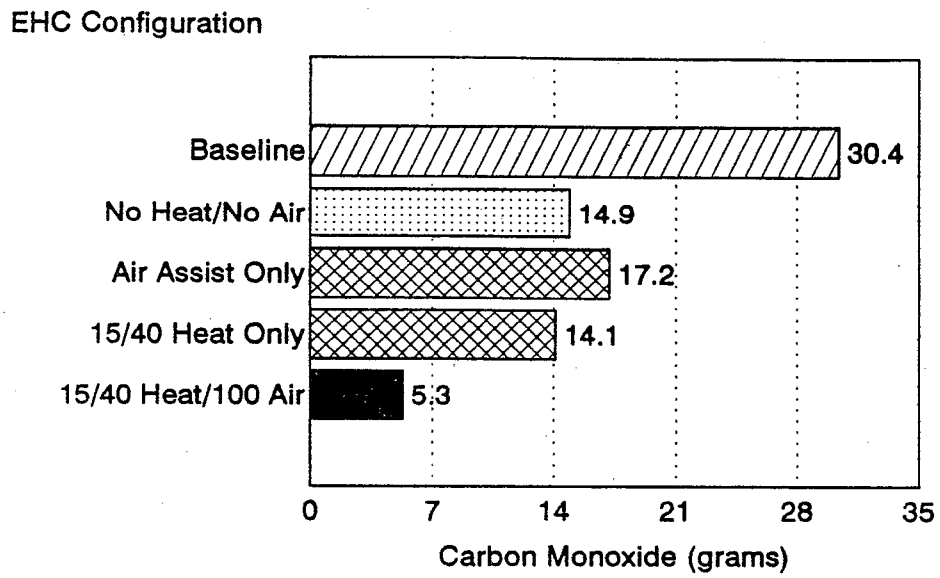
Figure 11
EMITEC EHC, M100 Toyota Corolla
Methanol Emissions, Bag 1



The unassisted catalyst reduced Bag 1 methanol emissions approximately 69 percent from baseline levels, from 19.87 grams to 6.20 grams. When air assist was used without resistive heating, Bag 1 methanol emissions increased above unassisted catalyst levels, to 7.37 grams. A significant reduction in unburned fuel emissions was obtained, however, when a 15/40 heat sequence was used; Bag 1 methanol emissions were reduced almost 70 percent from unassisted catalyst levels, from 6.20 grams to 1.88 grams. When both heat and air assist were applied to the catalyst during cold start, Bag 1 methanol was reduced to 0.71 grams, an 89 percent reduction from unassisted catalyst levels.

Figure 12 presents Bag 1 CO emissions from this testing.

Figure 12
EMITEC EHC, M100 Toyota Corolla
Carbon Monoxide Emissions, Bag 1



Bag 1 engine-out CO averaged 30.4 grams; this was reduced to 14.9 grams (51 percent reduction) when the EHC was used unassisted. Bag 1 CO increased to 17.2 grams when catalyst air assist (no resistive heating) was supplied. Resistive heating without air assist did not further reduce Bag 1 CO levels. When catalyst resistive heating was combined with air assist, Bag 1 CO was reduced to 5.3 grams, an 83 percent reduction from baseline.

A summary of Bag 1 emissions testing is given below.

Table 5

EMITEC EHC Evaluation
Bag 1 Emission Levels, M100 Toyota Corolla

Catalyst Configuration	HC* g	NOx g	CO g	CH_3OH g	HCHO mg	OMHCE g	NMHC g
Baseline	7.44	2.8	30.4	19.87	880	10.00	0.94
No heat/no air	2.37	1.6	14.9	6.20	245	3.15	0.30
Air only**	2.64	1.8	17.2	7.37	282	3.57	0.20
15/40 heat only	0.77	1.7	14.1	1.88	69	1.01	0.11
15/40 heat/air	0.31	1.8	5.3	0.71	28	0.40	0.05

* Gasoline-fueled vehicle measurement procedure with a propane-calibrated FID.
** Air assist for 100 seconds after key-on.

Bag 1 NOx was little affected by catalyst heat/air assist; the largest increase in Bag 1 NOx above unassisted catalyst levels noted here was 0.2 grams. Bag 1 OMHCE, NMHC, and methanol emissions were reduced in similar proportions with catalyst assist. (e.g. with catalyst resistive heating/air assist, Bag 1 OMHCE and methanol were reduced 87 and 88 percent respectively).

Table 6 presents composite FTP emissions from this testing.

Table 6

EMITEC EHC Evaluation
FTP Composite Emission Levels, M100 Toyota Corolla

Catalyst Configuration	HC* g/mi	NOx g/mi	CO g/mi	CH_3OH g/mi	HCHO mg/mi	OMHCE g/mi	NMHC g/mi
Baseline	1.63	0.6	5.6	4.26	249	2.17	0.24
No heat/no air	0.15	0.3	1.1	0.38	18	0.20	0.02
100 sec air only	0.20	0.4	1.4	0.49	20	0.24	0.02
15/40 heat only	0.05	0.3	1.0	0.12	6	0.07	**
15/40 heat and air	0.03	0.4	0.5	0.06	3	0.04	**

* Gasoline-fueled vehicle measurement procedure with a propane-calibrated FID.
** Less than 0.005 g/mi measured.

The reductions in Bag 1 methanol, CO, and formaldehyde emissions affected FTP composite emission levels. The heated catalyst was particularly effective at reducing formaldehyde emission levels. Formaldehyde was reduced to 3 milligrams/mile over the FTP when both heat and air assist were provided to the catalyst. This value represents an 83 percent reduction from unassisted catalyst levels and approximately a 99 percent reduction from baseline levels.

The resistively heated/air-assisted catalyst was very effective for control of Bag 1 methanol emissions occurring before catalyst light-off. The unassisted catalyst reduced methanol emissions over the FTP to 0.38 grams/mile, a 91 percent reduction from baseline. When heat and air assist were supplied to the catalyst, these emissions were further reduced to 0.06 grams/mile, a 99 percent reduction from baseline.

CO emissions over the FTP were also significantly reduced through the use of the EHC. CO emission levels over the FTP were reduced from 5.6 grams/mile (baseline) to 1.1 grams/mile (unassisted catalyst), an 80 percent reduction. When both heat and air assist were used during Bag 1, FTP composite CO emissions were reduced to 0.5 grams/mile, a 91 percent reduction from baseline.

Catalyst heating/air assist were provided at the start of the Bag 3 portion of the FTP in addition to Bag 1 in an attempt to further reduce FTP emissions of unburned fuel, CO, and formaldehyde. Bag 1 assist consisted of 15/40 resistive heating with 100 seconds of air assist; 5/30 heating was used at the beginning of Bag 3 in conjunction with 30 seconds of air assist after key-on. Table 7 below presents Bag 1 and Bag 3 emission levels from this testing. The four catalyst configurations presented in Table 7 are baseline (dummy catalyst), unassisted catalyst, Bag 1 heat and air assist only (15/40 heat, 100 seconds air), and Bags 1/3 heat and air assist (15/40 heat, 100 seconds air in Bag 1 and 5/30 heat, 30 seconds air in Bag 3). All emission levels are presented in grams per bag, except for formaldehyde, which is presented in milligrams.

Table 7

Bag 1 and 3 Heating and Air Assist
EMITEC EHC, M100 Toyota Corolla

Catalyst Configuration	HC* g	NOx g	CO g	CH_3OH g	HCHO mg	OMHCE g	NMHC g
Baseline:							
Bag 1 results	7.44	2.8	30.4	19.87	880	10.00	0. 4
Bag 3 results	4.77	2.7	15.1	12.23	875	6.06	0.72
No Heat/No Air:							
Bag 1 results	2.37	1.6	14.9	6.20	245	3.15	0.30
Bag 3 results	0.08	1.6	1.5	0.08	10	0.10	0.03
Bag 1 Heat/Air Assist:							
Bag 1 results	0.31	1.8	5.3	0.71	28	0.40	0.05
Bag 3 results	0.10	1.8	2.0	0.15	7	0.12	0.03
Bag 1 and 3 Heat/Air Assist:							
Bag 1 results	0.26	1.8	4.4	0.57	23	0.33	0.04
Bag 3 results	0.03	1.6	0.6	0.07	6	0.04	**

* Gasoline-fueled vehicle measurement procedure with a propane-calibrated FID.
** Less than 0.005 grams measured.

Bag 3 catalyst heat/air assist reduced Bag 3 CO and HC emissions below levels from unassisted catalyst testing. Bag 3 CO was reduced 60 percent, to 0.6 grams, when heat/air assist were provided. Emissions measured as HC were also substantially reduced, but methanol emissions were unchanged from unassisted catalyst levels.

The additional reductions in Bag 3 emissions only slightly reduced FTP composite emission levels, given in Table 8 below.

Table 8

Bag 1/3 Heating/Air Assist, FTP Composite Emissions
EMITEC EHC, M100 Toyota Corolla

Catalyst Configuration	HC* g/mi	NOx g/mi	CO g/mi	CH_3OH g/mi	HCHO mg/mi	OMHCE g/mi	NMHC g/mi
Baseline	1.63	0.6	5.6	4.26	249	2.17	0.24
No heat/no air	0.15	0.3	1.1	0.38	18	0.20	0.02
Bag 1 heat/ air assist	0.03	0.4	0.5	0.06	3	0.04	**
Bags 1/3 heat/ air assist	0.02	0.4	0.3	0.05	3	0.03	**

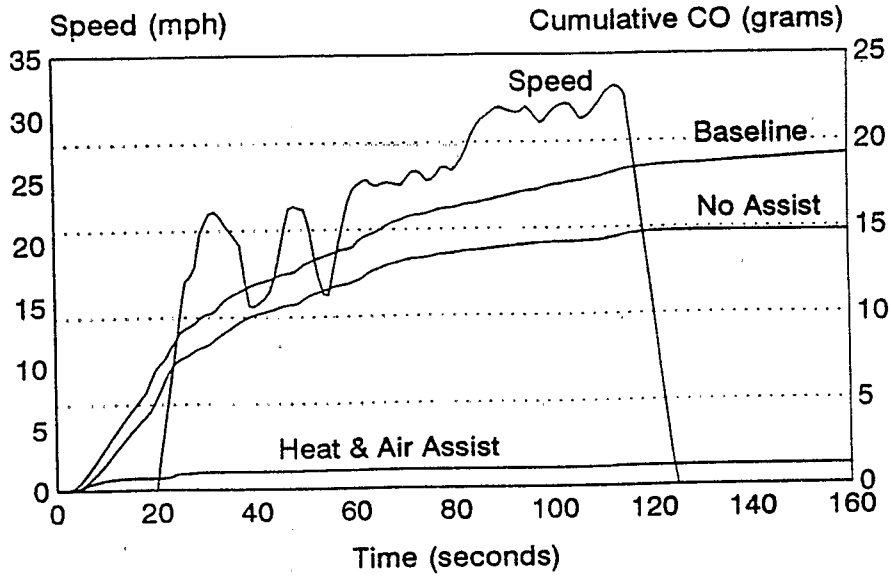
* Gasoline-fueled vehicle measurement procedure with a propane calibrated FID.
** Less than 0.005 grams/mile measured.

The reductions in unburned fuel emissions in Bag 3 resulted in a very slight reduction in FTP composite methanol levels, to 0.05 grams/mile. CO emissions over the FTP were reduced to 0.3 grams/mile, from 0.5 grams/mile. FTP levels of formaldehyde, however, remained unchanged when catalyst heat/air assist was provided during Bag 3.

Modal analysis (second-by-second emissions sampling/analysis) over the cold-start portion of the FTP was performed. Three catalyst configurations were used during this testing. Baseline was obtained with a dummy catalyst in place of the EHC system. The second configuration (No Assist) utilized the EHC catalyst without heat or air assist supplied to the catalyst. The final configuration used a 15/40 heat scheme and 100 seconds of air assist applied during Bag 1 only (Heat & Air Assist).

Figure 13 below presents cumulative CO emissions for each catalyst configuration over the first 160 seconds of the FTP cycle. Zero seconds here denotes key-on for Bag 1. Vehicle speed data is also included in this plot.

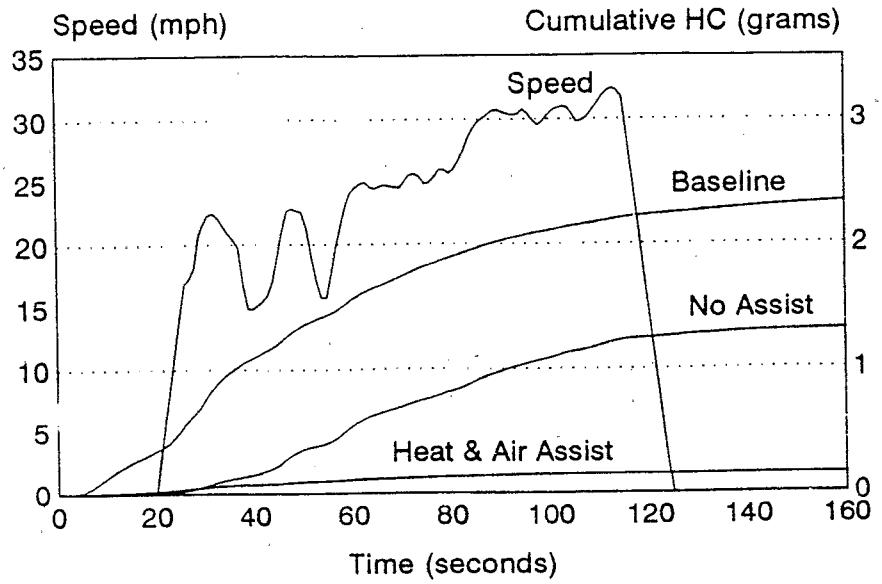
Figure 13
EMITEC EHC, First 160 Seconds of FTP Cycle Cumulative CO Emissions, M100 Toyota Vehicle



CO emissions conversion began after approximately 4 seconds into the driving cycle when the EHC was used without catalyst assist. This curve becomes horizontal (denoting 100 percent instantaneous conversion efficiency) after approximately 120 seconds of driving. When heat and air assist were supplied to the catalyst, cumulative CO levels diverged from unassisted catalyst levels after approximately 5 seconds. This trace becomes horizontal at the 25-second mark of the FTP, denoting 100 percent instantaneous conversion (and consequently lower emissions) for the remainder of the cycle.

Figure 14 below presents cumulative hydrocarbon emissions for the catalyst configurations described in Figure 13. The EHC, even in the absence of resistive heat/air assist, proved very efficient at controlling cold-start hydrocarbon emissions. Cumulative hydrocarbon emissions for the unassisted EHC begin to stabilize after approximately 120 seconds into the FTP. When resistive heat and air assist are provided during cold start, cumulative hydrocarbons are reduced to much lower levels. The emissions trace from assisted catalyst testing deviated from the unassisted catalyst trace after approximately 30 seconds, denoting a substantial hydrocarbon conversion benefit with resistive heating and air assist.

Figure 14
EMITEC EHC, First 160 Seconds of FTP Cycle
Cumulative HC Emissions, M100 Toyota Vehicle



VIII. Evaluation Highlights

1. The EMITEC electrically heated catalyst system proved to be very effective at controlling cold start emissions of formaldehyde from two M100-fueled vehicles. (e.g., Bag 1 emissions of formaldehyde from the M100 VW vehicle were reduced over 83 percent from unassisted catalyst levels when resistive heating/air assist were provided to the catalyst.)

2. The EHC efficiently reduced Bag 1 levels of unburned fuel when catalyst resistive heat/air assist were used. Bag 1 methanol emissions were reduced to 0.20 grams over Bag 1 on the VW vehicle, a 97 percent reduction from the unassisted catalyst level. Similar reductions were also noted with the Corolla vehicle, almost 89 percent below levels obtained with the unassisted catalyst.

3. Both catalyst heat/air assist were necessary in order to reduce CO emissions to very low levels for both test vehicles. Bag 1 CO emissions were reduced to 1.2 grams with the assisted EHC on the VW test vehicle (an improvement of approximately 90 percent from the 11.4 grams measured with the unassisted catalyst). CO cold start emissions from the Corolla vehicle were reduced 65 percent from unassisted catalyst levels when heat and air assist were provided.

4. The improvements in Bag 1 and Bag 3 emissions when catalyst resistive heat/air assist were used translated into substantial improvements in FTP composite emissions of OMHCE, CO, unburned fuel and formaldehyde. With the VW test vehicle, FTP composite emissions of unburned fuel, CO, and formaldehyde were measured at 0.03 grams/mile, 0.2 grams/mile, and 1 milligram/mile respectively. Composite NOx emissions remained relatively unchanged by the catalyst assists, at 0.9 grams/mile. FTP composite emissions from the M100 Corolla of unburned fuel, CO, and formaldehyde were measured at 0.05 grams/mile, 0.3 grams/mile, and 3 milligrams/mile. These levels met or approached California Ultra Low Emission Vehicle (ULEV) targets at low mileage for these pollutants.

IX. Future Efforts

Future efforts may be made to quantify the relationship between EHC heating/air assist and real-time emission rates of individual pollutants. A comparison and analysis of the light-off characteristics of several different resistively-heated catalysts may be made, making use of modal emissions analysis and exhaust temperature data.

X. Acknowledgements

The resistively heated catalyst system evaluated in this test program was supplied by EMITEC, a subsidiary of Interatom GmbH and Uni-Cardan AG, Germany. The M100 Volkswagen test vehicle was loaned to EPA by Volkswagen of America. The methanol-fueled Corolla vehicle was loaned to EPA by Toyota Motor Corporation.

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Appendix A

EMITEC EHC System Specifications

EMITEC Resistively Heated Quick Light-off Catalyst

Specification	Dimension
Substrate Diameter	70 mm
Substrate Length	25 mm
Substrate Volume	0.096 dm^3
Cells Per Square Inch	200
Geometric Surface Area (without coating)	0.2544 m^3
Cross Section	38.48 cm^3
Active Catalyst	60 g/ft^3 5:1 Pt:Rh
Rated Power Usage	3800 Watts
Approximate Heating Time to 400°C	7 seconds

EMITEC Main Catalyst

Catalyst No. 1

Substrate Diameter	90 mm
Substrate Length	90 mm
Substrate Volume	0.57 dm^3
Cells Per Square Inch	200

Catalyst No. 2

Substrate Diameter	105 mm
Substrate Length	150 mm
Substrate Volume	1.3 dm^3
Cells Per Square Inch	300