Development and Evaluation of Advanced Catalyst Technology for ULEV Emission Levels with Gasoline Fueled Vehicles

FINAL REPORT

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by

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ABSTRACT

The College of Engineering-Center for Environmental Research and Technology (CE-CERT) at the University of California, Riverside has conducted a development project to demonstration automotive emission rates on a conventional gasoline vehicle substantially below the ultra-low emission vehicle (ULEV) emission standards. The objective was to demonstrate emission rates of 0.025 gm/mi for non-methane organic gases (NMOG), 1.0 gm/mi carbon monoxide (CO), and 0.12 g/mi oxides of nitrogen (NOx). These emission rates are approximately 40% below the ULEV standards.

The technical approach involved the preparation of three prototype catalytic converters by Precision Combustion Inc. (PCI) based upon their Microlith™ technology. The Microlith™ technology uses a series of high cell density, short path length, and low thermal mass metal monoliths that provide high catalytic conversion efficiency while minimizing boundary layer build-up observed in conventional automotive monolithic substrate catalysts. The Microlith™ technology has higher mass and heat transfer rates than conventional monolith catalyst technology with resultant faster catalyst light-off times and higher conversions. The three prototype converter systems were a Microlith™/monolith cascade system with both catalysts mounted in the same converter can in a close-coupled configuration, a close-coupled Microlith™ followed by an underfloor monolith, and a stand-alone close-coupled Microlith™ catalytic converter. A standard monolithic converter was included in the test matrix as a baseline.

The catalytic converters were tested in a fresh stabilized condition and after 50,000 miles equivalent engine aging. Emission testing was performed on a 1997 Ford Escort. This vehicle is fitted with a 2.0 liter four cylinder engine with sequential fuel injection and provision for a close-coupled catalyst location approximately 4 inches from the exhaust manifold flange. This vehicle was certified to low emission vehicle (LEV) emission levels. The vehicle was fitted with an electronic air pump and an air injection manifold to achieve the fast cold-start catalyst light-off times required for ULEV emission levels.

After 50,000 miles equivalent aging, the best overall emission performance was provided by the Microlith™/monolith cascade system. Emission rates of 0.038 gm/mi NMOG, 0.328 gm/mi CO, and 0.058 gm/mi NOx were demonstrated. The NMOG emission rate did not meet our target of a 40% reduction from the ULEV standard. The CO and NOx emission rates exceeded our targeted reduction, with greater than 80% and 70% reductions from the ULEV standards, respectively. Emission reduction potentials were calculated assuming that the advanced Microlith™/monolith cascade converter system would be introduced starting with the 2000 model year on vehicles that are presently scheduled to meet ULEV emission standards. Maximum emissions reduction potentials for the SCAQMD were calculated to be 39 tons/year for NMOG, 5102 tons/year for CO, and 421 tons/year for NOx in 2006 and later years.

ACKNOWLEDGEMENTS

The following are acknowledged for their contribution to the successful completion of this project. Subir Roychoudhury and William Pfefferle of Precision Combustion Inc. provided the Microlith™ prototype catalytic converters and many helpful discussions during the course of this project. Dave Martis made the vehicle modifications to provide air addition during cold-start. Emission testing was conducted in the Vehicle Emissions Research Laboratory (VERL) at the College of Engineering-Center for Environmental Research and Technology (CE-CERT). Precision Combustion Inc provided co-funding for this project.

This report was submitted in fulfillment of AB2766/97012 and "Development and Evaluation of Advanced Catalyst Technology for ULEV Emission Levels with Gasoline Fueled Vehicles" by the College of Engineering-Center for Environmental Research and Technology under the partial sponsorship of the Mobile Sources Air Pollution Reduction Review Committee (MSRC). Work was completed as of December 31, 1997.

DISCLAIMER

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1.0 INTRODUCTION

Automotive catalyst technology to meet ultra-low emission vehicle (ULEV) emission levels for conventional gasoline fueled vehicles requires major improvements in catalytic activity and reactor engineering. A major challenge is in reducing vehicle cold-start emissions. ULEV emission levels can be exceeded in the first minute of the Federal Test Procedure (FTP) cold-start if the catalyst does not achieve its light-off temperature. To achieve these cold-start emission reductions, several approaches are actively being evaluated including electrically heated catalysts [1-3], fuel burners [4,5] and hydrocarbon adsorbers [6]. Some of these techniques have demonstrated the ability to substantially reduce cold-start emissions; however, they also add substantial complexity and cost to the emission control system. Additional work has concentrated on the development of advanced catalyst technology based on high loading of palladium [7,8]. These palladium catalysts have demonstrated improved warmed-up hydrocarbon activity and lower light-off temperatures compared to conventional platinum/rhodium catalysts. It must be recognized; however, that automotive catalyst light-off during vehicle cold-start is a dynamic process dependent not only on catalyst activity but the transfer of exhaust gas heat to the catalyst surface and the thermal mass of the catalyst/substrate combination. A major limitation of conventional ceramic or metal monolithic automotive catalyst technology is the large thermal mass associated with the catalyst substrate [9]. This results in a major delay in cold-start catalyst light-off times due to the large amount of exhaust energy required to heat the catalyst to reaction temperatures. The development of alternate catalyst/substrate technology with reduced thermal mass, high heat transfer rates and high catalyst activity could result in significant advancements in achieving emission levels at and below the ULEV standard.

Precision Combustion Inc. (PCI) has developed an alternative automotive catalyst technology called Microlith^{TM}, based upon a unique reactor engineering design. The advantages of the Microlith^{TM} automotive catalytic converter derive from a unique physical structure made possible by use of a novel proprietary catalyst coating process. The Microlith^{TM} technology developed by PCI uses a series of high cell density, short path length and low thermal mass metal monoliths that provide a high catalytic conversion efficiency while minimizing boundary layer build-up observed in conventional monolithic substrates with resultant lowering of mass and heat transfer rates[10]. The catalyst coating maintains a high open area even with cell densities as high as 388 cell per sq. cm and provides an adherent high activity coating that is resistant to loss of activity by sintering.

Conventional monolithic catalysts consist of metal or ceramic substrates having long flow channels, typically three to six inches in length, coated with a ceramic slip coat (washcoat) and a formulation containing precious metal catalysts. Automotive catalytic converter light-off occurs in a kinetically-limited regime, where catalyst surface temperature has an exponential effect upon reaction rate. After full light-off, conventional catalytic converters operate at temperature conditions where the actual catalytic reaction rate is faster than the rate at which reactants can be transported to the surface, i.e. the reaction is mass transfer limited. The reduced reaction rates of conventional monolith reactors is the result of the development of a boundary layer along the walls in the monolith channels, which limits the rate of mass transfer. Such boundary layers become fully developed within five to ten channel diameters of the entrance. The Microlith^{TM} converter avoids such boundary layer limitation by replacing the long channels of a conventional converter with a series of short substrates, each short enough to avoid substantial boundary layer build-up. As a result, Microlith^{TM} conversion rates as a function of converter length are much higher than conventional converters.

The Microlith^{TM} conversion rate is further enhanced through the use of high cell densities (e.g. 388 cells per sq. cm), allowing a much higher catalyst geometric surface area (GSA) per unit volume—up to four times that of a 62 cells per sq. cm ceramic monolith. The result is much higher conversion efficiencies than conventional monolithic catalysts with a smaller converter size. The smaller catalyst volume required for a given conversion also means that less precious metal is required. Alternatively, the same metal loading can be utilized to extend catalyst life. Use of less substrate material and less precious metal allow total costs to be below those of conventional designs.

The combination of low thermal mass, high heat transfer, and segmentation of the Microlith^{TM} assembly into a series of even lower thermal mass elements leads to a converter where each Microlith^{TM} element essentially immediately reaches the inlet gas exhaust temperature. The result is a catalytic converter which can achieve light-off times equivalent to those of electrically heated converters.

Precision Combustion, Inc has utilized the technological advantages of the Microlith™ to develop advanced automotive catalytic converters involving both a “stand-alone” Microlith™ and a Microlith™ in combination with a conventional monolithic catalyst. The stand-alone Microlith™ provides ultra-fast light-off, smaller catalyst volume, and high warmed-up conversion compared to conventional automotive converters. This smaller volume can be translated into improved emission performance since the Microlith™ converter is more likely to be placed in an optimum location without the packaging constraints of conventional systems. The Microlith™/monolith combination (often refereed to as a “cascade” system), places the Microlith™in front of the monolith in the same catalytic converter. This configuration utilizes the Microlith™’s ultra-fast light-off characteristics to light-off the conventional monolith without the requirement for a separate electrically-heated light-off converter.

2.0 OBJECTIVE AND APPROACH

The objective of this project was to demonstrate the ability of standard gasoline fueled vehicles equipped with the Microlith™ automotive catalytic converter technology to meet and exceed the ULEV emission levels. The goal was to demonstrate the ability to achieve non-methane organic gases (NMOG) emission levels of 0.25 g/mi, carbon monoxide (CO) emission levels of 1.0 gm/mi, and oxides of nitrogen (NOx) emission levels of 0.12 gm/mi. These values are approximately 40% below the 50,000 mile ULEV standard. The technical approach involved:

1. Procurement and instrumentation of a test vehicle.

2. Baseline emission testing of vehicle to determine optimum catalytic converter location and operating conditions.

3. Fabrication of prototype catalytic converter systems.

4. Emission testing and optimization of prototype catalytic converter systems.

5. Engine aging of prototype converters to 50,000 miles equivalent.

6. Emission testing of 50,000 mile aged prototype catalyst systems.

3.0 METHODOLOGY

3.1 Test Vehicle

The test vehicle chosen for this project was a 1997 Ford Escort certified to the California low emission vehicle (LEV) standards. Specifications for the engine are listed below:

Engine Type:	Overhead-cam in-line 4 cylinder with OBD II
Displacement:	2.0 liter
Valves:	8
Horsepower (SAE net):	110 @ 5,000 rpm
Torque (SAE net lb.ft.):	125 @ 3,750 rpm
Fuel system:	Sequential electronic fuel injection
Engine control:	EEC-V computer

This vehicle came equipped with a single 96 in.^{3} close-coupled catalytic converter with the inlet face of the catalyst 4 inches from the exhaust manifold flange. Prior to instrumentation and baseline testing, the vehicle was driven on the road for approximately 1000 miles to stabilize operation.

The vehicle was fitted with a three-stage electronic air pump to provide air injection into the exhaust manifold during cold-start. As discussed in the result section, this provides an overall lean (excess air) environment to the catalyst during the engine rich cold-start condition for faster catalyst light-off. The pump is operated at 12 volts and a maximum current of 40 amperes. The maximum flow rate of the pump is 622 liters/min. A series of tests were conducted varying the air injection rate and injection time during cold-start. An injection rate of approximately 370 liters/min for 45-55 seconds was found to give optimum cold-start hydrocarbon (HC) and CO performance with a minimal negative impact on NOx emissions (see Results section). A photograph of the air pump and air distribution system is presented in Figure 1. Air is distributed to the exhaust manifold through a 2.54 cm diameter air rail. The air rail has four 6.35 mm diameter injection tubes. One injection tube is inserted into each of the four exhaust ports.

3.2 Prototype Catalytic Converters

The four prototype converters prepared for testing in this program are described below:

- **Standard ceramic monolith catalytic converter for baseline testing**
  - 1.6 liter 62 cells per cm^2 ceramic monolith
    - Pd-only formulation with 11.14 gm of Pd
- **Microlith™/Monolith (cascade) in a single catalytic converter**
  - 0.11 liter Microlith™
    - 5.3/4.6/0.2 Pt/Pd/Rh formulation with 3.85 gm of platinum group metals
  - 1.6 liter 62 cells per cm^2 ceramic monolith
    - Pd-only formulation with 11.14 gm of Pd

  The Microlith™ is mounted in the inlet of the catalytic converter. The monolith is mounted ½ inch behind the Microlith™.
- **Close-coupled Microlith™ followed by a standard monolith in underfloor location**
  - 0.11 liter Microlith™
    - 4.6/5.1/0.2 Pt/Pd/Rh formulation with 4.0 gm of platinum group metals
  - 1.6 liter 62 cells per cm^2 ceramic monolith
    - Pd-only formulation with 11.14 gm of Pd

  The Microlith™ is mounted in the close-coupled configuration. The monolith is mounted 15 inches behind the Microlith™ in an underfloor location.
- **Microlith™-only catalytic converter**
  - 0.82 liter Microlith™
    - 4/5.7/0.3 Pt/Pd/Rh formulation with 10.46 gm of platinum group metals

Schematics of the prototype converters are presented in Figure 2 and a photograph is presented in Figure 3. Each converter was configured such that the inlet face of the first catalytic unit was 4 inches from the exhaust manifold flange.

Each converter system was fitted with pre- and post-catalyst sampling taps and a thermocouple located 1 inch in front of the inlet catalyst face (3 inches from the exhaust manifold flange).

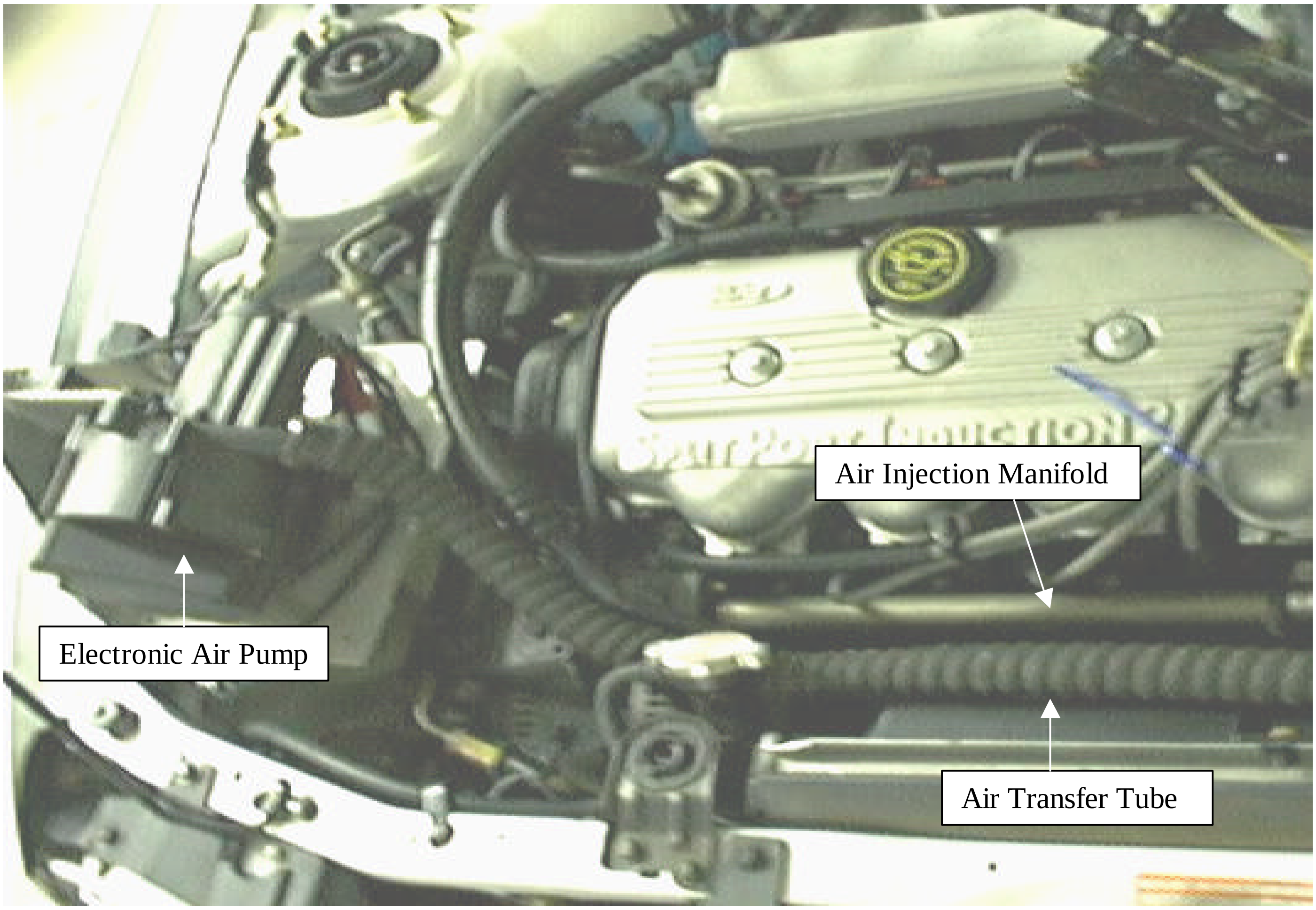
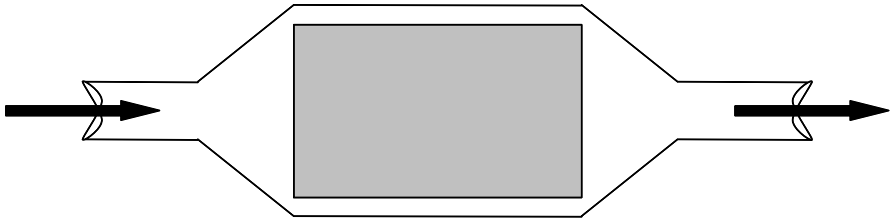
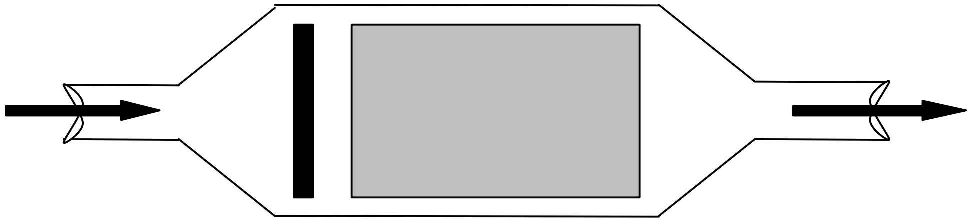


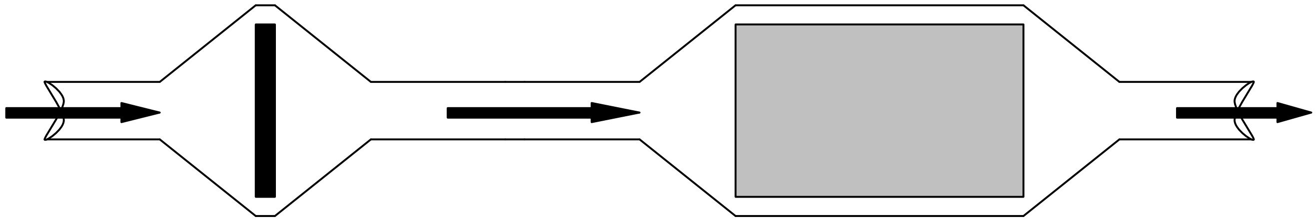
Figure 1. Photograph of Escort 2.0L engine with electronic air pump and air injection manifold



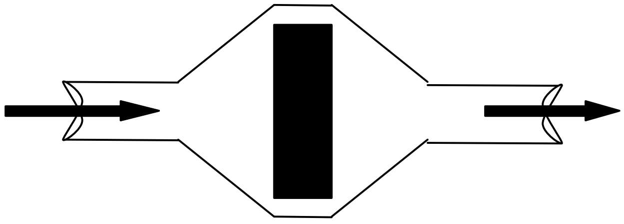
Standard Ceramic Monolith Catalytic Converter



Microlith™/Monolith (cascade) in a Single Catalytic Converter



Close-coupled Microlith™ followed by a Standard Ceramic Monolith in Underfloor Location



Microlith™-only Catalytic Converter

Figure 2. Schematic of prototype catalytic converters

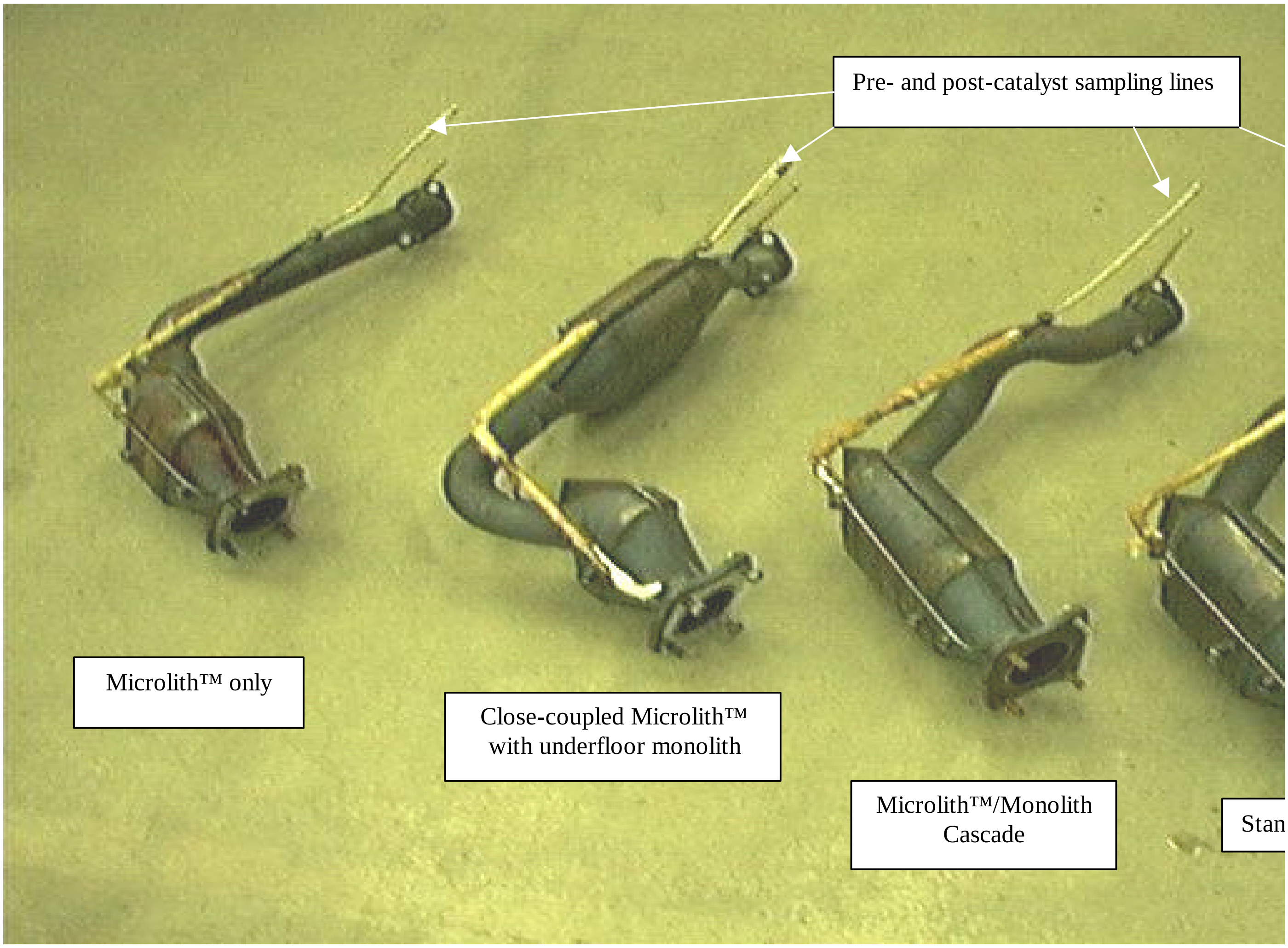


Figure 3. Photograph of prototype catalytic converters

3.3 Engine Aging of Prototype Converters to 50,000 Mile Equivalent

Prototype converters were engine aged to 50,000 mile equivalent at Southwest Research Institute. Aging was performed with a 7.5L Ford V-8 engine equipped with sequential multi-port fuel injection and an exhaust splitter system. The aging cycle used is defined by General Motors in the Society of Automotive Engineering paper[11] and is referred to as the Rapid Aging Test A (RAT-A). Details of the cycle are given in Table 1.

Step	Description
1	Closed-loop, stoichiometric operation for 40 seconds, catalyst inlet temperature of 800 °C, measured 6” upstream of catalyst face
2	Power enrichment mode, 3% carbon monoxide for 6 seconds
3	Power enrichment with air injected at converter inlet to provide 3% carbon monoxide and 3% oxygen for 10 seconds
4	Closed-loop, stoichiometric operation with air injection at the converter inlet to provide 3% oxygen for 4 seconds

Table 1. Description of engine Rapid Aging Test A (RAT-A)

Actual catalyst inlet and bed temperatures measured during aging are presented in Figure 4. Catalyst inlet temperatures were approximately 60 °C below the targeted value of 800 °C (1472 °F) during Step 1, while maximum catalyst bed temperatures reached 927 °C (1700 °F) during Step 3. The four prototype converters were aged simultaneously with the exhaust split to provide equal flow through each converter, approximately 52.5 scfm per converter. Fuel used during aging was certification grade gasoline meeting the 1996 California Phase II specifications with a sulfur content of 40 ppm. The catalysts were aged for 50 hours using this cycle that is deemed to be equivalent to 50,000 miles of vehicle aging.

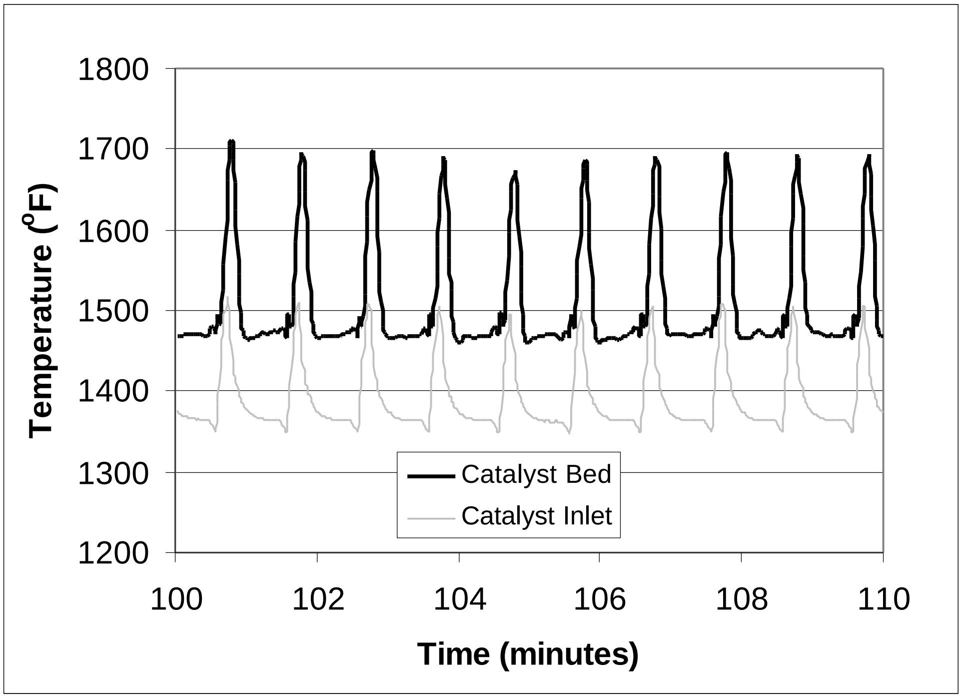


Figure 4. Measured catalyst inlet and bed temperatures during aging

3.4 Emission Testing

All testing was conducted with the College of Engineering-Center for Environmental Research and Technology's (CE-CERT's) 48 inch electric dynamometer according to test procedures for measuring gaseous exhaust emissions outlined in the Code of Federal Regulations[12] (CFR Part 86, Subpart B). All emission testing was conducted at 70±2°C over the urban dynamometer driving schedule (UDDS) of the FTP. The test fuel was procured from Phillips Chemical Company and met specifications for California phase II reformulated gasoline. Fuel analysis results are presented in Table 2.

Property	**Test Result**
API Gravity	59.7
RVP, psi	6.9
Octane, (R+M)/2	91.7
Carbon, wt.%	84.3
Hydrogen, wt.%	13.7
Sulfur, ppm mass	32.5
Aromatics, vol.%	24.2
Olefins, vol.%	5.8
Saturates, vol.%	66.3
MTBE, vol.%	10.9
Benzene, vol.%	0.95
Distillation, ^{o}F	
IBP	101
T10	139
T50	203
T90	300
EP	379
Loss, %	0.9
Residue, %	1.0

Table 3. Fuel analysis results

Oxygenated organic samples for the calculation of NMOG were collected utilizing Waters Sep-Pak Silica cartridges coated with acidified 2,4-dinitrophenyl hydrazine (DNPH) from the constant volume sampling system through a heated line (100 ^{o}C). DNPH cartridges were analyzed using the Auto/Oil Phase II protocol.[13]

4.0 RESULTS AND DISCUSSION

4.1 Baseline Emission Test Results

Two FTP emission tests were conducted with the original equipment emission control system to assess system performance and determine modifications required to meet ULEV emission standards. Results are summarized in Table 3. The vehicle meets the LEV emission requirements for which it was certified but is higher than the ULEV emission standards. Initial analysis of the results presented in Table 3 show that the ULEV hydrocarbon emissions are being exceeded during the cold-transient phase, presumably due to delayed catalyst light-off.

This is confirmed by an analysis of the second-by-second hydrocarbon emissions results. Figure 5 presents cumulative weighted engine-out (EO) and tailpipe (TP) hydrocarbon emissions for the cold-transient phase of the FTP. The 0.04 gm/mi ULEV emission level for hydrocarbons is exceeded approximately 30 seconds into the cold-transient phase of the FTP. Further increases in tailpipe hydrocarbon emissions are very low after catalyst light-off occurs at approximately 35 seconds into the cold-transient phase of the FTP.

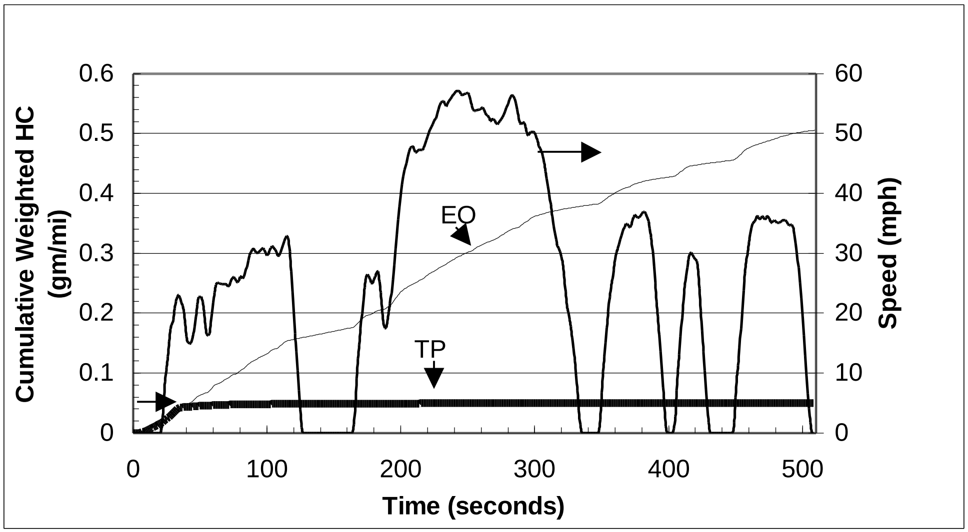


Figure 5. Cumulative weighted HC emissions during the cold-transient phase of FTP

Table 3. Baseline FTP emission results with 1997 Ford Escort

Test No.	THC (gm/mi)				NMHC (gm/mi)				CO (gm/mi)				
	CT	CS	HT	Total	CT	CS	HT	Total	CT	CS	HT	Total	CT
4001	0.246	0.004	0.001	0.053	0.230	0.004	0.000	0.050	2.237	0.055	0.088	0.515	0.09
5022	0.276	0.025	0.014	0.074	0.270	0.024	0.012	0.071	1.775	0.044	0.057	0.406	0.09
Average	0.261	0.015	0.008	0.064	0.250	0.014	0.006	0.060	2.006	0.050	0.073	0.461	0.09

Figure 6 presents air/fuel ratio, exhaust temperature (3 inches from the exhaust manifold and 1” in front of the catalyst inlet face), and hydrocarbon conversion efficiency results during the cold-transient phase of the FTP. In order to achieve hydrocarbon light-off, temperatures greater than 250-300 °C and air/fuel ratios greater than or equal to stoichiometric (= 14.5) are required. The air/fuel trace shows open-loop rich operation during cold-start with a brief excursion to lean conditions approximately 20 seconds into the test. Closed-loop stoiciometric operation is achieved approximately 35 seconds into the test. Exhaust gas temperatures exceed 250°C approximately 20 seconds into the test.

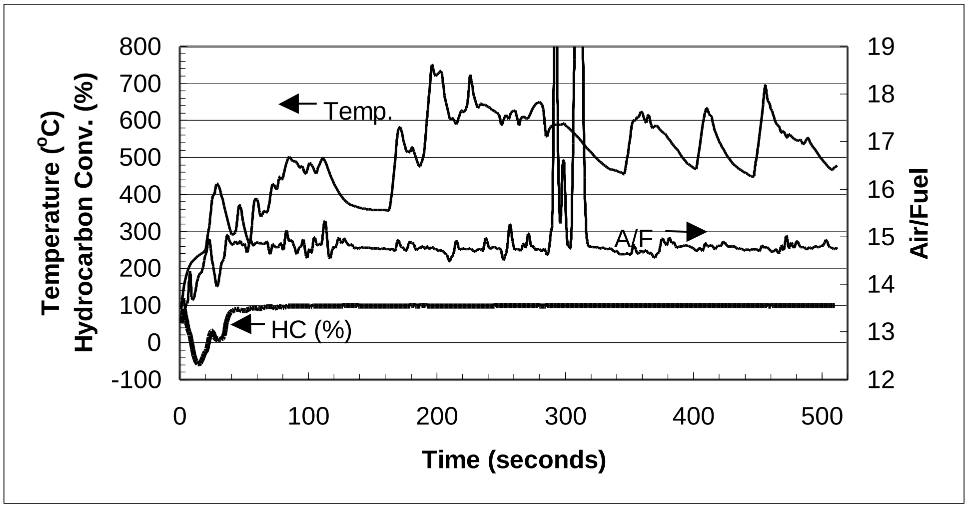


Figure 6. Exhaust temperatures, air/fuel ratio, and hydrocarbon conversion during the cold-transient phase of the FTP

The hydrocarbon conversion results show an initial removal of hydrocarbons for the first 10 seconds of cold-start. This is the result of hydrocarbon adsorption on the cold catalyst surface. These adsorbed hydrocarbons are desorbed after approximately 10 seconds as the catalyst warms up. Hydrocarbon conversion due to oxidation starts approximately 22 seconds into the test and then declines with light-off (50% conversion) occurring at approximately 35 seconds.

An analysis of these results indicates that hydrocarbon light-off is being controlled by air/fuel ratio and not catalyst temperature. This is shown more clearly in Figure 7 where results for the first 100 seconds of the cold-transient phase are presented. Catalyst inlet temperatures exceed 250 °C after approximately 20 seconds. Initial hydrocarbon conversion at 22 seconds corresponds with the transient lean excursion of the air/fuel. Hydrocarbon conversion subsequently drops between 25 and 30 seconds, even though the temperature is increasing. This drop in hydrocarbon conversion is associated with rich engine operation. Final hydrocarbon light-off occurs at approximately 35 seconds and coincides with closed-loop stoichiometric engine control.

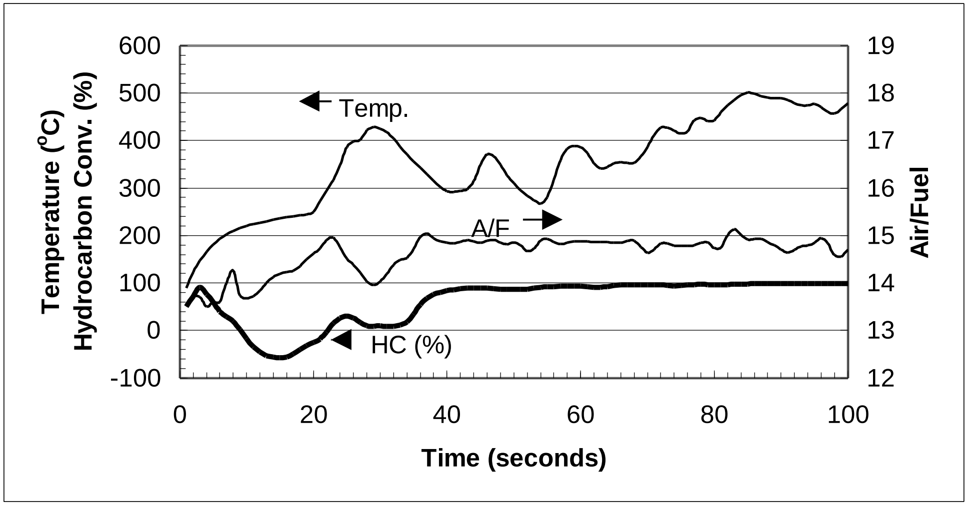


Figure 7. Exhaust temperatures, air/fuel ratio, and hydrocarbon conversion for the first 100 seconds of the cold-transient phase of the FTP

The above analysis indicates that the faster light-off times required to achieve ULEV emission values require air addition during cold-start to provide a stoiciometric or lean exhaust prior to closed-loop engine operation. The results presented in Figures 6 and 7 show that after closed-loop operation is achieved, the air/fuel control is very tight, resulting in hydrocarbon conversions approaching 100%.

4.2 Optimization for Ultra-Low Emission Level

Light-off times of 20 seconds or less are required to meet ULEV emission levels. As shown above for the original equipment configuration, catalyst light-off is inhibited by fuel enrichment during the first 35 seconds of cold-start. To overcome this limitation, the vehicle was fitted with an electronic air pump to provide air injection during cold-start. The air injection system has been described in Section 3.1.

Figure 8 presents air/fuel ratio and hydrocarbon conversion traces for the first 100 seconds of the cold-transient phase with and without air injection. As discussed in Section 4.1, the results without air addition show an initial adsorption and desorption of hydrocarbons from the catalyst surface. Hydrocarbon light-off occurs at approximately 35 seconds and corresponds with closed-loop stoichiometic operation of the engine.

With air addition, the air/fuel ratio in front of the catalyst is substantially lean of stoichiometry until after closed-loop operation and the air injection is turned off at approximately 55 seconds. The variability of the air/fuel during the first 55 seconds results from the fact that the electronic air pump delivers a constant volume of air. This dilutes the exhaust to varying degrees as a function of engine speed. The hydrocarbon conversion results with air addition are significantly better than those without air addition. Although adsorption of hydrocarbons is observed during the first 5 seconds of the test, the amount of desorbed hydrocarbons which are unreacted over the catalyst (indicated by negative hydrocarbon conversion) is much smaller. Hydrocarbon light-off (50% conversion) occurs at approximately 15 seconds with air addition compared to 35 seconds without air addition.

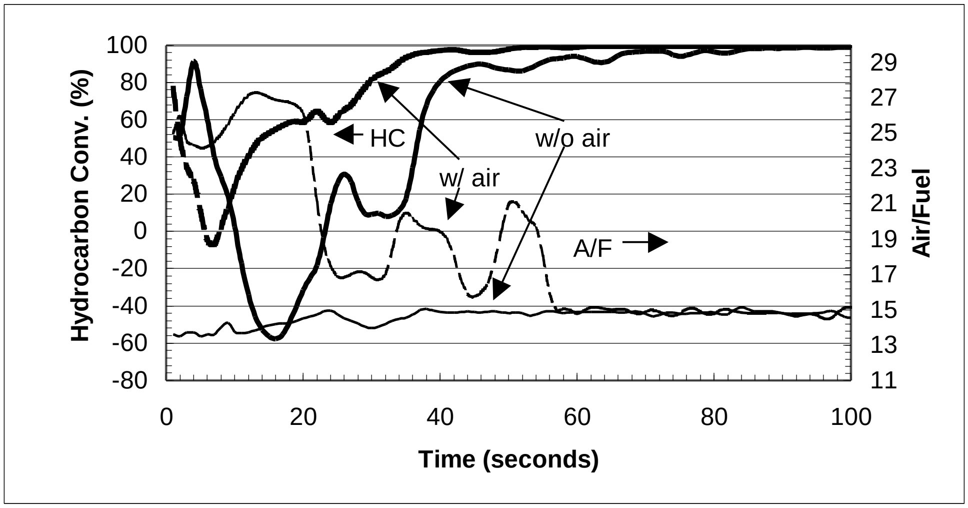


Figure 9. Air/Fuel ratio and hydrocarbon conversion for first 100 seconds of cold-transient phase of FTP with and without air addition

The effects of air addition on emission rates during the cold-transient phase of the FTP are summarized in Table 4. Total hydrocarbon (THC) and non-methane hydrocarbon (NMHC) emission rates are reduced by more than 50 % with air addition and CO emission rates by almost a factor of ten. Air addition does result in an increase in the cold-transient NOx emission rate, but the levels are still substantially below those required to meet the ULEV standards.

	Emission Rate during Cold-Transient Phase of FTP (gm/mi)			
	THC	NMHC	CO	NOx
Without Air	0.246	0.230	2.237	0.095
With Air	0.096	0.089	0.271	0.197

Table 4. Effects of air addition on cold-transient emission rates

4.3 Emission Results for Fresh/Stabilized Prototype Converters

FTP emission results for fresh/stabilized prototype converters are presented in Table 5. Each converter system was operated on the vehicle for approximately 10 hours prior to testing to establish a stabilized performance level. All tests were performed with air injection for the first 45 seconds of the FTP test. It should be noted that for the fresh/stabilized tests, oxygenate analyses were not performed and, therefore, THC and NMHC results are presented. It would be expected, and is shown with the aged catalyst results discussed in Section 4.4, that the NMOG emission rates do not differ substantially for the THC emission rates. The baseline monolith, Microlith™/monolith cascade, and close-coupled Microlith™ with underfloor monolith systems have emission levels well below the ULEV standards. The stand-alone close-coupled microlith™ meets the ULEV standard for THC and CO, but is approximately 50% above the NOx standard. Even though this converter meets the CO requirements, its emission levels for this pollutant are substantially higher than the other converters.

A detailed analysis was conducted comparing the performance of the stand-alone Microlith™ and the Microlith™/monolith cascade system to determine where the deficiencies in performance occur with the stand-alone Microlith™. Figure 9 presents THC, CO, and NOx conversion efficiencies for the stand-alone Microlith™ and the Microlith™/monolith cascade system during the cold-transient and cold-stabilized phases of the FTP. Both systems perform equally well in converting hydrocarbons, but the CO and NOx results show substantial differences in performance. Whereas the Microlith™/monolith cascade system has very little CO breakthrough during transients, the stand-alone Microlith™ shows substantial breakthrough under these conditions. Both systems show substantial NOx breakthrough under transient conditions, but again the breakthrough is much larger for the stand-alone Microlith™. The poorer CO performance of the stand-alone Microlith™ system indicates inadequate oxygen storage and release capability for this system. This will also adversely affect the NOx performance.

Table 5. FTP emission results for fresh/stabilized prototype catalytic converters

Catalyst	THC (gm/mi)				NMHC (gm/mi)				CO (gm/mi)			
	CT	CS	HT	Total	CT	CS	HT	Total	CT	CS	HT	Total
Monolith Baseline	0.096	0.008	0.002	0.024	0.089	0.004	0.001	0.021	0.271	0.044	0.013	0.082
Micolith/Monolith Cascade	0.076	0.016	0.001	0.024	0.066	0.009	0.000	0.019	0.271	0.070	0.014	0.096
Close-coupled Microlith + Underfloor Monolith	0.106	0.023	0.012	0.037	0.088	0.017	0.007	0.029	0.326	0.020	0.017	0.082
Close-coupled Microlith Stand-alone	0.089	0.018	0.024	0.034	0.071	0.007	0.014	0.022	1.400	0.357	0.515	0.616

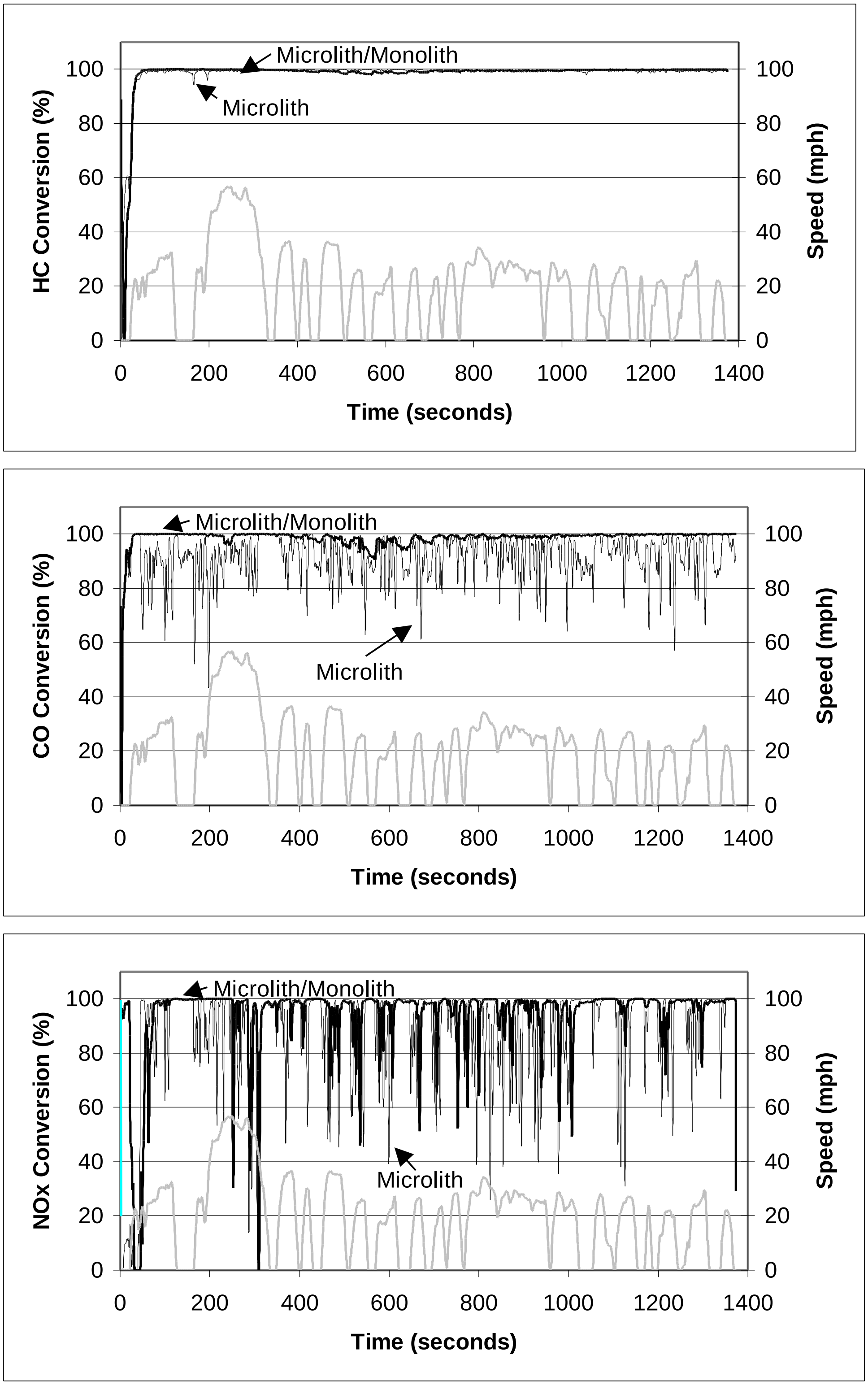


Figure 9. HC, CO, and NOx conversion efficiencies of Microlith™/monolith and stand-alone Microlith™ during the cold-transient and cold-stabilized phases of FTP

4.4 Emission Results for 50,000 Mile Aged Converters

Emission standards for low emission vehicles are set for 50,000 and 100,000 miles. Emission testing for this study was conducted after aging the prototype catalytic converters to 50,000 miles equivalent. 50,000 mile aging was chosen over 100,000 mile because it is felt that the 50,000 mile standards are more stringent than the 100,000 mile standards as summarized below:

- Ultra-low emission standards (ULEV)

	NMOG (gm/mi)	CO (gm/mi)	NOx (gm/mi)
50,000 miles	0.040	1.7	0.2
100,000 miles	0.055	2.1	0.3

Prototype catalysts were aged on the Rapid Aging Test A (RAT-A) developed by General Motors and described in detail in Section 3.3. This is a severe high temperature aging cycle with maximum catalyst temperatures reaching 927 ^{o}C.

Emission test results after 50,000 miles equivalent aging are summarized in Table 6. Each prototype converter system was tested three times. All tests were conducted with air addition for the first 45 seconds of the cold-transient phase. The results presented in Table 6 show the baseline monolith and the Microlith™/monolith cascade systems are at or below the 50,000 mile ULEV emission standard for NMOG, CO, and NOx. The close-coupled Microlith™ plus underfloor monolith NMOG emission rate is slightly higher than the ULEV standard (0.054 gm/mi vs. 0.040 gm/mi), but the CO and NOx emission rates are substantially lower than the ULEV standard. The stand-alone close-coupled Microlith™ has NMOG and CO emission rates which meet the low-emission vehicle (LEV) standard but a high NOx emission rate of 0.579 gm/mi.

The best overall emission performance is demonstrated by the Microlith™/monolith cascade system. This system has a slightly lower NMOG and a significantly lower NOx emission rate than the baseline monolith catalyst system. The baseline monolith does have the lowest CO emission rate, but both systems have CO emission rates less than 20% of the ULEV emission standard.

None of the prototype catalyst systems met our objective of demonstrating NMOG emission rates of 0.025 gm/mi or less. However, the Microlith™/monolith cascade system has a CO emission rate of 0.328 mg/mi and a NOx emission rate of 0.058 mg/mi. These emission rates represent larger than an 80% reduction in CO and a 70% reduction in NOx compared to the ULEV standard and substantially exceed the objectives for these pollutants. These results indicate that it may be possible to achieve the 0.025 gm/mi NMOG objective with optimization of engine calibration with a possible tradeoff of some NOx performance. Unfortunately, changes in engine calibration were beyond the scope of this project.

Table 6. FTP emission results for 50,000 mile aged prototype catalytic converters

Catalyst	Test	THC (gm/mi)				NMOG (gm/mi)				CO (gm/mi)		
	No.	CT	CS	HT	Total	CT	CS	HT	Total	CT	CS	HT
Monolith Baseline	1007	0.174	0.004	0.006	0.040	0.181	0.011	0.006	0.043	1.127	0.094	0.072
	1012	0.137	0.006	0.007	0.034	0.144	0.015	0.007	0.038	0.846	0.099	0.069
	2026	0.160	0.000	0.002	0.034	0.167	0.009	0.004	0.039	0.746	0.132	0.068
	Average	**0.157**	**0.003**	**0.005**	**0.036**	**0.164**	**0.012**	**0.006**	**0.040**	**0.906**	**0.108**	**0.070**
Micolith/Monolith Cascade	1014	0.154	0.004	0.004	0.035	0.153	0.007	0.004	0.036	1.140	0.129	0.090
	1019	0.145	0.007	0.006	0.035	0.140	0.010	0.007	0.035	0.933	0.135	0.103
	2031	0.191	0.000	0.002	0.040	0.189	0.004	0.004	0.042	1.402	0.103	0.082
	Average	**0.163**	**0.004**	**0.004**	**0.037**	**0.161**	**0.007**	**0.005**	**0.038**	**1.058**	**0.122**	**0.092**
Close-coupled Microlith + Underfloor Monolith	1042	0.223	0.004	0.017	0.053	0.215	0.007	0.015	0.051	1.527	0.159	0.442
	1048	0.186	0.000	0.012	0.042	0.181	0.006	0.011	0.043	1.126	0.120	0.130
	2049	0.293	0.000	0.013	0.064	0.282	0.006	0.011	0.064	2.968	0.059	0.107
	Average	**0.234**	**0.001**	**0.014**	**0.053**	**0.226**	**0.006**	**0.012**	**0.054**	**1.874**	**0.113**	**0.226**
Close-coupled Microlith Stand-alone	1032	0.228	0.052	0.073	0.094	0.201	0.028	0.054	0.070	3.886	2.860	2.478
	1038	0.194	0.050	0.073	0.076	0.167	0.027	0.054	0.062	3.475	2.669	2.959
	2040	0.196	0.037	0.077	0.081	0.168	0.013	0.058	0.057	4.090	2.186	2.412
	Average	**0.206**	**0.046**	**0.074**	**0.084**	**0.179**	**0.023**	**0.055**	**0.063**	**3.981**	**2.572**	**2.616**

As discussed above, the NMOG emission rate of the close-coupled Microlith™ plus underfloor monolith is above the ULEV emission standard, but the CO and NOx emission rates are less than 40% of the ULEV standards. These results again indicate that optimization of engine calibration could possibly be utilized to lower the NMOG emission rate with a tradeoff of NOx performance. Further work in this area would be warranted as this system offers substantial advantages in vehicle packaging due to the small size of the close-coupled Microlith™ converter (see Figures 2&3). As discussed in Section 4.3, the lower performance of the close-coupled stand-alone Microlith™ appears to result from a lack of sufficient oxygen storage component. It is recommended that additional work be done on this formulation to improve the oxygen storage and release performance.

An interesting observation is made in comparing the emission results from the fresh/stabilized catalysts presented in Table 5 with those of the 50,000 mile aged catalysts in Table 6. As would be expected, the hydrocarbon and CO emission rates increase for all catalysts in going from the fresh/stabilized to the aged condition. Interestingly, the NOx emission rates show mixed behavior. The NOx emission rates for the baseline monolith and the Microlith™/monolith cascade systems actually decrease with aging, while the close-coupled Microlith™ plus underfloor monolith stays approximately the same and the close-coupled stand-alone Microlith™ increases with aging. One possible explanation for the higher NOx emission rates in the fresh/stabilized condition for the baseline monolith and the Microlith™/monolith cascade systems is their very high activity for CO oxidation. CO is the major reductant for NOx conversion. It has been shown previously[14] that catalysts with very high CO oxidation activity have poorer NOx reduction activity. Under these conditions, NOx conversion is limited because the CO reacts with oxygen much faster than it reacts with NOx. The improvement in NOx performance with catalyst aging may result from thermal deactivation of sites for CO oxidation. This will effectively increase the concentration of CO available for NOx reduction and result in higher NOx conversion efficiency.

5.0 EMISSIONS REDUCTION BENEFITS

The emission reduction target for this project was to achieve emission levels after 50,000 miles aging of 0.025 gm/mi NMOG, 1.00 gm/mi CO, and 0.12 gm/mi NOx, approximately 40% below the ULEV standards. The best prototype catalyst system, the Microlith™/monolith cascade system, gave 50,000 mile emissions of 0.038 gm/mi NMOG, 0.328 gm/mi CO, and 0.058 gm/mi NOx. Although the actual results fall below our targets for NMOG reduction, we have greatly exceeded the reduction targets for CO and NOx emissions. The 50,000 mile CO emission rate represents greater than an 80% reduction and the NOx emission rate greater than a 70% reduction compared to the ULEV standards.

Calculations have been performed to determine the emissions reduction benefits for the SCAQMD that would result from the introduction of this technology. The following assumptions were made in these calculations:

- Vehicle populations and average miles traveled in the SCAQMD were obtained from the California Air Resources Boards EMFAC7G emissions inventory model.
- The advanced Microlith™/monolith cascade technology is introduced starting with the 2000 model year for automobiles.
- The advanced Microlith™/monolith cascade technology is introduced at a rate equivalent to the rate of introduction of ULEV automobiles. These rates are 2% of new cars sold in the year 2000, 5% in the year 2001, 10% in the year 2002, and 15% in the year 2003 and later years.
- The emissions benefits are the difference between the 50,000 mile ULEV standards and those demonstrated in this project.
- Emission rates for the advanced catalyst technology system as a function of mileage were calculated by a linear extrapolation between the fresh/stabilized results (Table 5) and the 50,000 mile aged results (Table 6).
- Emissions benefits were only calculated for the first 50,000 miles of vehicle operation since testing was not performed at higher mileage.

Based upon these assumptions, Table 7 presents a summary of the emissions reduction benefits associated with introduction of the advanced Microlith™/monolith cascade catalyst system.

Table 7. Emissions reduction benefits in the SCAQMD associated with introduction of advanced Microlith™/monolith cascade catalyst system starting with the 2000 model year.

Year	**Emission Reductions (tons/year)**		
	NMOG	**CO**	**NOx**
2000	2.3	193	13
2001	7.3	659	47
2002	16	1568	114
2003	28	2884	218
2004	35	3954	311
2005	38	4731	384
2006+	39	5102	421

The emission reduction benefits are fairly modest in the first few years due to the limited number of vehicles introduced. After seven years (year 2006), the reduction benefits reach a maximum and continue at this rate for the following years.

The estimated emission reduction benefits presented in Table 7 are conservative. The assumptions used to calculate these benefits included the replacement of vehicles scheduled to meet the ULEV standards with vehicles fitted with the advanced catalyst technology. The percent of vehicles scheduled to meet the ULEV standard is small (2% in the year 2000 and increasing to a maximum of 15 % in 2003 and subsequent model years). Much larger emissions reduction benefits could be realized by demonstrating that this advanced catalyst technology would allow certification of presently schedule LEV vehicles to a ULEV or lower standard. At present, 75% of new cars sold in 2003 and later years are scheduled to be at the LEV standard. Future work should be directed at this target.

7.0 SUMMARY AND CONCLUSIONS

The College of Engineering-Center for Environmental Research and Technology at the University of California, Riverside has conducted a development project to demonstration automotive emission rates with a conventional gasoline vehicle that are substantially below the ULEV emission standards. The objective was to demonstrate emission rates of 0.025 gm/mi for NMOG, 1.0 gm/mi CO, and 0.12 g/mi NOx. These emission rates are approximately 40% below the ULEV standards.

The technical approach involved the preparation of three prototype catalytic converters by Precision Combustion Inc. based upon their Microlith™ technology. The Microlith™ technology uses a series of high cell density, short path length, and low thermal mass metal monoliths that provide high catalytic conversion efficiency while minimizing boundary layer build-up observed in conventional automotive monolithic substrate catalysts. The Microlith™ technology has higher mass and heat transfer rates than conventional monolith catalyst technology with resultant faster catalyst light-off times and higher conversions. The catalyst coating on the Microlith™ maintains a high open area even with cell densities as high as 388 cells per square cm (conventional automotive monoliths have cell densities of 62-93 cells per square cm) and provides an adherent high activity coating resistant to loss of activity by sintering. The three prototype converter systems were a Microlith™/monolith cascade system with both catalysts mounted in the same converter can in a close-coupled configuration, a close-coupled Microlith™ followed by an underfloor monolith, and a stand-alone close-coupled Microlith™ catalytic converter. A standard monolithic converter was included in the test matrix as a baseline.

The catalytic converters were tested in a fresh stabilized condition and after 50,000 miles equivalent engine aging. The 50,000 miles equivalent aging was done using a high temperature (maximum catalyst temperature of 927 ^{o}C) accelerated aging cycle. Emission testing was performed on a 1997 Ford Escort. This vehicle is fitted with a 2.0 liter four cylinder engine with sequential fuel injection and provision for a close-coupled catalyst location approximately 4 inches from the exhaust manifold flange. This vehicle was certified to LEV emission levels. Baseline testing in its original equipment configuration confirmed the LEV emission rate and demonstrated that air addition would be necessary to achieve the fast cold-start catalyst light-off times required for ULEV emission levels. The vehicle was fitted with an electronic air pump and an air injection manifold. Optimization testing demonstrated that the best cold-start emission performance was obtained with air injection for the first 45 seconds of cold-start.

Based upon emission testing of the prototype catalytic converters, the following conclusions are drawn:

- Air addition during the first 45 seconds of cold-start is necessary to achieve the catalyst light-off times required to meet ULEV emission rates.

- In the fresh/stabilized state, three prototype converter systems demonstrated emission rates significantly below ULEV levels. These converter systems were the baseline monolith system, the Microlith™/monolith cascade system, and the close-coupled Microlith™ followed by an underfloor monolith system.

- In the fresh/stabilized condition, the stand-alone close-coupled Microlith™ catalytic converter had hydrocarbon and CO emission rates below the ULEV standard, but the NOx emission rate was above the ULEV standard. The performance of this converter system appears to be poorer than the other systems due to lower oxygen storage and release capability.

- After 50,000 miles equivalent aging, two converter systems demonstrated emission rates at or below the ULEV standards. These were the baseline monolith system and the Microlith™/monolith cascade system.

- The best overall performance was provided by the Microlith™/monolith cascade system with emission rates of 0.038 gm/mi NMOG, 0.328 gm/mi CO, and 0.058 gm/mi NOx. The NMOG emission rate did not meet our target of a 40% reduction from the ULEV standard. The CO and NOx emission rates exceeded our targeted reduction with greater than 80% and 70% reductions from the ULEV standards, respectively.

- Based upon assumptions that the advanced Microlith™/monolith cascade converter system would be introduced starting with the 2000 model year on vehicles that are presently scheduled to meet ULEV emission standards, maximum emissions reduction potentials for the SCAQMD are calculated to be 39 tons/year for NMOG, 5102 tons/year for CO, and 421 tons/year for NOx in 2006 and later years.

8.0 RECOMMENDATIONS FOR FUTURE WORK

The best emission performance was obtained with the Microlith™/monolith cascade converter system. The NMOG emission reductions fell short of our targeted 40% reduction from the ULEV standard, but the CO and NOx reductions greatly exceeded our targets. It is felt that the very low NOx emission results obtained with this converter system indicate the possibility of lowering the NMOG emission rate by changes in vehicle calibration. Generally, one can tradeoff NOx reduction performance with hydrocarbon and CO oxidation performance by changes in air/fuel calibration. In the present study, the only vehicle modifications were the addition of an air pump. It is recommended that future studies look at changes in vehicle calibration to achieve the 40% reduction in NMOG while still maintained the targeted reductions in CO and NOx.

It is also recommended that the effects of vehicle calibration on the performance of the close-coupled Microlith™ followed by an underfloor monolith system be explored. This system had a NMOG emission rate above the ULEV standard at 0.053 gm/mi, but the CO and NOx emission rates were well below the standard at 0.508 gm/mi and 0.071 gm/ mi, respectively. This system has significant advantages in packaging in the engine compartment due to the small size of the close-coupled Microlith™. Further development and demonstration that this system can achieve ULEV or lower emission standards is recommended. The use of this system with engine/vehicle families that do not have enough space to fit a standard monolith in a close-coupled configuration could significantly increase the percent of vehicles certified to ULEV standards.

The emissions reduction benefits of this project are based upon demonstrating emission rates significantly below the ULEV standards. Additional, and potentially larger, emissions reduction benefits could be achieved by demonstrating that a larger fraction of the automobile fleet could be converted from the LEV category to the ULEV category and that light-duty trucks (including sport utility vehicles) can be certified to the automobile LEV and ULEV standards. It is recommended that future development work be conduced to demonstrate that light-duty trucks can be certified to the automobile LEV and ULEV standards using the Microlith™ advanced catalyst technology.

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