CONTROL OF BENZENE EMISSIONS FROM LIGHT-DUTY MOTOR VEHICLES

By

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FINAL REPORT

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FOREWORD

This project was conducted for the State of California Air Resources Board (ARB) by the Department of Emissions Research, Southwest Research Institute (SwRI). The report is submitted in fulfillment of ARB Contract Number A6-204-32, "Control of Benzene Emissions from Light-Duty Motor Vehicles" by Southwest Research Institute, 6220 Culebra Road, San Antonio, Texas. The program was initiated July 18, 1987, and completed September 30, 1990. It was identified within Southwest Research Institute as Project 08-1815. The ARB Contract Manager for the program was initially Joseph Pantalone and finally Mr. Manjit Ahuja of the Research Division, Sacramento, California. The ARB Project Technical Monitor was initially Mr. Jack Kitowski and finally Mr. Juan Osborn, both of the Mobile Source Division, El Monte, California. SwRI Project Manager was Dr. Lawrence R. Smith. The SwRI principal researcher was Martin J. Heimrich.

Several manufacturers were contacted and asked to supply prototype emission control technologies for study in this program. Corning Incorporated responded with a cordierite substrate coated with a zeolite molecular sieve for cold-start hydrocarbon collection. Allied Signal Automotive Catalyst Company submitted a prototype catalyst formulation that attempted to inhibit the formation of benzene. Nippon Shokubai Company provided SwRI with a high temperature warm-up catalyst for use in a close-coupled (to the exhaust manifold) position. Union Carbide Corporation donated a molecular sieve for use as an evaporative emission adsorption material. Finally, the electrically-heated catalysts used in this program were submitted by Camet Company. SwRI and ARB recognize and appreciate the support that these companies gave to this study.

ABSTRACT

Several strategies to reduce the total amount of exhaust and evaporative benzene emissions from light-duty gasoline-fueled vehicles have been investigated. A literature search was performed to determine automotive benzene emission levels and technologies for benzene emission control. Laboratory vehicle emission tests were performed to demonstrate benzene control technologies. Exhaust benzene emission control was addressed by reducing total hydrocarbon emissions (including benzene), and focused on developing strategies for specifically controlling the high level of cold-start emissions. Catalyst formulations were investigated for improved benzene conversion efficiencies. High temperature catalysts were close-coupled to the exhaust manifold to promote quicker catalyst light-off. Zeolite molecular sieves were evaluated for evaporative emission control and the results were compared to those using conventional coal- and wood-based activated carbon.

A cold-start hydrocarbon collection system was developed for this program. Hydrocarbon emissions were collected by a zeolite molecular sieve element for subsequent release to an active catalyst. Preliminary Federal Test Procedure (FTP) emission tests demonstrated a reduction in cold-start hydrocarbon emissions.

Electrically-heated catalyst systems with cold-start air injection were optimized for this program. FTP emission tests demonstrated that vehicles equipped with unaged electrically-heated catalyst systems are potentially capable of meeting the California Ultra-Low Emission Vehicle (ULEV) emission standards. Exhaust hydrocarbon speciation was performed on two vehicles, a 1990 Buick LeSabre and a 1990 Toyota Celica, equipped with optimized electrically-heated catalyst systems.

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SUMMARY

Benzene has been identified as a toxic air contaminant by the State of California Air Resources Board (ARB) and the U.S. Environmental Protection Agency (EPA). The ARB has proposed a number of methods for the reduction of benzene from mobile sources, including fuel modifications, tightening of total hydrocarbon emission standards, and developing of technology for selective reduction of benzene. This study has attempted to identify information which may be useful in developing emission control technologies.

The primary objective of this project was to determine how benzene and total organic gas emissions from gasoline-powered light-duty vehicles can be reduced through the development of a total emission control system optimized for reducing such emissions, without sacrificing control of other pollutants. The main focus of the program was control of exhaust hydrocarbon emissions, but evaporative emission control was also investigated. In this program prototype benzene control systems were investigated and then installed on two vehicles for short-term evaluations at Southwest Research Institute (SwRI) and extended evaluations by the ARB.

At the start of this investigation, a literature search identified information on benzene emissions and their control. Both exhaust and evaporative emission references were investigated.

Exhaust benzene emissions were reported by several researchers to be related to the levels of benzene and other aromatics in the fuel. Benzene emissions from automotive engine exhaust tended to increase with benzene content in the fuel. High level aromatics (such as toluene, ethyl benzene, o-xylene, etc.) had an average effect on exhaust emissions of about 8 percent of that of benzene. Research suggested that exhaust benzene emissions were expected to decrease with total hydrocarbon exhaust emissions.

Evaporative benzene emissions were reported to be directly related to benzene levels in the fuel. Literature reviews revealed few evaporative control technologies specific to benzene. Contacts with emission control manufacturers led to an investigation of an alternative evaporative emission adsorbent. Experimentation with a molecular sieve was performed, but without improvement over activated carbon which is currently used in evaporative emission control canisters. Manufacturers of activated carbon generally felt that current technology is sufficient to control benzene emissions. Literature suggesting alternate control technologies was limited.

Cold-start emissions were identified to be the major contributor to exhaust benzene and total hydrocarbon emissions. For modern vehicles equipped with catalytic converters, emissions following the cold-start typically account for 70 to 80 percent of the total hydrocarbon emissions. A cold-start is defined by the Code of Federal Regulations (CFR) as an engine start following a 12- to 36-hour continuous vehicle soak in a constant temperature environment of 20°C to 30°C (68°F to 86°F). Vehicle hydrocarbon emissions (including benzene) are excessively high following the cold start because the catalyst is not active and the engine requires a rich fuel-air ratio to maintain cold driveability. The exhaust emission control strategies studied in this program were, therefore, either designed to control cold-start hydrocarbon emissions or to specifically lower benzene emission levels.

Exhaust emission control systems were adapted to a demonstration vehicle. Control technologies investigated include a system to collect and subsequently oxidize cold-start hydrocarbon emissions, a high-temperature catalyst close-coupled to the exhaust manifold, a close-coupled catalyst used in conjunction with an underbody catalyst, and an experimental underbody catalyst designed to reduce benzene formed by dealkylation of higher aromatics (within the catalyst). An electrically-heated catalyst, which is heated prior to engine starting, was successfully demonstrated late in the investigative portion of the program.

The cold-start hydrocarbon collection system was developed as part of this program. Its function was to collect the initial hydrocarbon emissions and store them until they could be released to an active catalyst. The prototype collection element was produced by a commercial firm. The hydrocarbon collection system and strategy used in this program were developed by SwRI. Demonstration hardware was designed and tested for collection with encouraging results. Development of this control strategy under ARB project funds was discontinued because of cost considerations.

A high-temperature close-coupled catalyst was obtained from a catalyst company for evaluation in this study. A close-coupled catalyst would tend to heat up quickly, and therefore be able to control cold-start emissions sooner. The close-coupled catalyst configuration evaluated in this program performed best as a warm-up catalyst in conjunction with an underbody converter. This warm-up plus underbody converter was initially recommended for benzene emission control prior to the SwRI evaluation of the electrically-heated catalyst.

The experimental low benzene forming catalyst was obtained from a catalyst company for evaluation in this program. This catalyst was formulated with an element selected to poison the formation reaction of benzene within the catalyst. When placed in an underbody location (as was done in this program), the experimental catalyst is not specifically a cold-start control strategy. This catalyst was evaluated because of its potential for limiting the formation of benzene from the dealkylation of higher aromatics in the exhaust.

Each of these experimental benzene emission control strategies was evaluated with limited success. At this time, a commercial prototype of an electrically-heated catalyst became available for this program. The electrically-heated catalyst was a metal foil supported catalyst that was heated electrically prior to engine starting. Cold-start benzene emissions could be controlled by a potentially active catalyst. This catalyst required an elaborate electrical heating controller, which was developed by the catalyst manufacturer. Initial evaluation of the electrically-heated catalyst suggested air injection would be required for the system to substantially lower benzene and total hydrocarbon emissions.

SwRI initiated an internal study to determine the feasibility of cold-start air injection, and if feasible, develop a strategy for demonstration. This SwRI study resulted in an effective air injection control strategy for the preheated catalyst. The remainder of the ARB benzene control technology study was redirected toward further development and demonstration of the electrically-heated catalyst.

Two current-technology production vehicles, a 1990 Buick LeSabre and a 1990 Toyota Celica, had electrically-heated catalyst systems installed. The Buick LeSabre was evaluated with the heated catalyst placed directly in front of the main production catalytic converter while the Toyota Celica was evaluated with the electrically-heated catalyst placed between the main close-coupled catalytic converter and a smaller downstream production catalytic converter. Laboratory studies involved examination of heating strategies to minimize electrical energy requirements, a variety of off-board battery and recharging configurations to determine their effect on emissions, and multiple air injection strategies to achieve minimum hydrocarbon emissions. The vehicle conversions exhibited FTP emissions which show promise of meeting the California Ultra-Low Emission Vehicle (ULEV) standards, and have contributed to adoption of low emission standards by the ARB.

I. INTRODUCTION

The primary objective of this project was to determine how benzene and total organic gas emissions from gasoline-powered light-duty vehicles could be reduced, through the development of a total emission control system optimized for reducing such emissions, without sacrificing control of other pollutants. The main focus of the program was control of exhaust hydrocarbon emissions, but evaporative emission controls were also investigated. A number of prototype benzene control systems were investigated. The program concluded with the selection of a control system and the installation of the system on two vehicles for short-term evaluations at Southwest Research Institute (SwRI) and extended evaluations by the State of California Air Resources Board (ARB).

Initial program activities included a literature search and contact with emission control product manufacturers. During the literature search, several possible exhaust benzene control technologies were identified. Strategies identified and subsequently investigated in the laboratory included a system to first collect and then oxidize cold-start hydrocarbons, a high-temperature catalyst close-coupled to the exhaust manifold for quick light-off, and an experimental underbody catalyst intended to reduce the formation of benzene from the dealkylation of higher exhaust aromatics. A dual-bed catalyst system with air injection between the pieces was identified as a possible control system, but was not evaluated due to potential increases in oxides of nitrogen emissions. During the later stages of the program, an additional control strategy, a catalyst that was heated electrically prior to engine starting, was identified and evaluated.

A review of the literature and discussions with evaporative emission control product manufacturers led to the identification and evaluation of two potential evaporative emission control strategies. These strategies included an alternative material for hydrocarbon adsorption and an alternative canister design. A discussion comparing wood- and coal-based activated carbons currently used in evaporative emission canisters has also been included in this study.

Following preliminary investigations of the benzene exhaust emission control strategies, two current-technology vehicles were fully equipped with electrically-heated catalyst systems. A superior evaporative emission control technology was not identified, therefore; no evaporative emission control system modifications were made. Electrically-heated catalysts provided significant improvements in cold-start benzene and total hydrocarbon exhaust emission control. The vehicles equipped with these catalysts demonstrated potential for meeting future California Ultra-Low Emission Vehicle (ULEV) emission standards and have contributed to the adoption of future regulations by the State of California.

II. LITERATURE SEARCH SUMMARY AND EMISSION CONTROL INDUSTRY COMMENTS

Benzene has been identified as a toxic air contaminant by the Environmental Protection Agency (EPA) and the California Air Resources Board. Light-duty gasoline trucks and passenger cars account for 54 percent of all benzene emitted in the State of California.(1)* This value is even higher, 93 percent, if all on-road vehicles, off-road vehicles, trains, ships, aircraft, mobile equipment, and utility equipment sources are included in the estimate.(2,3) Benzene emissions from mobile sources can be grouped into four areas: (1) vapor loss during refueling, (2) diurnal and hot soak evaporative losses, (3) evaporative losses during vehicle operation (running losses), and (4) exhaust emissions. Exhaust emissions have been estimated to account for 70 percent of the mobile source emissions, while refueling and evaporative losses account for 10 and 20 percent, respectively.(4) Running loss emissions were not accounted for at the time of this estimate. In Europe, exhaust benzene emissions were found to account for as much as 81 to 89 percent of total benzene emissions. In this case, refueling benzene losses were small, approximately 1 to 2 percent. Evaporative losses accounted for 10 to 18 percent of the total.(5) Estimations of relative benzene contributions vary, but all identify exhaust sources as the major component.

The Air Resources Board has proposed a number of methods for the reduction of benzene from mobile sources, including fuel modifications, tightening of total hydrocarbon emission standards, and development of technology for selective reduction of benzene. The literature search attempted to identify information which could be useful in developing benzene-selective emission control technology. While considerable information was found on benzene emissions from mobile sources, only limited information was available for selective benzene control.

This review has been divided into two segments: (1) Benzene Exhaust Emission Control, and (2) Benzene Evaporative Emission Control. The control of benzene during refueling was beyond the scope of this review and not addressed. Control of benzene losses during refueling has been addressed by both EPA and the ARB. EPA has proposed on-board vehicle vapor recovery systems to eliminate total hydrocarbon vapor losses (including benzene) during refueling, while the ARB has proposed Phase II recovery systems at all California refueling stations in order to increase control of benzene emissions. These control systems are expected to significantly reduce refueling benzene losses.

Contacts with companies manufacturing vehicle catalysts and a review of the literature were conducted in order to obtain existing information for benzene exhaust emission control. Information provided by the ARB, SwRI reports, and papers identified during a computer-assisted literature search were reviewed.

The computerized literature search was performed using two information services, namely those of DIALOG Information Services, Inc., and Systems Development Corporation's ORBIT. Databases searched within the DIALOG system were NTIS, CA SEARCH, COMPENDEX®, Ei ENGINEERING MEETINGS®, and DOE ENERGY. The SAE Global Mobility Database was accessed through the ORBIT information system.

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*Numbers in parentheses designate references at the end of this report.

A. Benzene Exhaust Emission Control

A number of companies were contacted to determine if they had existing technology for selective control of benzene in vehicle exhaust emissions. Individuals contacted, along with their respective companies, are listed in Table 1. For the most part, these companies had little or no information regarding selective benzene control and generally indicated that benzene would be reduced in conjunction with any reductions in total hydrocarbons. These reductions would be accomplished by modifications of conventional catalysts, i.e., increased loadings, etc. All indicated a need for specific vehicle- or engine-out emissions data before recommending any catalyst changes. In all, four companies indicated that they have technology which may assist in the reduction of benzene exhaust emissions (as well as total hydrocarbon emissions). These companies were Allied Signal, Corning Incorporated, Nippon Shokubai, and Camet (at a later time in the program).

TABLE 1. EXHAUST AFTERTREATMENT TECHNOLOGY CONTACTS

Name	Company	Comments
Dr. Jerry Summers Dr. Mike Henk	Allied Signal	Supplied candidate catalysts
Mr. Louis Socha	Corning Incorporated	Supplied prototype cold-start device
Mr. Yoshiyuki Nakanishi Mr. Koichi Saito	Nippon Shokubai	Supplied high temperature warm-up catalyst
Mr. William Whittenberger	Camet Co.	Supplied electrically-heated catalysts (EHCs)
Dr. Joseph Kubsh	W.R. Grace & Co.	Supplied EHC with Camet
Mr. Charles Penquite	Engelhard Corp.	No additional information
Mr. Thomas Kreuzer	Degussa Corporation	No additional information
Mr. Kent Wiberg	EKA Nobel	No additional information
Mr. Koichi Matsuo	Mitsui Mining & Smelting	No additional information
Mr. John Howitt	Selee Corporation	No additional information
Mr. R. Glen Reid	Johnson Matthey	No additional information

Mr. Yoshiyuki Nakanishi and Mr. Koichi Saito of Nippon Shokubai supplied a high-temperature catalyst that was placed near the exhaust manifold. This configuration took advantage of the higher exhaust temperatures near the engine to oxidize hydrocarbon and other emissions. Results of the SwRI testing are given in Section III of this report.

Allied Signal has been working with European automotive companies on benzene emission concerns and has indicated a strong interest in developing an improved catalyst formulation for benzene control. They have offered their expertise in this area, and provided

SwRI with a catalyst formulation that attempts to poison the dealkylation of exhaust aromatics. During rich operation, some catalyst formulations have been found to increase benzene emissions by dealkylation of other aromatics in the exhaust. The results of the feasibility experiments on this experimental low-benzene catalyst are given later in this report.

A promising technology was offered by Corning Incorporated. Corning has been developing an adsorption element that would be placed in the exhaust stream to collect cold-start hydrocarbon emissions, including benzene. The adsorption element would store and eventually release the collected hydrocarbons to a fully active catalytic converter. Development will be required to optimize the temperatures at which hydrocarbons are adsorbed by and desorbed from the cold-start device, as well as the hydrocarbon collection capacity. A summary of the development work done by SwRI on the cold-start hydrocarbon collection system is included, along with results of the feasibility testing, in Section III.

Camet Company supplied electrically-heated catalysts for this study late in the program. At the time of the initial feasibility study and contacts with manufacturers, the heated catalyst was not available. It was not until after other control technologies were evaluated that the electrically-heated catalyst was tested in this program. More information concerning the application of electrically-heated catalysts in this program begins in Section VI.

The necessity for reduced cold-start emissions is evident after recognizing that cold-start hydrocarbon emissions account for a majority of the FTP 3-bag hydrocarbon emissions. Studies at SwRI for the U.S. EPA(6,7,8) and at NIPER for the Coordinating Research Council(2) have shown that for a number of vehicles, the cold-start transient portion (Bag 1) of the FTP test is the major contributor to the FTP benzene emission rate. The higher relative concentration of hydrocarbons in the first bag is due to the time required for the catalyst to "light-off" following a cold start. The catalyst remains essentially inactive for one to two minutes after a cold start. Most of the FTP hydrocarbons, therefore, originate from the initial portion of the first segment of the FTP. Examples can be found in the baseline tests in Section III.

Exhaust benzene emissions have been reported by researchers to be related to the benzene and total aromatic content of the fuel. Benzene itself has the greatest effect on benzene exhaust emissions on the basis of equal volume percent in fuel.(9) Benzene exhaust emissions tend to increase with increases in benzene fuel content, but fuel benzene content is not the only source of increased exhaust benzene emissions. In one study, tests showed that all fuel aromatic species studied (benzene, toluene, ethylbenzene, o-xylene, and heavy reformates that contain nine or more carbon atoms) caused benzene exhaust emissions in five modern production vehicles. The non-benzene aromatic compounds had an average effect of about 8 percent of that of benzene.(9)

Increases in the total aromatic content of gasoline also increased the amount of benzene emitted in the exhaust.(10,11,12,13) Benzene appears to be produced from the dealkylation of higher aromatics. Data compiled from several studies to determine automobile benzene emissions suggest that benzene reductions are roughly proportional to total hydrocarbon emission reductions.(13) In a study using five 1985 and 1986 model vehicles, the reduction in benzene emissions across the catalyst ranged from about 70 to 90 percent.(9) At the lower HC emission rates, benzene emissions can be more difficult to control catalytically than total exhaust hydrocarbons because benzene is generally less reactive.

U.S. gasoline can contain from nearly zero to 4 volume percent benzene.(4) The average was reported, in the mid 1980s, to be in the range of 1.2 volume percent to 1.33 volume percent.(4,13) Currently, the ARB has data showing the average California fuel benzene levels to be approximately 2 percent by volume.(14) Aromatic levels in gasoline were found to range from 28 weight percent to 44 weight percent in Southern California.(15) As a note, several western European countries have adopted a 5 volume percent benzene limit on gasoline.

Benzene and other aromatics are a source of high octane components for gasoline.(11) Unleaded premium gasolines typically have a higher aromatic level than unleaded regular gasolines. Leaded gasolines typically have a lower aromatic level than unleaded gasoline, because more of the octane requirement is provided by the lead.

In one study, researchers demonstrated that benzene exhaust emission rates increased by 0.75 weight percent of the total hydrocarbons for an increase of one volume percent of benzene in the fuel.(4) In addition, increasing the aromatic content of the test fuel from 25 volume percent to 40 volume percent increased the benzene emission by 1.3 weight percent of the total hydrocarbon. Of the five cars used in this study, the three-way catalyst plus oxidation systems tended to reduce tailpipe benzene emissions slightly better than three-way systems alone. The dual bed configuration was also recognized as a more efficient strategy for benzene control in a study by Lyons.(1)

B. Benzene Evaporative Emission Control

Commercial manufacturers and material suppliers were contacted regarding evaporative benzene emission control technology. Individuals contacted and their respective companies are listed in Table 2. None of the companies had developed technology that was specific to benzene evaporative applications. Mr. Joseph Ausikaitis and Mr. Steve Dunne of Union Carbide Corporation suggested a novel material for evaporative hydrocarbon emission collection, however. This material is a molecular sieve and was a possible replacement for activated carbon. SwRI received a sample of the material from Union

TABLE 2. EVAPORATIVE EMISSION CONTROL TECHNOLOGY CONTACTS

Name	Company	Comments
Mr. Joseph Ausikaitis Mr. Steve Dunne	Union Carbide Corporation	Supplied molecular sieve material
Mr. Hal Moore Mr. John Urbanic	Calgon Carbon Corporation	Supplied carbon technology
Mr. Bruce Bragg	Westvaco Corporation	No additional information
Mr. Frank Schwartz	North American Carbon	No additional information

Carbide, and it was tested to determine its working capacity as compared to that of activated carbon. The results of these evaluations are presented in Section IV of this report.

Manufacturers of activated carbon generally felt that the current technology is sufficient to control benzene emissions. Mr. John Urbanic of Calgon Carbon Corporation has supplied SwRI with technical data concerning activated carbon and benzene adsorption. Mr. Frank Schwartz of North American Carbon questioned if any improvements were possible or necessary.

Limited literature data were available on benzene evaporative emissions. In several studies on benzene emissions from passenger cars, evaporative benzene emissions were found to be directly related to the benzene level in the gasoline.(4,5,13) Evaporative benzene emissions accounted for 10 to 18 percent of the total benzene emissions.(5) In a study of five European vehicles with a variety of emission control and fuel systems, the evaporative portion of benzene emissions was estimated at 20 percent for a gasoline benzene level of 1.5 volume percent.(4) It should be noted that these European vehicles were not equipped with evaporative emission canisters and are not expected to represent current U.S. evaporative emission data.

A study of 45 vehicles (model years ranging from 1975 to 1982) indicates that benzene and hydrocarbon evaporative emission rates have decreased with improved control technology.(13) In a study of four domestic vehicles, benzene made up 0.5 percent to 2.2 percent of the total evaporative hydrocarbons when tested with gasoline benzene levels ranging from 1.5 to 1.9 weight percent. Benzene emissions were 3.5 to 7.1 percent of evaporative hydrocarbons from gasoline containing benzene levels of 5.8 to 7.1 weight percent.(13)

III. EXHAUST EMISSION CONTROL TECHNOLOGIES INVESTIGATED

Several exhaust emission control technologies were investigated during this task of the program. Experimental catalysts and novel materials for emission control systems were donated by several manufacturers. Some manufacturers even initiated their own in-house investigations. The technologies studied for benzene emission control included dual-bed catalysts, cold-start hydrocarbon collection, experimental low-benzene catalyst formulations, and high-temperature warm-up catalysts. System design considerations were explored prior to the build-up and demonstration of the cold-start hydrocarbon collection system. Tests were run to evaluate the effectiveness of the experimental low-benzene emitting catalyst. In addition, a demonstration vehicle was equipped with a high temperature warm-up catalyst to determine the emissions benefit of the close-coupled catalytic converter. After these evaluations, performance and cost comparisons were made. Other control strategies, including preheated catalysts, were reviewed.

A. Demonstration Vehicle and Test Fuel

A vehicle was borrowed from an SwRI commercial client (with permission) for the demonstration of the selected control technologies. This demonstration vehicle was a 1986 Honda Accord LXi equipped with a four-cylinder engine (119 CID), an electronic port fuel injection system, and a three-way catalyst. A description of the vehicle is presented in Table 3.

TABLE 3. DEMONSTRATION VEHICLE DESCRIPTION

Item	1986 Honda Accord LXi
Body Style	3-Door Hatchback
Odometer	23334 Miles
Transmission	Manual
No. of Gears	5
VIN	JHMBA5342GC043618
Texas License No.	535-LNG
Tires	P185/70R13
Inertia Weight	2875 lbs
Accessories	Air Conditioning Power Steering Power Brakes
Engine Family	GHN2.0V5FNF3
Engine Displacement	119CID
No. of Cylinders	4
Fuel System	Electronic Port Fuel Injection
Ignition System	Electronic Ignition
Emission Control	Three-Way Catalyst
Evaporative Family	86FG

The fuel used for the demonstration testing was an emissions grade test fuel, coded EM-780-F. The hydrocarbon composition of the test fuel is given in Table 4. Fuel benzene concentration by volume was 0.8 percent; toluene was 15.3 percent. A copy of the fuel analysis record sheet can be found in Appendix A.

TABLE 4. HYDROCARBON COMPOSITION OF GASOLINE EMISSIONS TEST FUEL

Hydrocarbon Composition	
Olefins, %	1.0
Aromatics, %	31.1
Saturates, %	67.9

B. Dual-Bed Catalysts for Benzene Control

Several sources found in the literature, along with commercial contacts in the emission control industry, indicated that a vehicle equipped with a three-way plus oxidation catalyst (dual-bed catalyst) tended to have lower benzene emissions than a vehicle equipped with three-way catalyst (TWC) alone. As a result, SwRI originally proposed a cold-start hydrocarbon collection system in conjunction with an oxidation catalyst to oxidize stored hydrocarbons. This initial concept was changed to a proposed system that would not utilize a dual-bed catalyst. Instead of purging collected hydrocarbons to an oxidation segment of a dual-bed catalyst, the collected hydrocarbons would be returned to the intake system of the engine. This change in program direction was made in light of a letter received from Mr. K.D. Drachand of the Mobile Source Division of the Air Resources Board. The ARB letter requested a change in control technology to eliminate any possible NO_X production from the oxidation of ammonia. This letter from Mr. Drachand is included in Appendix B. A dual-bed catalyst was originally selected so that existing engine and fuel system calibrations would not have to be altered, thus avoiding possible driveability and emission problems.

In addition, Allied Signal provided SwRI with a small matrix of six three-way and oxidation catalysts for possible evaluation. One experimental three-way segment, which was designed for possible benzene emission reduction, was tested by SwRI. The remaining catalyst combinations were not tested because they included oxidation segments and/or represented past technology.

C. Cold-Start Hydrocarbon Collection - Theory of Operation

A tentative concept for the routing and collection of cold-start exhaust hydrocarbons with a three-way (only) catalyst is shown in Figure 1. Following a cold-start, the exhaust flows through the converter, bringing it to operating temperature as quickly as possible. At first there is little catalytic activity, because the temperature has not risen significantly. The raw exhaust gases then travel through a cold-start storage device (CSD) where hydrocarbons can be adsorbed. When the temperature of the catalyst is sufficient to oxidize the raw engine exhaust hydrocarbons, the CSD is bypassed and ambient air is purged through the CSD. The

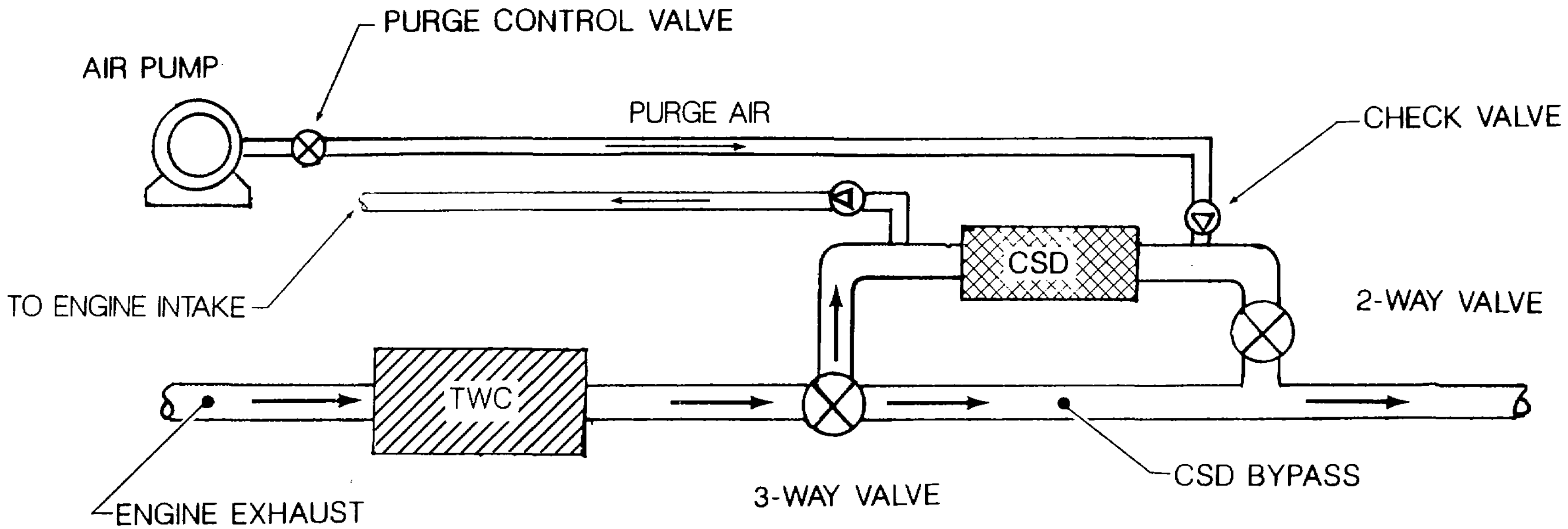


FIGURE 1. PRELIMINARY COLD-START DEVICE EXHAUST ROUTING

CSD sees no additional raw exhaust, only the ambient purge air. The purge air is routed from the CSD to the intake of the engine where the air and purged hydrocarbons re-enter the engine and are ultimately admitted to a hot catalyst. In summary, when the catalyst reaches a predetermined temperature, the CSD is bypassed and purging follows. Purge air originates from an air pump mounted on the vehicle. The purge air would flow until the CSD is completely purged. Possible exhaust routing valve positions are given in Table 5.

TABLE 5. POSSIBLE EXHAUST ROUTING VALVE POSITIONS

Valve	Cold-Start Device Mode	
	HC Collection	**HC Purge**
Three-way	To CSD	To CSD Bypass
Two-way	Open	Closed
Purge Control	Off	Purge On

A number of items will need to be addressed in the design of a roadworthy hydrocarbon collection system. These future design considerations primarily deal with calibration issues such as purge rates, signaling temperatures, and CSD desorption temperature.

D. Cold-Start Hydrocarbon Collection - Feasibility Demonstration

An exhaust system was fabricated for testing the hydrocarbon collection system. The demonstration exhaust system was located along the left side of a demonstration vehicle. The length and heat loss of the exhaust system was expected to be similar to that of an actual underbody system. An external exhaust system was chosen to minimize the cost for obtaining basic feasibility data.

Demonstration experiments were performed using the experimental hardware. The vehicle used to demonstrate feasibility was the 1986 Honda Accord LXi, a description of which was given earlier. The stock catalyst was used for the initial demonstrations. Cold-start constant speed runs were initially performed to determine the temperature distribution of the exhaust system, the light-off temperature of the catalytic converter, and the purge temperature of the CSD. The constant speed tests provided useful information for the FTP cycle tests that followed. Photographs of the CSD hardware used in the feasibility testing are shown in Figure 2.

After the temperature distribution was determined on a constant speed run, the demonstration testing continued using the FTP driving schedule. Using the original stock catalytic converter and the FTP driving schedule, catalyst light-off time was determined. This light-off time was assumed to occur at the same catalyst bed temperature at which light-off occurred during the constant speed runs. (Light-off was easily seen on the constant speed runs by a sharp drop in hydrocarbon emission concentrations downstream of the catalyst). The Honda Accord with the stock catalyst experienced light-off approximately 190 seconds into the cold transient portion of the FTP. (Determining light-off times for a catalyst driven

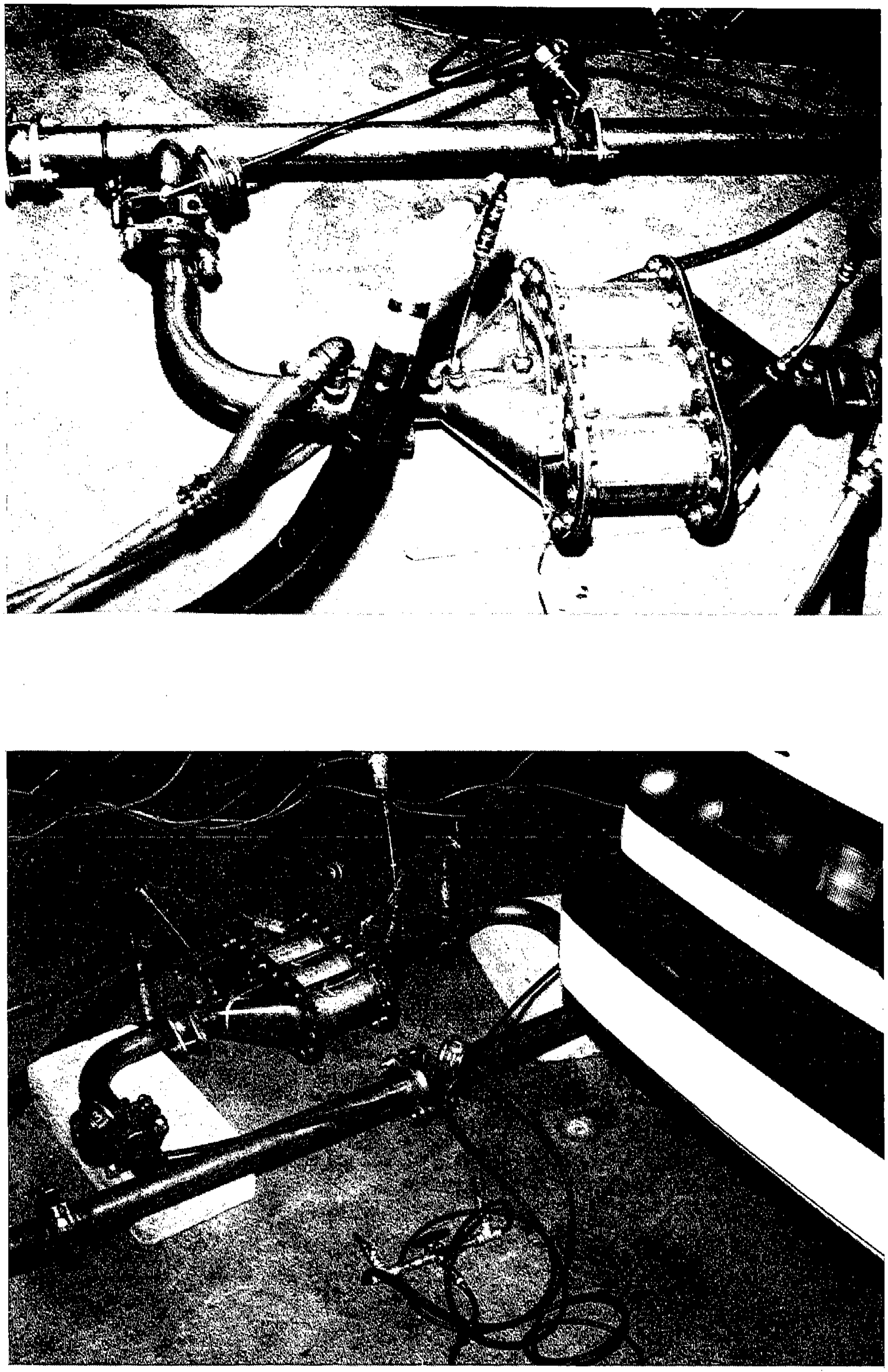


FIGURE 2. COLD-START DEVICE FEASIBILITY EXPERIMENT

over a transient speed cycle is difficult because hydrocarbon emission concentrations fluctuate).

Sample bags were taken during the FTP runs with the CSD. To analyze the cold-start emissions more precisely, the cold transient segment (Bag 1) of the FTP was split into two parts. Bag 1A was defined as the first 140 seconds of the cold transient and Bag 1B as the remaining portion of the cold transient (140-505 seconds). The sum of the mass emissions from Bags 1A and 1B equals the mass emissions of a conventional Bag 1. Computer printouts of the emission test and fuel economy results for the demonstration vehicle, with and without the CSD, are located in Appendix C.

Raw hydrocarbon concentrations were measured before and after the CSD. Hydrocarbon adsorption and desorption by the CSD were easily seen on the strip chart recorder output. The CSD clearly adsorbed exhaust hydrocarbons for 80 seconds after the cold-start. CSD bed temperature reached approximately 42°C after 80 seconds. This temperature is below the desorption temperature of 70°C. Exhaust manifold gas temperature and catalyst bed temperature were 540°C and 270°C, respectively at the 80-second point. From 80 to 140 seconds into the cold transient, the hydrocarbon concentrations at the inlet and outlet of the CSD container were essentially equal and frequently crossed. During this period, the CSD apparently had reached its hydrocarbon collection capacity. To assure that the acceleration loading on the vehicle would be identical for the constant speed tests, the vehicle followed the same acceleration trace to bring the vehicle speed to 30 mph.

Two FTP emission collection tests were performed. The first test collected the cold-start hydrocarbons for 140 seconds. The second test collected for 70 seconds. No significant difference was noted on the strip chart recorder output of continuous raw exhaust nor in the mass of hydrocarbons collected in the sample bags. It would appear that any additional amounts of cold-start hydrocarbons adsorbed (or possibly desorbed) during the period between 70 seconds and 140 seconds were very small.

Table 6 shows the mass emissions of each of the segments of the FTP for the stock catalytic converter, with and without hydrocarbon collection. The last column gives the weighted 3-bag FTP mass emission rate in units of grams/mile. It can be seen that the FTP weighted mass hydrocarbon emissions were reduced by 21 percent. To date, only preliminary CSD feasibility experiments have been performed. FTP purging of the CSD was not attempted because of cost considerations. It was beyond the scope of this study to further develop the cold-start hydrocarbon collection system.

The cold-start hydrocarbon collection system still requires on-vehicle purging control and automatic valve actuation before the system can be run independently. The supplier of the hydrocarbon collection element has stated that improvements in the HC collection capacity are possible.

TABLE 6. FTP COLD-START DEVICE DEMONSTRATION HYDROCARBON EMISSIONS

Cold-Start Device	Test Date	HC Mass Emissions, grams Bag 1A[a]	1B[b]	2	3	FTP Weighted 3-Bag HC Emissions, g/mi
No	5/24/88	1.72	0.72	0.37	0.30	0.210[c]
Yes	5/20/88	1.11[f]	0.59	--	--	0.169[d]
Yes	5/23/88	1.11[g]	0.44	--	--	0.161[e]

[a] Bag 1A - cold transient 0-140 sec.
[b] Bag 1B - cold transient 140-505 sec.
[c] Baseline test results consistent with past history of vehicle.
[d,e] Projected FTP results using mass emissions from Bag 2 and Bag 3 of baseline test (5/24/88)
[f] CSD hydrocarbon collection for 140 seconds.
[g] CSD hydrocarbon collection for 70 seconds.

FTP desorption of collection element was not attempted.

E. Experimental Low Benzene Emitting Catalyst

Allied Signal Corporation provided a catalyst designed to reduce benzene emissions by poisoning the dealkylation process by which higher aromatics are converted to benzene within the catalyst. The low benzene catalyst is an experimental three-way formulation. Specifications are given in Table 7.

TABLE 7. EXPERIMENTAL LOW-BENZENE CATALYST SPECIFICATIONS

Noble Metal Loading	50 g/ft^3
Platinum/Rhodium	5/1
Cell Density	400 cells/in^2
Diameter	3.66 inches
Length	3.0 inches

SwRI tested the low benzene catalyst to obtain FTP performance data for this study. After the baseline tests were conducted, two tests were run with the low benzene catalyst in the standard underbody position. The baseline tests were run with the aged stock catalytic converter, and the results are given in Table 8. The low benzene catalyst test results are given in Table 9. Average emission rates for the stock catalyst (baseline) and the average rates for the low benzene catalyst are compared in Table 10. The low benzene catalyst did

TABLE 8. BASELINE BENZENE AND REGULATED EMISSIONS FOR A 1986 HONDA ACCORD WITH THE STOCK CATALYTIC CONVERTER

	Mass Emissions, grams (except as noted)				FTP Weighted 3-Bag, g/mi (Except as Noted)	
	Bag 1		Bag 2	Bag 3		
	Bag 1A	Bag 1B				
Stock Catalytic Converter Test 1-1, 7/12/88						
Benzene, mg	99.3		16.6	21.3	Benzene, mg/mi	9.65
Toluene, mg	394.8		3.5	16.2	Toluene, mg/mi	24.1
HC	3.15		0.56	0.33	HC	0.28
CO	30.08		9.71	3.65	CO	3.34
NO_x	2.20		0.34	1.00	NO_x	0.25
Stock Catalytic Converter Test 2-1, 7/18/88						
Benzene, mg	46.0	28.8	15.9	12.8	Benzene, mg/mi	7.5
Toluene, mg	217.0	79.8	18.2	21.7	Toluene, mg/mi	21.3
HC	1.90	0.76	0.33	0.29	HC	0.22
CO	18.96	6.12	6.20	3.08	CO	2.53
NO_x	0.90	1.54	0.30	1.01	NO_x	0.26
Stock Catalytic Converter - Average Emissions						
Benzene, mg	87.1		16.2	17.1	Benzene, mg/mi	8.6
Toluene, mg	345.8		10.9	19.0	Toluene, mg/mi	22.7
HC	2.91		0.45	0.31	HC	0.25
CO	27.58		7.96	3.37	CO	2.94
NO_x	2.32		0.32	1.01	NO_x	0.26

TABLE 9. BENZENE AND REGULATED EMISSIONS FOR AN EXPERIMENTAL LOW BENZENE EMITTING CATALYST

	Mass Emissions, grams (Except as Noted)			FTP Weighted 3-Bag, g/mi (Except as Noted)	
	Bag 1	Bag 2	Bag 3		
Low Benzene Catalyst Test 1-1					
Benzene, mg	113.2	105.2	49.1	Benzene, mg/mi	24.4
Toluene, mg	416.0	136.0	99.8	Toluene, mg/mi	49.9
HC	3.23	1.95	1.14	HC	0.54
CO	22.23	8.04	3.71	CO	2.65
NO_x	2.94	0.50	2.09	NO_x	0.40
Low Benzene Catalyst Test 2-1					
Benzene, mg	111.1	273.2	50.9	Benzene, mg/mi	47.3
Toluene, mg	446.8	264.1	109.7	Toluene, mg/mi	70.1
HC	3.50	2.05	1.14	HC	0.57
CO	23.56	8.58	3.22	CO	2.78
NO_x	3.11	0.59	1.44	NO_x	0.37
Low Benzene Catalyst - Average Emissions					
Benzene, mg	112.2	189.2	50.0	Benzene, mg/mi	35.9
Toluene, mg	431.4	200.0	104.8	Toluene, mg/mi	60.0
HC	3.37	2.00	1.14	HC	0.56
CO	22.90	8.31	3.47	CO	2.72
NO_x	3.03	0.55	1.77	NO_x	0.39

not perform as well as the stock catalytic converter. Carbon monoxide emissions dropped 7.5 percent when compared to the stock catalytic converter, but benzene, toluene, total hydrocarbon, and NO_x emission rates increased significantly. Based on the noble metal loading and volume, the experimental low benzene catalyst had the potential of reducing emissions to the levels achieved by the stock catalytic converter. Apparently the attempt to poison the formation reaction of benzene within the catalyst adversely affected conversion of most species, especially HC and NO_x. The FTP test results for the stock catalytic converter and the experimental low benzene catalyst are located in Appendices F and G, respectively.

TABLE 10. COMPARISON OF THE EMISSION RESULTS FOR THE STOCK CATALYTIC CONVERTER AND THE EXPERIMENTAL LOW BENZENE CATALYST[a]

	Emissions, g/mi			Emissions, mg/mi		Fuel Economy, mi/gal
	HC	**CO**	**NO_x**	**Benzene**	**Toluene**	
Stock Catalytic Converter Average (Baseline)	0.25	2.94	0.26	8.6	22.7	24.57
Low Benzene Catalyst Average	0.56	2.72	0.39	35.9	60.0	25.26

[a] The low benzene catalyst is an experimental formulation.

F. High-Temperature Warm-Up Catalyst

Nippon Shokubai of Japan supplied SwRI with a high-temperature catalyst designed for automotive use. The catalyst had a three-way formulation with reasonably high loading. Specifications for the high-temperature warm-up catalyst provided by Nippon Shokubai are given in Table 11.

TABLE 11. HIGH-TEMPERATURE CATALYST SPECIFICATIONS

Cell density	300 cells/in^2
Precious metal loading	40 g/ft^3
Platinum/Rhodium ratio	5/1
Diameter	3.66 inches
Length	4.00 inches
Normal Bed Temperature	<900°C
Max. Bed Temperature	950°C

Since the high-temperature catalyst could withstand a higher temperature than standard catalysts, this catalyst was mounted at the exit of the exhaust manifold. At this location, the catalyst receives exhaust gas at a higher temperature, which would assist catalyst light-off activity. No bypass was incorporated in this demonstration. A bypass system may be required if unacceptable deterioration of the high-temperature warm-up catalyst occurs. Continued flow of high-temperature exhaust gases would tend to age the warm-up catalyst.

1. Close-Coupled Plus Underbody Catalyst Configuration

The high-temperature light-off catalyst, which was mounted at the exit of the exhaust manifold, was run in conjunction with the stock catalytic converter. The first test in this sequence of experiments was an FTP with the stock catalytic converter in the standard underbody position. This and another standard configuration test were averaged and used as a baseline for comparing the subsequent tests that involve the high-temperature light-off catalyst. The baseline test results were given in Table 8. After the baseline, three tests were run with the high temperature light-off catalyst and the stock catalytic converter in place. All tests were run measuring the regulated emissions (HC, CO, and NO_X) along with benzene and toluene. The results of the high-temperature light-off experiments are given in Table 12. Table 13 presents a comparison of the average baseline and average high-temperature catalyst FTP emission rates.

From Table 13 it is seen that the FTP weighted 3-bag results were significantly reduced using the added high-temperature catalyst, by an average of 69% for HC, 57% for CO, and 62% for NO_X. A hydrocarbon reduction analysis (stock catalyst data from Table 8 to the stock plus high-temperature catalyst results in Table 12) reveals that the major reductions in total HC occurred in bags 1B, 2, and 3. Bag 1A, where the cold-start emissions occur, had a relatively moderate percent reduction in total HC. The average reductions in total HC emissions for the three tests performed were 46 percent for Bag 1A, 85 percent for Bag 1B, 94 percent for Bag 2, and 88 percent for Bag 3. The benzene and toluene emissions using the high-temperature manifold catalyst (run in conjunction with the underbody catalytic converter) were reduced by 40 percent and 42 percent respectively. These figures are based on the average emission rates for the two baselines and the average rates for the three tests done on the high-temperature manifold and underbody catalysts.

2. Close-Coupled Catalyst Configuration

After the three tests of the high-temperature catalyst, an additional test was performed to assess the performance of the high-temperature catalyst run without the aid of the stock catalyst. Table 14 contains the test results of the high-temperature catalyst without the underbody catalyst. A comparison of the average stock catalyst results and the high-temperature warm-up catalyst run alone is given in Table 15. The HC and CO emission rates were generally lower for the experiment using only the high-temperature catalyst (mounted at the exhaust manifold). The HC emission rate was 60 percent lower for the high-temperature catalyst than for the stock catalyst. Carbon monoxide emissions were 43 percent lower. In contrast, the FTP weighted emission rate was 116 percent higher for NO_X with only the high-temperature catalyst on the vehicle. The high-temperature catalyst when tested separately from the stock catalyst gave a 27 percent reduction in benzene emissions and a 35 percent reduction in toluene when compared to the baseline test results. These benzene and toluene reduction figures are based on the test data reported in Tables 13 and

TABLE 12. BENZENE AND REGULATED EMISSIONS FOR THE HIGH-TEMPERATURE WARM-UP CATALYST PLUS STOCK CATALYTIC CONVERTER

	Mass Emissions, grams (Except as Noted)				FTP Weighted 3-Bag, g/mi (Except as Noted)	
	Bag 1A	Bag 1B	Bag 2	Bag 3		
High-Temperature Catalyst + Stock Catalyst Test 1-1, 7/19/88						
Benzene, mg	45.6	6.6	35.8	8.4	Benzene, mg/mi	8.5
Toluene, mg	147.8	32.7	20.5	3.6	Toluene, mg/mi	13.5
HC	1.10	0.14	0.01	0.02	HC	0.07
CO	14.22	1.21	3.09	0.98	CO	1.39
NO_x	0.22	1.09	0.15	0.07	NO_x	0.10
High-Temperature Catalyst + Stock Catalyst Test 2-1, 7/20/88						
Benzene, mg	51.4[a]	0.18	0	8.4	Benzene, mg/mi	3.7[a]
Toluene, mg	153.9[a]	28.1	0	4.3	Toluene, mg/mi	10.9[a]
HC	1.13	0.14	0.03	0.05	HC	0.08
CO	11.59	1.61	3.19	0.76	CO	1.25
NO_x	0.03	0.98	0.18	0.23	NO_x	0.09
High-Temperature Catalyst + Stock Catalyst Test 2-2, 7/21/88						
Benzene, mg	59.1	1.28	0	0	Benzene, mg/mi	3.5
Toluene, mg	170.0	26.1	25.1	2.5	Toluene, mg/mi	15.0
HC	1.14	0.11	0.04	0.04	HC	0.08
CO	11.71	1.24	2.41	0.68	CO	1.13
NO_x	0.25	0.82	0.12	0.33	NO_x	0.10
High-Temperature Catalyst + Stock Catalyst - Average Emissions						
Benzene, mg	52.4	2.7	11.9	5.6	Benzene, mg/mi	5.2
Toluene, mg	157.2	29.0	15.2	3.5	Toluene, mg/mi	13.1
HC	1.12	0.13	0.03	0.04	HC	0.08
CO	12.51	1.35	2.97	0.81	CO	1.26
NO_x	0.17	0.96	0.15	0.21	NO_x	0.10

[a] Benzene and toluene mass emissions for Bag 1A are estimated from Tests 1-1 and 2-2.

TABLE 13. COMPARISON OF THE EMISSION RESULTS FOR THE STOCK CATALYTIC CONVERTER AND THE STOCK PLUS HIGH-TEMPERATURE CATALYST

	Emissions, g/mi			Emissions, mg/mi		Fuel Economy, mi/gal
	HC	CO	NO_X	Benzene	Toluene	
Stock Catalytic Converter Average (Baseline)	0.25	2.94	0.26	8.6	22.7	24.57
Stock & High-Temperature Catalyst Average	0.08	1.26	0.10	5.2	13.1	25.18

TABLE 14. BENZENE AND REGULATED EMISSIONS FOR THE HIGH-TEMPERATURE WARM-UP CATALYST ALONE

	Mass Emissions, grams (Except as Noted)				FTP Weighted 3-Bag, g/mi (Except as Noted)	
	Bag 1A	Bag 1B	Bag 2	Bag 3		
High-Temperature Catalyst Test 1-1, 7/22/88						
Benzene, mg	39.6	11.5	16.6	14.0	Benzene, mg/mi	6.3
Toluene, mg	137.7	50.8	12.2	0	Toluene, mg/mi	14.8
HC	1.07	0.26	0.10	0.15	HC	0.10
CO	11.40	2.62	4.96	2.28	CO	1.67
NO_X	0.33	2.27	1.50	2.49	NO_X	0.55

TABLE 15. COMPARISON OF THE EMISSION RESULTS FOR THE STOCK CATALYTIC CONVERTER AND THE HIGH-TEMPERATURE WARM-UP CATALYST ALONE

	Emissions, g/mi			Emissions, mg/mi		Fuel Economy, mi/gal
	HC	CO	NO_X	Benzene	Toluene	
Stock Catalytic Converter Average (Baseline)	0.25	2.94	0.26	8.6	22.7	24.57
High-Temperature Catalyst Alone	0.10	1.67	0.55	6.3	14.8	27.44

15. Complete FTP summaries of the regulated emissions and fuel economy results by bag for the high-temperature warm-up catalyst are located in Appendix H.

G. Performance and Cost Comparison of Exhaust Benzene Emission Controls

A summary of the average results of the different exhaust benzene control technologies is given in Table 16. The high-temperature catalyst in conjunction with the stock catalyst provided the best performance. When the high-temperature catalyst was run without the underbody catalyst, HC and CO emissions were reduced (compared to the stock catalyst in the underbody location). The high-temperature catalyst alone did not provide as much NO_X reduction as the underbody catalyst. Performance of the high-temperature catalyst in an underbody location was not assessed.

During the feasibility experiment, the cold-start hydrocarbon collection device demonstrated a 21 percent improvement over the original catalyst configuration for HC control during a 3-bag FTP. The CO and NO_X emission rates for the cold-start collection device are projected values calculated using the CO and NO_X emissions from bags 1A and 1B of the CSD test and bags 2 and 3 of the baseline test. The stabilized portion and the hot transient portion of the FTP were not run on the emission collection tests because a complete on-vehicle control system was not available. The manual system was run only through the cold transient segment. The projected performance of the CSD system (which uses the original catalyst) did not match the overall performance of the high-temperature catalyst run in conjunction with the original underbody catalyst. Significant reductions in CO and NO_X are not expected with this collection element. Cold-start hydrocarbon collection was successfully demonstrated. As previously stated, the supplier of the CSD adsorption elements indicated that improved collection capacities of the elements have been realized since the feasibility testing, however no vehicle data are available.

Currently, the prototype hydrocarbon collection system is not roadworthy. Preliminary collection system results show a reduction in HC levels during cold-start operation. Assuming collected hydrocarbons can be purged successfully after the cold-start, the emission rates for hot operation of the CSD-equipped vehicle could be expected to be similar to current production systems.

The hydrocarbon collection approach demonstrated a great improvement in hydrocarbon emission control during cold-start operation. In contrast, the high-temperature catalyst (with the stock catalytic converter) demonstrated the largest relative reductions during hot operation, as shown in Table 12. (For this discussion, hot operation is defined as bags 1B, 2, and 3.) On a bag-by-bag analysis, the greatest relative reductions for HC and CO occurred during hot engine operation. Reductions in bag 1A emissions were significant on an absolute basis. It appears that when the high-temperature and underbody catalysts reach their normal operating temperatures, they perform very efficiently together.

Noteworthy is the fact that the high-temperature catalyst was new during the test. Its performance may deteriorate with aging. It is also possible that the higher backpressure, caused by having two catalysts in the exhaust system, contributed in part to the lower FTP NO_X emissions. The backpressure increase was evidently not large enough to affect performance in a major way, because the difference in fuel economy compared to the baseline test was insignificant.

TABLE 16. SUMMARY OF EXHAUST BENZENE EMISSION CONTROL EXPERIMENTS

	FTP Weighed 3-Bag Emissions					
	Stock Catalytic Converter (Baseline) for CSD[a]	**Cold-Start Hydrocarbon Collection Device (CSD)**	**Stock Catalytic Converter (Baseline)**	**Low Benzene Catalyst**	**Stock & High-Temperature Catalysts**	**High-Temperature Catalyst Alone**
Benzene, mg/mi	NA	NA	8.6	35.9	5.2	6.3
Toluene, mg/mi	NA	NA	22.7	60.0	13.1	14.8
HC, g/mi	0.21	0.17[b]	0.25	0.56	0.08	0.10
CO, g/mi	2.63	2.61[b]	2.94	2.72	1.26	1.67
NO_x, g/mi	0.37	0.31[b]	0.26	0.39	0.10	0.55
Fuel Economy, mi/gal	25.13	25.25[b]	24.57	24.26	25.18	27.44

[a] Separate baseline for CSD because CSD analysis was done at a different time.

[b] Projected FTP result using mass emission from Bag 2 and Bag 3 of CSD baseline test (5/24/88).

It is evident that NO_X emissions for the stock configuration could have been improved with increased catalyst size or noble metal loading. Note that the stock and high-temperature catalyst demonstrated lower NO_X emissions together than separately (Table 16). The demonstration vehicle in the stock catalyst configuration did, however, meet the NO_X emission standard of 1.0 grams per mile by a considerable margin.

The light-off time of the high-temperature catalyst possibly could have been decreased by optimizing the system. A catalyst with a different volume, surface area, or cell density may lead to improved light-off. A quicker light-off would help reduce the emissions further in Bag 1, and would improve the FTP emission rate significantly because most of the hydrocarbon emissions occur during the cold-start.

Finally, the emission results for the experimental low benzene catalyst were all higher, except for CO, which was slightly lower. The formulation of this experimental catalyst may have reduced the formation of benzene within the catalyst, but it evidently did not reduce the benzene and total hydrocarbons in the exhaust gas. It was suspected from Allied Signal's own in-house tests that this new formulation may decrease the total effectiveness of the catalyst on the regulated emissions. Because the catalyst is currently not as effective as the original catalyst, its use was not recommended for the future prototype vehicles.

Since the high-temperature catalyst is similar to conventional catalysts, SwRI expects its cost to be similar to current production catalytic converters of similar size, loading, and substrate material. The cold-start hydrocarbon collection system, on the other hand, is more complex. It requires a monolithic element and a container (just like a catalytic converter), control valves, a heat exchanger, an air pump, a controlling mechanism to operate the valves, and a temperature or time measuring device. In all, it would be several times more expensive than a production exhaust aftertreatment system (catalyst, possibly an air pump, etc.), and additional development work still remains to be done on the system. The feasibility data on the system strongly suggest that it could be made to work effectively. The development of the remainder of the system defined is certainly desirable and achievable, but not as a part of this program as it was proposed. Further development of the cold-start device system should be a separate program.

H. Other Cold-Start Emission Control Strategies

As previously mentioned, the cold-start emissions are a major contributor to the FTP hydrocarbon emission rate for light-duty gasoline vehicles. Cold-start emission reduction, especially total hydrocarbons and benzene, has been the focus of this program. The idea of bringing the catalytic converter (or other catalytic device) to full operating temperature at an accelerated rate has surfaced several times. Variations include a warm-up catalyst with or without a bypass mechanism to divert flow after warm-up. Examples of this concept, including a warm-up bypass catalyst, a warm-up non-bypass system, a close-coupled catalytic converter, and an electrically preheated underbody catalytic converter will be discussed briefly.

1. Warm-up Bypass Catalyst

In one variation of a warm-up bypass catalyst, a small catalyst is positioned in or near the exhaust manifold near the exhaust ports. This small, quickly heated catalyst reaches an efficient operating temperature sooner than an underbody catalyst located downstream. To protect the warm-up catalyst from possible overheating and unnecessary aging, a bypass mechanism is activated after the underbody catalyst has reached an efficient operating temperature. The bypass mechanism is simply a high-temperature valve (or combination of valves) that diverts flow either to the warm-up catalyst or to a bypass path. The bypass mechanism would ideally have a low heat capacity so the mechanism would not absorb exhaust heat that would be better used to bring the warm-up catalyst up to temperature quickly. In the bypass mode the exhaust is directed to a conventional underbody catalyst.

2. Warm-Up Catalyst Without Bypass

A warm-up catalyst without bypass employs a small, quickly heated catalyst in or close to the exhaust manifold and a slightly reduced underbody catalytic converter. The warm-up catalyst (mounted at the exhaust manifold) does not have a bypass mechanism and assists the underbody catalytic converter at all times. The warm-up catalyst reaches an efficient temperature quickly, as in the other systems. The warm-up catalyst must be durable at high operating temperatures. This style system was tested in Task 1 of the program, and the results were presented in this section.

3. Close-Coupled Catalytic Converter

A close-coupled catalytic converter is simply a converter mounted at the exhaust manifold. The converter must be able to operate at high temperatures without appreciable deterioration because a bypass mechanism is not employed. There is no second catalyst in the system. At least one manufacturer used this system in its 1987 and 1988 models. Certification results show improved emission control.

4. Electrically Preheated Catalytic Converter

Another concept for reducing cold-start emissions is to electrically (or otherwise) preheat a catalytic converter prior to a cold-start. Cold-start emissions could then be treated immediately by an active converter. Power requirements for heating the converter would depend upon the heat capacity and the thermal conductivity of the catalytic element. Experimental units that incorporate metal substrates were just being developed for methanol vehicles at the time of the demonstration testing. Work has been done to minimize warm-up time and power requirements. This technology was identified as a possible strategy for reducing benzene emissions and was investigated in subsequent efforts for this program (Sections VI through X).

These control strategies are similar in nature. Strategy nomenclature differs from different sources, but conceptually they are alike. All these systems can potentially reduce total hydrocarbon cold-start emissions. It is unknown, however, whether or not dealkylation of aromatics in the raw exhaust will occur and form benzene during rich cold-start operation. Cold-start emissions were focused upon in this report, but improvements in general emissions are obviously also achieved with efficiently tuned engines, reliable and precise fuel and ignition systems, and well maintained vehicles.

IV. EVAPORATIVE EMISSION CONTROL TECHNOLOGIES INVESTIGATED

Alternatives to current evaporative emission control technologies were less numerous than for alternatives to exhaust emission control technology. The literature search identified no more than that which is already commonly used, namely activated carbon. As part of this study, one manufacturer submitted a sample of a molecular sieve for possible use as an evaporative emission adsorbent. The butane working capacity of this material was compared to that of activated carbon in our study. A multi-chamber carbon canister was fabricated to see if geometry changes could improve evaporative control. In addition to this experimentation, a comparison of wood- and coal-derived activated carbon, originally studied at SwRI for EPA(16,17), has been reviewed.

A. Alternate Hydrocarbon Adsorption Material for Evaporative Canisters

Union Carbide provided SwRI with an alternative material for possible use as a hydrocarbon adsorbent for evaporative emission control. A molecular sieve was considered for evaporative emission control and was tested to determine its butane working capacity. In all the butane working capacity measurements, the canisters were loaded with butane at a rate of 1 liter per minute until breakthrough occurred at the exit of the canister. Breakthrough, in the case of the butane measurements, was defined as the point at which the vapors at the exit of the canister reached a concentration of 1,000 ppmC, as determined with an FID hydrocarbon analyzer. Typically, the hydrocarbon level at the exit of the canister remained well below 100 ppmC until breakthrough, at which point the level rose to well above 1,000 ppmC within a matter of seconds. Each canister was purged for 20 minutes at 10 liters per minute before the next loading with butane. The canisters were weighed after both loading and purging, with the difference in weights giving the working capacity. Working capacity measurements were also attempted with benzene vapors (in zero air), however, meaningful data could not be obtained due to the inability to load and purge necessary quantities of benzene to and from the various adsorption materials. In addition, a surface area analysis was performed on the adsorption materials. A Micromeritics Digisorb 2300 was used to determine the specific surface area. This instrument uses mixtures of nitrogen and helium gas cooled to liquid nitrogen temperature. Nitrogen can determine the area of the surface with any cracks or pores larger than the diameter of diatomic nitrogen. The average error for this analytical procedure was about 1 m^2/g. Table 17 shows the performance of the alternate evaporative emission control material and compares it to wood-based carbon. It can be seen that the capacity of the alternative adsorption material, in the form tested, is far below that of carbon. This alternative material was not recommended for a benzene evaporative control medium because of its low butane working capacity.

TABLE 17. BUTANE WORKING CAPACITY COMPARISON FOR WOOD-BASED CARBON AND AN ALTERNATIVE ADSORBENT

Material	Volume, L	Mass, g	Surface Area, m^2/g	Butane Working Capacity, grams		
				Initial[a]	Cycle A	Cycle B
Carbon (wood-based)	0.586	176.1	1383	31.2	27.3	30.2
Molecular Sieve	0.626	352.2	564[b]	8.0	6.4	6.0

[a] No prior exposure to butane.
[b] Surface area measured by supplier.

B. Multiple Chamber Canister Evaluation

An experiment was performed to determine if increasing the number of chambers within the canister would affect the butane working capacity of the activated carbon inside. A dual chamber canister was modified by dividing each of the original chambers in half. The new container geometry had a total of four chambers. See Figure 3 for photographs of the modified canister container design. The modified container held the same amount of activated carbon as the original production design, but the vapors had to flow through more channels before they finally exited the canister.

The results of the multi-chamber canister geometry experiment are shown in Table 18. The nearly identical working capacities for each of the container geometries indicate that canister performance is a strong function of carbon quantity and type, but a weak function of more complicated container geometry.

TABLE 18. BUTANE WORKING CAPACITY FOR A PRODUCTION CANISTER AND A MULTIPLE CHAMBER CANISTER

Container Style	Activated Carbon		Butane Working Capacity,[a] grams	
	Volume, cm^3	Mass, grams	Cycle A	Cycle B
Production[b]	1469	546.7[c]	63.9	62.7
Multiple Chamber[d]	1469	546.7	62.2	62.5

[a] Loading rate of 1 liter/minute; purge rate of 10 liters/minute for 20 minutes.
[b] Production canister contained two chambers.
[c] New activated carbon preconditioned with two butane working capacity test cycles.
[d] Four chamber canister design.

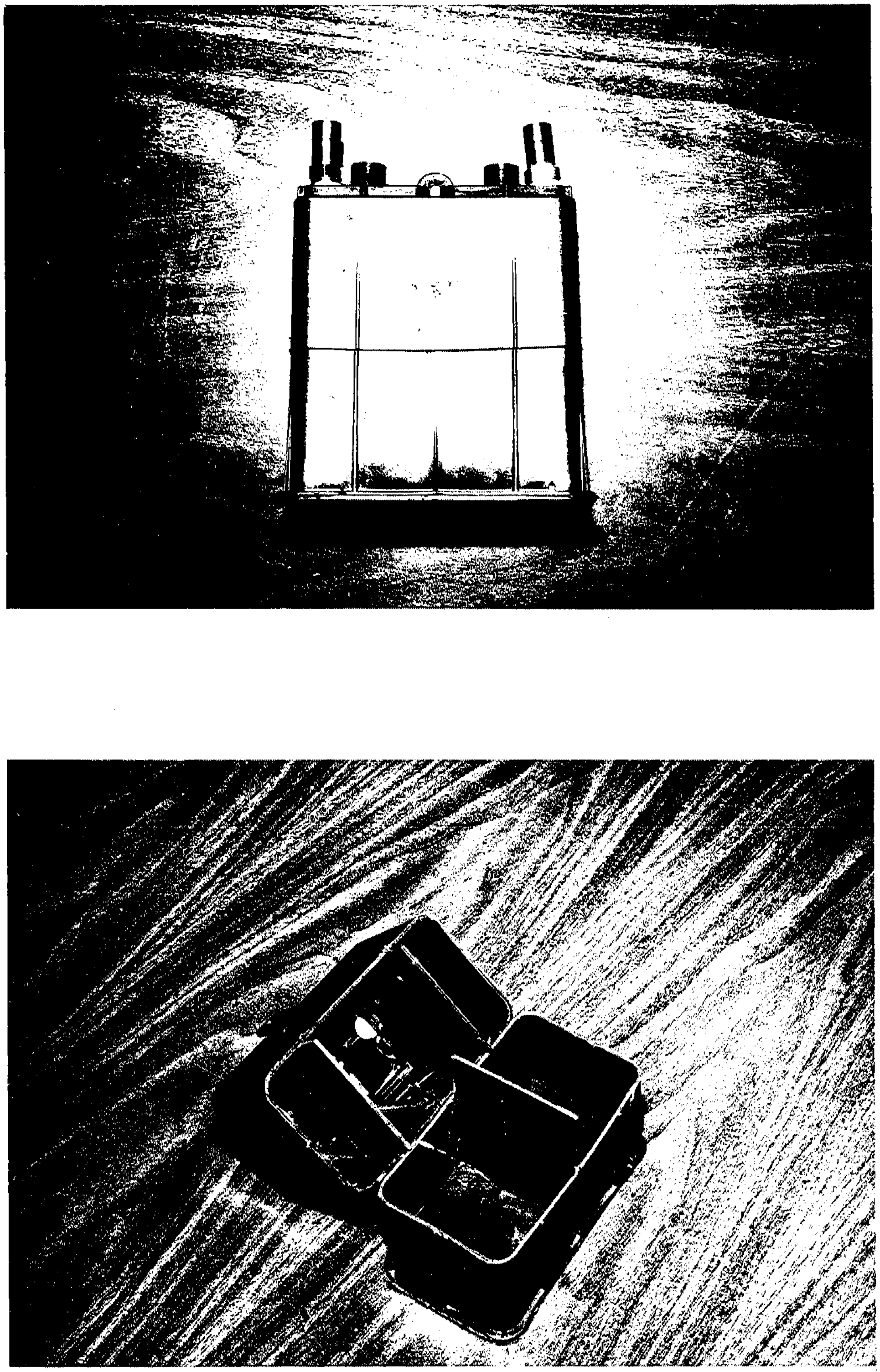


FIGURE 3. MODIFIED CARBON CANISTER WITH MULTIPLE CHAMBERS

C. Wood- and Coal-Based Activated Carbon Comparison

A comparison of wood-based and coal-based activated carbon working capacities was performed by SwRI under a contract for EPA.(16,17) In this experiment, the canisters were loaded with a hydrocarbon blend instead of pure butane. The composition of the hydrocarbon blend (by volume) was approximately 16 percent butane, 4 percent isobutylene, and 0.7 percent toluene. The remainder was nitrogen carrier gas. The flowrate of hydrocarbon vapors plus nitrogen carriers to a series of twelve mini-canisters was on the order of 70 milliliters/min.

Working capacities for four different canister materials are shown in Table 19. For the hydrocarbon blend described earlier, the working capacity for both the coal-based carbons was superior to that for the wood-based carbons.

TABLE 19. WORKING CAPACITIES FOR DIFFERENT CANISTERS EXPOSED TO A HYDROCARBON BLEND

Manufacturer	Activated Carbon Type	Approximate Density, g/mL	Working Capacity, mg HC Blend[a]/g Carbon
Chrysler 1	Wood	0.27	196
Chrysler 2		0.27	168
Ford 1	Coal	0.40	197
Ford 2		0.40	201
Ford 3		0.40	197
Ford 4		0.40	195
GM 1	Wood	0.29	136
GM 2		0.29	137
GM 3		0.29	137
Toyota 1	Coal	0.42	193
Toyota 2		0.42	190
Toyota 3		0.42	194

[a]Blend of butane, isobutylene, and toluene.

In an experiment conducted for the benzene control program, two different wood-based activated carbons were compared for their relative butane working capacities. The first sample was a powdered wood-based activated carbon in the form of carbon pellets. The second sample was a wood-based activated carbon with the appearance of fine chips. Each type of carbon was placed in a reusable round canister. A photograph of the apparatus used is shown in Figure 4. The butane working capacities along with surface area measurements are presented in Table 20. In the BET surface area measurement, the wood-based carbon chips had a 4.3 percent higher surface area than the wood-based carbon pellets. The improved butane working capacity performance is most likely due to an increased number of active adsorption sites (for butane) on the GM wood-based activated carbon. The BET four point surface analysis test results for each of the adsorbers are included in Appendix I. (BET surface area analysis is named with the initials of the inventor).

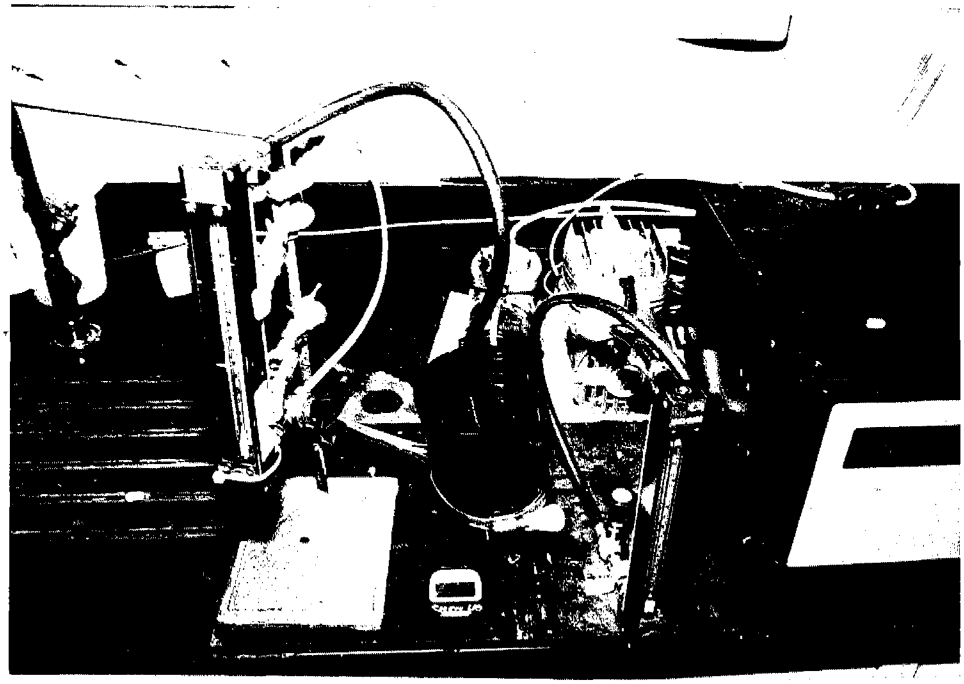


FIGURE 4. BUTANE WORKING CAPACITY TEST APPARATUS

TABLE 20. BUTANE WORKING CAPACITY FOR TWO WOOD-BASED ACTIVATED CARBONS

Activated Carbon				Butane Working Capacity,[a] grams	
Type	Volume, cm^3	Mass,[b] grams	Surface Area,[c] m^2/g	Cycle A	Cycle B
Ford (powdered wood pellets)	542.8	176.1	1323	16.2	16.6
GM (wood chips)	651.0	176.1	1383	25.3	25.9

[a] Unused activated carbons preconditioned with one butane working capacity test.
[b] Mass of clean, untested carbon.
[c] Surface area by BET surface area analysis.

V. INITIAL RECOMMENDATIONS FOR LOW BENZENE EMISSION VEHICLE DEMONSTRATION

Based on the findings of the literature search, contacts with manufacturers of emission control components, and the feasibility experiments performed for this study, SwRI recommended the following items to be incorporated into the design of the low benzene emitting vehicle. These were the initial recommendations before any work was performed on the preheated catalyst in this study. As described in the following sections of this report, the electrically-heated catalyst was eventually chosen as the cold-start benzene emission control strategy for our demonstration vehicles.

A. Exhaust Benzene Emissions

The high-temperature warm-up catalyst (placed at the exit of the exhaust manifold) in conjunction with an underbody catalyst was recommended as the most effective emission control strategy. This catalyst system was identified to be the most effective in this study, prior to the evaluation of the electrically-heated catalyst. The warm-up plus underbody catalyst system still appears to be the most feasible unheated cold-start benzene control strategy.

B. Evaporative Benzene Control

It was recommended that a high surface area activated carbon be used for control of evaporative emissions. Our research has shown that coal-based activated carbon has a greater butane working capacity than wood-based carbon. Further improvements in hydrocarbon adsorption capacity could be achieved with larger canisters, if required. Alternate adsorption materials were investigated but no improved materials were identified.

C. Vehicle Selection

SwRI recommended that the demonstration vehicles(s) selected for the low benzene emission control system be California certified and be as representative as possible of future technology. It was suggested that the selected vehicle(s) have a certification hydrocarbon emission rate that was not usually high or low. Other recommendations included ample space for ease of modification and low cost. As an example, SwRI envisioned a current model subcompact with a four-cylinder engine, closed-loop fuel injection, and a three-way catalyst system.

VI. ELECTRICALLY-HEATED CATALYST FOR COLD-START BENZENE EMISSION CONTROL

Late in the technology investigation portion of this study, the electrically-heated catalyst became available for evaluation. The Air Resources Board directed SwRI to evaluate this catalyst based on the encouraging results obtained by EPA.(18,19) A prototype electrically-heated catalyst was obtained from a commercial catalyst supplier for this task of the program and evaluated on an available test vehicle. The electrically-heated catalyst would eventually be selected by the Air Resources Board as the control technology for exhaust benzene emissions.

A. Initial Electrically-Heated Catalyst Test Results

An electrically-heated catalyst was installed on a 1986 Toyota Camry obtained for this demonstration. This catalyst was supplied by Camet Company, a unit of W. R. Grace. The Camet catalytic converter was composed of two separate sections, the larger section being a metal substrate catalyst without heating ability. Its other section was a catalyzed metal substrate capable of being heated electrically. This catalytic converter could be mounted on the vehicle with the heated catalyst portion facing to the front or to the rear of the exhaust system.

For our application, the Camet converter was mounted on the vehicle such that the electrically-heated portion was at the rear (downstream). This initial configuration was recommended by Camet. The basis of this recommendation was that a rear-mounted heated catalyst element may be more durable, because it would be subjected to less poisoning.

The heating control system was set up to heat the catalyst for 15 seconds before cold-starting the engine. After the engine has started, the catalyst heating element is reactivated for a period of 30 seconds. When the engine is shut off, a timer was activated. If the vehicle was restarted within 30 minutes, the heating of the catalyst before and after starting was proportionally reduced. For example, if the engine was restarted 10 minutes after it was last shut off, the catalyst would undergo pre-start heating for 5 seconds instead of the full 15 seconds and post-start heating for 10 seconds instead of the full 30 seconds. The electrical heating times for this application were built into the controller by Camet Company.

An FTP emissions test was performed on the Toyota Camry with the Camet catalyst. The unaged Camet catalyst in a non-preheated configuration provided better emission control than the original Toyota catalyst. These results are given in Table 21. The Camet catalyst was then tested with electrical preheating. Heated catalyst test results showed no improvement over the unheated Camet catalyst test.

The Toyota Camry then underwent a 500-mile service accumulation to age the new Camet catalyst. Two FTP tests were performed on the vehicle after the 500 miles were accumulated, one with and one without the electrical heating of the catalyst. Aged catalyst test results (Table 21) showed no improvement in hydrocarbon emission control as a result of catalyst preheating, similar to the new catalyst results.

TABLE 21. INITIAL ELECTRICALLY-HEATED CATALYST TEST RESULTS 1986 TOYOTA CAMRY

Test No.	Description	Emissions, g/mi			Fuel Economy, mi/gal	Benzene Emissions, mg/mi	Toluene Emissions, mg/mi
		HC	CO	NO_x			
TCOEM21U	OE[a] Catalyst	0.21	2.83	0.45	28.2	7.6	16.9
TCCAM00U	Camet Catalyst New, Unheated	0.13	1.16	0.14	29.4	6.9	11.6
TCCAM01H	Camet Catalyst New Heated[b]	0.15	1.40	0.14	28.7	10.4	14.5
TCCAM02H	Camet Catalyst 500 mi. Heated	0.16	2.20	0.19	28.5	7.4	13.3
TCCAM02U	Camet Catalyst 500 mi. Unheated	0.13	1.78	0.19	29.9	6.9	13.2

[a] OE-original equipment.
[b] Catalyst heating durations; 15 seconds before cold-start, 30 seconds after cold-start, 5 seconds before hot-start, 10 seconds after hot-start.

One possible explanation for the lack of improvement in the heated catalyst test is that there was insufficient oxygen in the exhaust during cold-start operation. Obviously, oxygen is required to oxidize excess hydrocarbons and carbon monoxide. Even a warm catalyst cannot reduce hydrocarbon and carbon monoxide emission levels without oxygen.

Oxygen is scarce in the exhaust gases during a cold start because the engine fuel system is calibrated to run rich during this period (generally required for acceptable driveability). Cold-start hydrocarbon and carbon monoxide emissions can improve if the fuel system brings the air-fuel ratio to stoichiometry as soon as possible after the cold start, or if air is injected into the exhaust stream ahead of the catalyst during cold-start operation. Available exhaust oxygen is required before a warm catalyst will benefit cold-start emissions.

Although it was conjectured that supplementary oxygen during the cold-start could improve conversion performance, this ARB-funded benzene emission study was not able to fund an air injection study to determine feasibility of such an approach. Other sources of funding were pursued, but without success. At this time, SwRI approved an Internal Research proposal to continue the electrically-heated catalyst work with an air injection feasibility study.

B. SwRI-Sponsored Air Injection Demonstration

The Advisory Committee for Research at SwRI awarded funding to the Department of Emissions Research to determine the feasibility of air injection to the electrically-heated catalyst for reducing cold-start benzene emissions. This SwRI internal research project demonstrated successful emission reductions with air injection to the preheated catalyst. A report (20) describing all important aspects of this feasibility study is provided in its entirety in Appendix H.

In summary, an air injection strategy was developed to determine if cold-start air injection would improve FTP exhaust emissions. The strategy developed injected air at a rate of 140 liters per minute (5 cubic feet per minute) for a period of 140 seconds following the cold-start. Air injection began as the engine cranked for starting. Air injection and catalyst heating experiments were performed to determine effects on emission control. Four catalyst preheating and air injection configurations were tested. FTP exhaust emissions were determined for the no-heat-no-air, heat only, air only, and heat-plus-air catalyst configurations.

Following the determination of an optimal air injection flowrate and duration, FTP emission tests were conducted. The 1986 Toyota Camry, equipped with the prototype electrically-heated catalyst, was the demonstration vehicle. Benzene and toluene emissions were measured in addition to the regulated emissions (HC, CO, NO_X). FTP emissions for each of the four catalyst preheating and air injection configurations are given in Table 22. The California emission standards for the ultra-low emission vehicle (ULEV) are also listed in the table. Catalyst preheating combined with air injection produced emissions that were near or equivalent to the ULEV standards.

As shown in Table 22, the lowest FTP emission rates for HC, CO, benzene, and toluene were achieved with catalyst preheating and secondary air injection. Emissions of NO_X, however, were minimized with the catalyst preheating alone (no air injection). This is because the heated catalyst was an active NO_X reduction catalyst without the addition of air. A slight increase in NO_X emissions occurred with the heat-plus-air configuration during the cold transient portion of the FTP, when the secondary air was injected.

TABLE 22. FTP AIR INJECTION AND HEATED CATALYST EXPERIMENTS 1986 TOYOTA CAMRY

Test Description	FTP Emissions, g/mile					
	THC	NMHC	CO	NO_X	Benzene	Toluene
No Heat, No Air	0.12	0.12	1.13	0.22	0.0078	0.0140
Heat, No Air	0.10	0.09	1.50	0.12	0.0066	0.0091
Air, No Heat	0.13	0.12	1.48	0.23	0.0071	0.0113
Heat and Air	0.07	--	0.40	0.25	--	--
Heat and Air	0.05	0.03	0.35	0.22	0.0017	0.0012
Heat and Air	0.04	0.03	0.49	0.25	0.0038	0.0018
Heat and Air	0.04	0.03	0.26	0.27	0.0022	0.0026
(Average)	**0.05**	**0.03**	**0.38**	**0.25**	**0.0026**	**0.0019**
California ULEV Standards	--	0.04[a]	1.70	0.20	--	--

[a] NMOG Standard
Air Injection: 140 L/min, 140 sec. for cold-start, no air during hot-start.
Heating: 15 sec. before cold-start, 30 seconds after cold-start,
5 seconds before hot-start, 10 seconds after hot-start,

The SwRI internally-sponsored air injection feasibility study was highly successful. Air injected into an electrically-heated catalyst was shown to be an effective technology for controlling hydrocarbon, benzene, and carbon monoxide emissions on gasoline-fueled vehicles. An electrically-heated catalyst with air injection represents a possible control technology for meeting lower emission standards, but much development work on the part of manufacturers remains to be done. The ARB-sponsored benzene control study was continued because a benzene (and total hydrocarbon) emission control strategy was identified. Conversion and optimization of two current-technology vehicles to air injected electrically-heated catalyst emission control systems followed the SwRI internal demonstration.

VII. ELECTRICALLY-HEATED CATALYST SYSTEM CONVERSIONS ON TWO CURRENT-TECHNOLOGY VEHICLES

Following the feasibility demonstration and experimentation to obtain an understanding of the heated catalyst technology application, two current-technology vehicles were equipped with electrically-heated catalyst and air injection systems. The systems were designed and calibrated for each vehicle application. This section describes the emission control system conversions.

A. Vehicles

A 1990 Buick LeSabre and a 1990 Toyota Celica were used for demonstration of the electrically-heated catalyst systems. These vehicles were selected by the Air Resources Board because of their low emissions and excellent in-use emission performance record. Certification emission test results(21) for the LeSabre and Celica are given in Table 23. The LeSabre is equipped with a 3.8 liter V-6 engine having sequential multipoint electronic fuel injection, while the Celica utilizes a 2.2 liter in-line four-cylinder engine with multipoint electronic fuel injection. Descriptions of the LeSabre and Celica are given in Table 24. Photographs of the demonstration vehicles are shown in Figure 5.

TABLE 23. CERTIFICATION EMISSIONS

Vehicle	FTP Emissions, g/mi		
	HC	CO	NO_x
1990 Buick LeSabre (L2G3.8W8XEB7)	0.11	1.60	0.20
1990 Toyota Celica (LTY2.2V5FCC3)	0.12	1.80	0.10

B. Electrically-Heated Catalysts

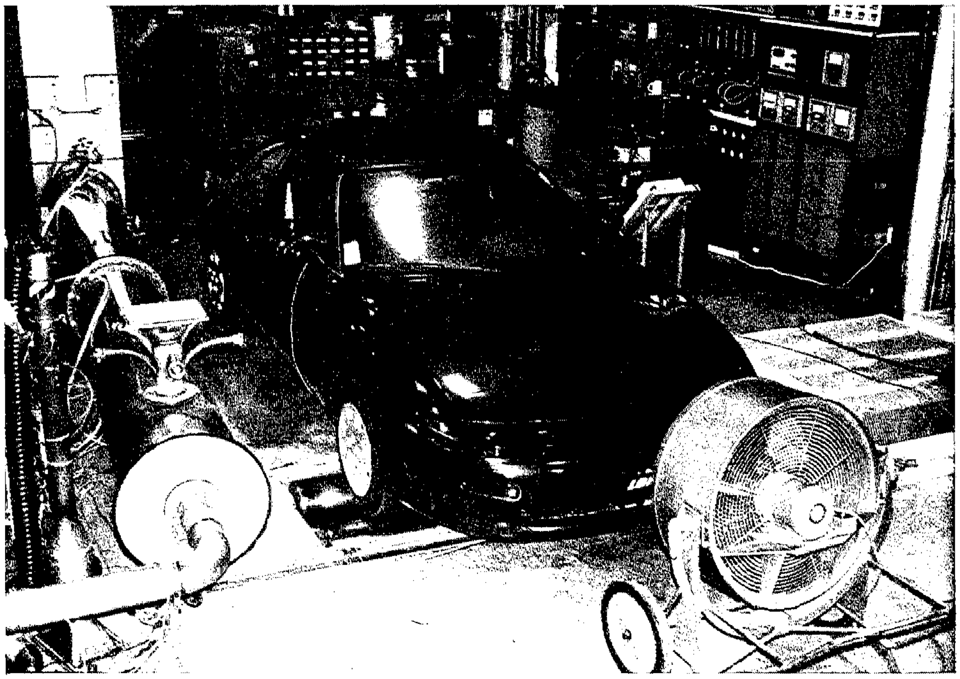
Electrically-heated catalysts were installed on the Buick LeSabre and Toyota Celica. Each electrically-heated catalyst was incorporated as a supplement to the original catalytic converter system. The Buick and Toyota catalytic converters were not removed or reconfigured, in order to maintain original emission system control characteristics during warmed-up operation. The electrically-heated catalysts for this study consisted of three-way formulations applied on a metal substrate, and were unaged at the time of installation on the vehicles. Near the conclusion of testing, the electrically-heated catalyst on the Celica was replaced with a larger unit (unaged) to further reduce emission levels. The larger electrically-heated catalyst improved the emissions on the Celica, and was used for the remainder of the program.

TABLE 24. VEHICLE DESCRIPTIONS

Item	Buick LeSabre	Toyota Celica
Model Year	1990	1990
Body Style	4-door sedan	2-door coupe
Odometer[a]	336 km (209 miles)	145 km (90 miles)
Transmission	Automatic	Automatic
No. of Gears	4	4
VIN	1G4HP54C91H430188	JT2ST87FL0005692
Tires	P205/75R14	P185/65R14
Accessories	Air Conditioning Power Steering Power Brakes Auto. Overdrive Transmission	Air Conditioning Power Steering Power Brakes Auto. Overdrive Transmission
Engine Family	L2G3.8W8XEB7	LTY2.2V5FCC3
Engine Displacement	3.8 liter	2.2 liter
No. of Cylinders	6	4
Fuel System	Electronic Sequential Port Fuel Injection	Electronic Port Fuel Injection
Ignition System	Electronic Distributorless Ignition	Electronic Ignition
Catalyst (Production)	Underbody Three-Way Catalyst	Close-Coupled and Underbody Three-Way Catalysts
Chassis Dynamometer:		
Inertia Setting	1644Kg (3525 lbs)	1364 Kg (3000 lbs)
Road Load @ 50 mph	5.7 kW (7.3 hp)	4.3 kW (5.7 hp)

[a] Odometer mileage at start of SwRI testing.

1990 Buick LeSabre



1990 Toyota Celica

FIGURE 5. DEMONSTRATION VEHICLES FOR ELECTRICALLY-HEATED CATALYST CONVERSIONS

A total of three catalysts, therefore, were obtained for this study. Descriptions of the electrically-heated catalysts are given in Table 25 and a photograph of the one used on the Buick is shown in Figure 6. The other electrically-heated catalysts were similar in appearance.

C. Heating Controllers

Heating control for the electrically-heated catalysts was obtained with on-vehicle MOSFET (metal-oxide semiconductor field-effect transistor) semiconductor-based controllers. The power controllers modulate electrical energy based on a temperature feedback from the electrically-heated catalyst and voltage feedback from the battery. The controllers supply electrical power to the catalyst if the bed temperature is below (or drops below) the design setpoint (approximately 370°C for the LeSabre and Celica applications). Power to the catalyst is limited if the battery voltage goes below a minimum threshold. A bank of 18 MOSFET switches within each controller regulates power on-time by pulse width modulation operating at a frequency of 60 Hertz. Power levels can be regulated from 0 to over 99 percent using pulse width modulation. A photograph of a power controller is given in Figure 7. Supplemental information on the electrically-heated catalyst power controller can be obtained from the manufacturer's product manual.(22)

D. Air Injection Pumps

For the demonstration vehicles, air pumps are required for a complete on-vehicle electrically-heated catalyst control system. Secondary air provides the required oxygen for control of cold-start HC and CO emissions. Air pumps were installed on the LeSabre and Celica. Initial air pumps had a nominal flowrate of 160 liters per minute (L/min) at 12 volts direct current when measured with a volumetric flow gas meter dumping to atmosphere. Later in the study, while at the ARB, the initial air pumps were replaced with high-flow units that had a flowrate of over 300 L/min. The vehicle air pumps were experimental prototypes and were purchased for this study.

Air injection ahead of the electrically-heated catalyst is required only for a short period following the cold start. Some applications, such as the LeSabre, may exhibit additional emission control with a brief period of hot-start air injection. For the LeSabre and Celica applications at SwRI, air injection was started at engine cranking and continued for 50 to 75 seconds following the cold-start. Hot-start air injection times ranged from 0 to 20 seconds, depending on the air schedule being investigated. The time-based air injection was controlled by a manual on-off switch for more flexibility during early research calibration studies. An automatic time-based air control switch was incorporated into the power controller by the catalyst manufacturer following the initial testing portion of this demonstration at SwRI.

Photographs of the SwRI-installed air pumps on the LeSabre and Celica are given in Figure 8. The air pump was located within the engine compartment on the Buick, while for the Toyota, it was mounted behind the front bumper because of space limitations.

E. Air Injection Management Valves

Solenoid-operated valves were used to manage the air injection. The air management electrical valve opened when the pump was activated to allow air flow to the exhaust system, and closed when the pump was deactivated to prevent exhaust leaks and damage to the

TABLE 25. ELECTRICALLY-HEATED CATALYST DESCRIPTIONS

Electrically-Heated Catalyst	Vehicle Application		
	Buick LeSabre	Toyota Celica	Toyota Celica
Model Number	10-9	10-7	10-10
Serial Number	004	003	008
When Used	EHC tests L-H-02 through LS-AH-16	EHC tests C-AH-02 through C-VAH-24	EHC tests C-VAH-25 through CS-VAH-27
Substrate:			
Material	Stainless Steel	Stainless Steel	Stainless Steel
Thickness	0.0016 inch	0.0016 inch	0.0016 inch
Core Geometry:			
Cell Density	520 cells/in^2	520 cells/in^2	520 cells/in^2
Wall Thickness	0.0017 inch	0.0017 inch	0.0017 inch
Core Frontal Area	11.88 in^2	8.27 in^2	12.87 in^2
Core Length	2.00 inches	1.75 inches	2.18 inches
Coating:			
Washcoat Type	Alumina/Ceria	Alumina/Ceria	Alumina/Ceria
Washcoat Loading	28 mg/in^2	28 mg/in^2	28 mg/in^2
Fresh Surface Area	@ 200 m^2/gram	@ 200 m^2/gram	@ 200 m^2/gram
Precious Metals:			
Precious Metal Types	Platinum/Rhodium	Platinum/Rhodium	Platinum/Rhodium
Loading (combined)	40 gm/ft^3	40 gm/ft^3	40 gm/ft^3
Precious Metal Ratio	5 to 1	5 to 1	5 to 1
Electrical Data:			
Actual Voltage, volts	7.12	7.34	6.81
Actual Current, amps	769	757	780
Heating Duration	15 seconds	15 seconds	15 seconds
Temperature at 15 sec.	330 °C (526°F)	354°C (670°F)	273°C (542°F)

Description provided by Camet Co.
EHC - Electrically-heated Catalyst

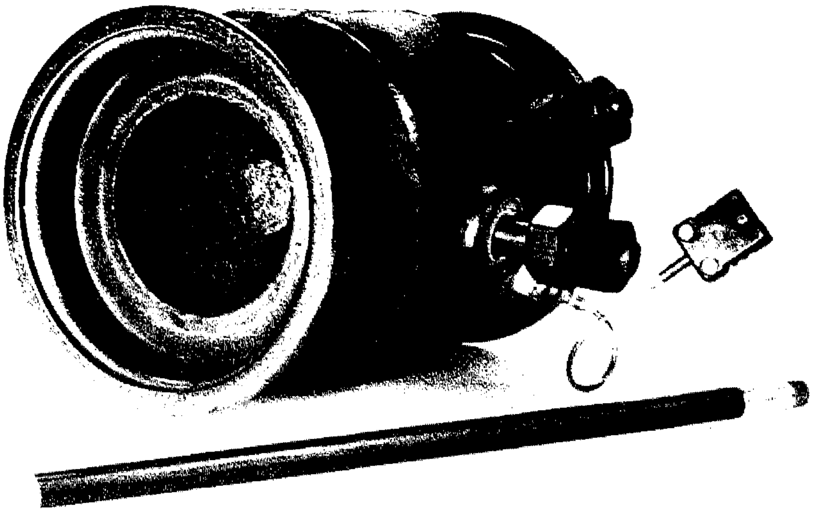


FIGURE 6. ELECTRICALLY-HEATED CATALYST

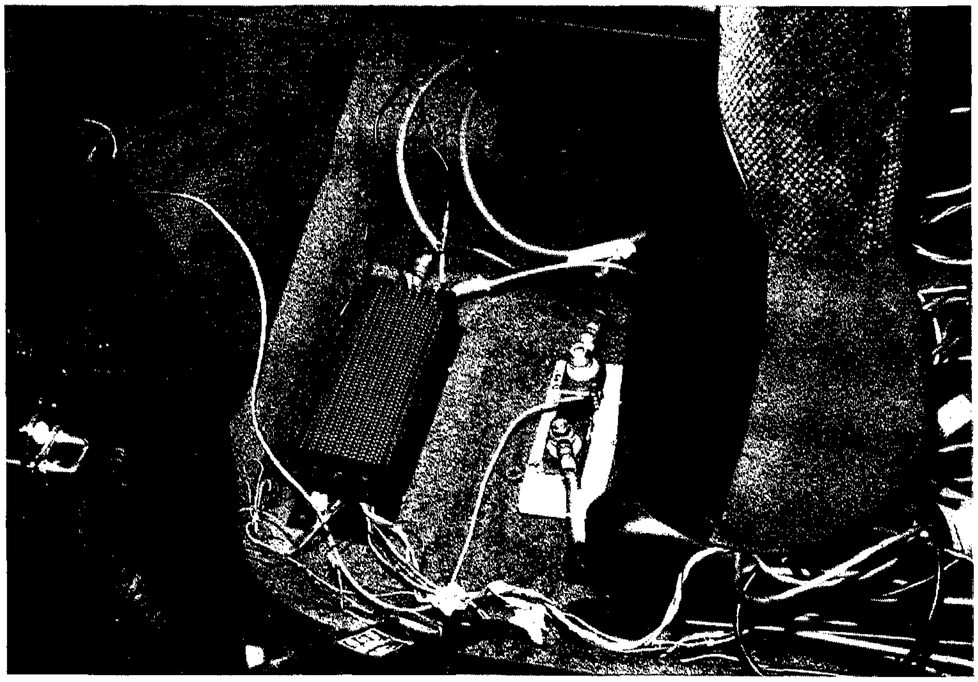
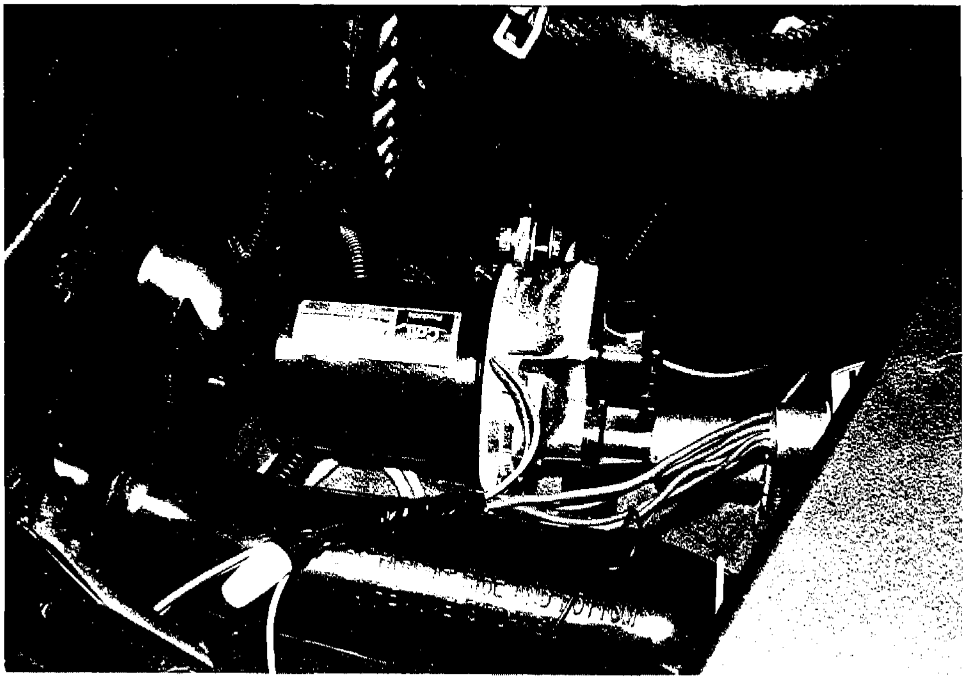
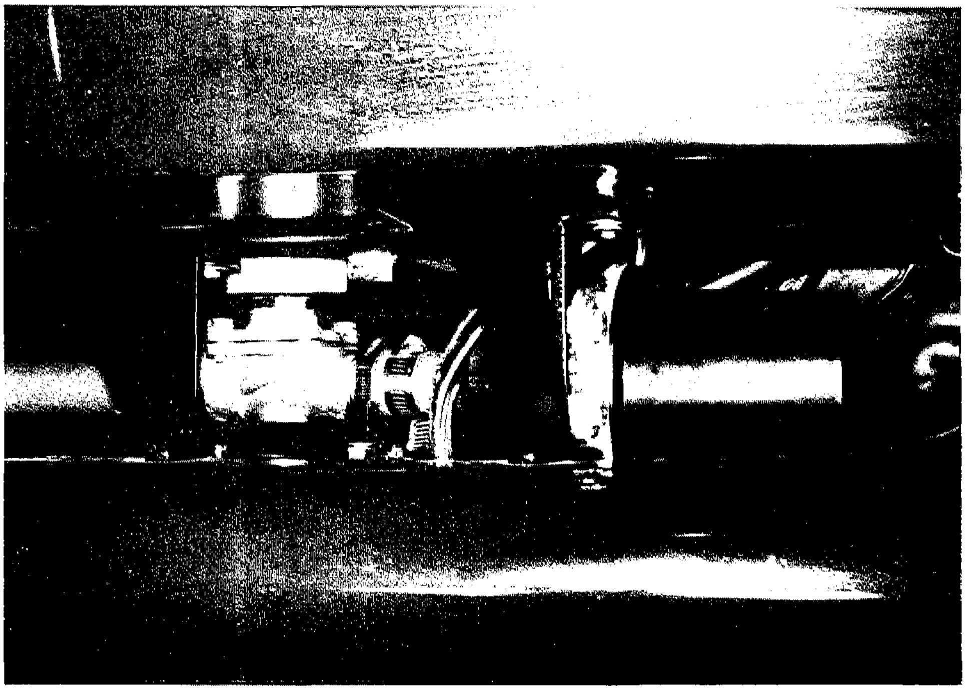


FIGURE 7. POWER CONTROLLER FOR ELECTRICALLY-HEATED CATALYST



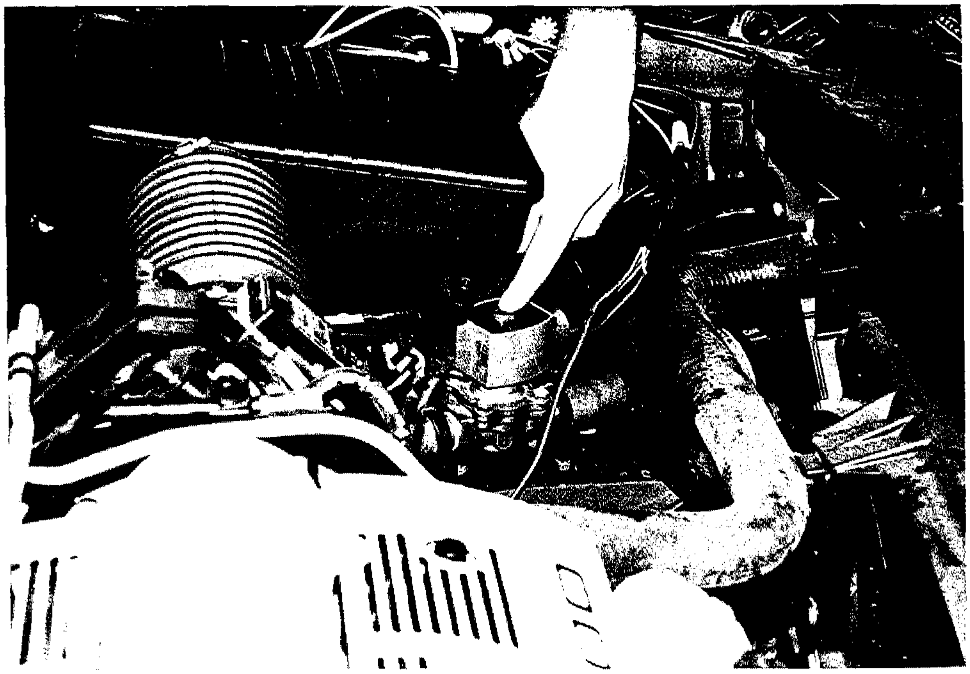
Buick LeSabre Air Pump Installed Under the Hood



Toyota Celica Air Pump and Control Valve Installed Behind Front Bumper

FIGURE 8. AIR INJECTION PUMPS

pump. Check valves were not used in the final design because preliminary experiments revealed that check valves can impose a high resistance to flow and limit the quantity of air injected into the exhaust system. It was also discovered that the check valve evaluated did not seal properly, allowing exhaust gases to escape and air to enter the exhaust system. Measurements confirmed high levels of oxygen in the raw exhaust gas associated with the leaking valve. For these reasons, the electrical solenoid was selected to control the secondary air. A low-cost check valve that sealed properly would have been ideal for this application. The air injection control valve selected for LeSabre and Celica conversions was a 12-volt valve with a 19 mm (¾-inch) flow path. A photograph of the valve installed on the Buick LeSabre is shown in Figure 9.

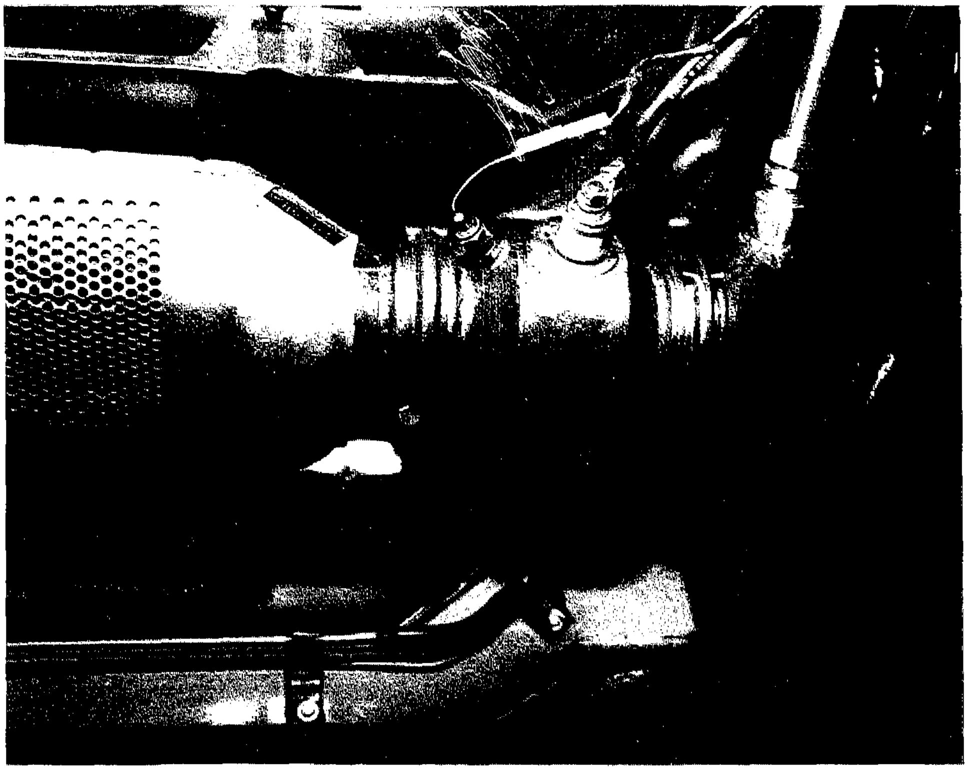


Buick LeSabre

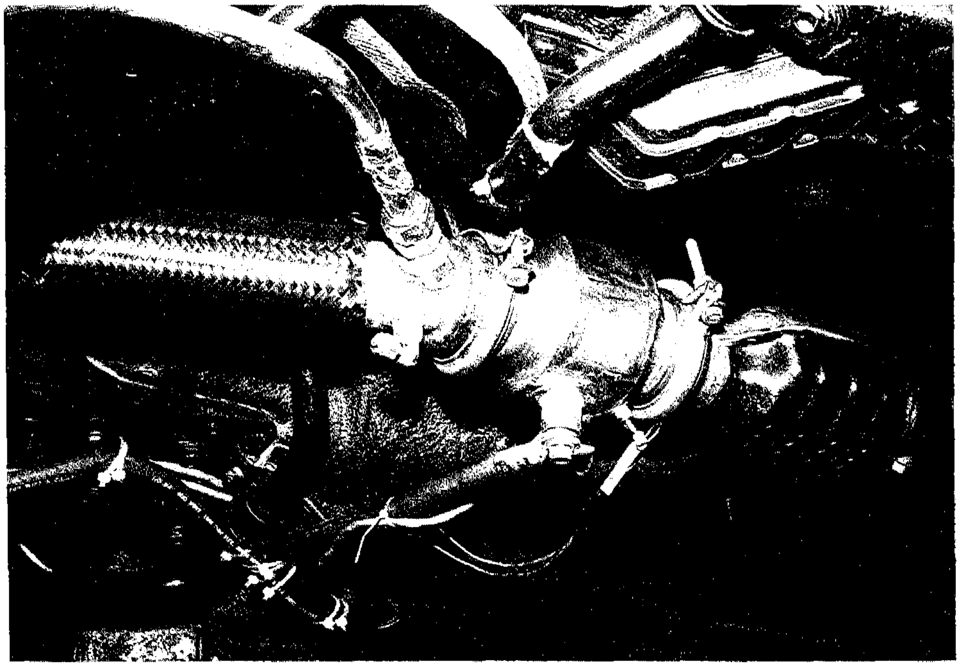
FIGURE 9. AIR INJECTION CONTROL VALVE

F. Air Injection Ports

Air was injected just ahead of the electrically-heated catalyst as can be seen in Figure 10. The entry point for the air was placed downstream from the engine oxygen sensor. Based on air-fuel ratio and continuous exhaust gas measurements, there is no evidence that the injected air changed the actual engine air-fuel ratio. A photograph showing the inside of the exhaust pipe at the point of injection is shown in Figure 11. Steel tubing was used near the hot exhaust pipe.

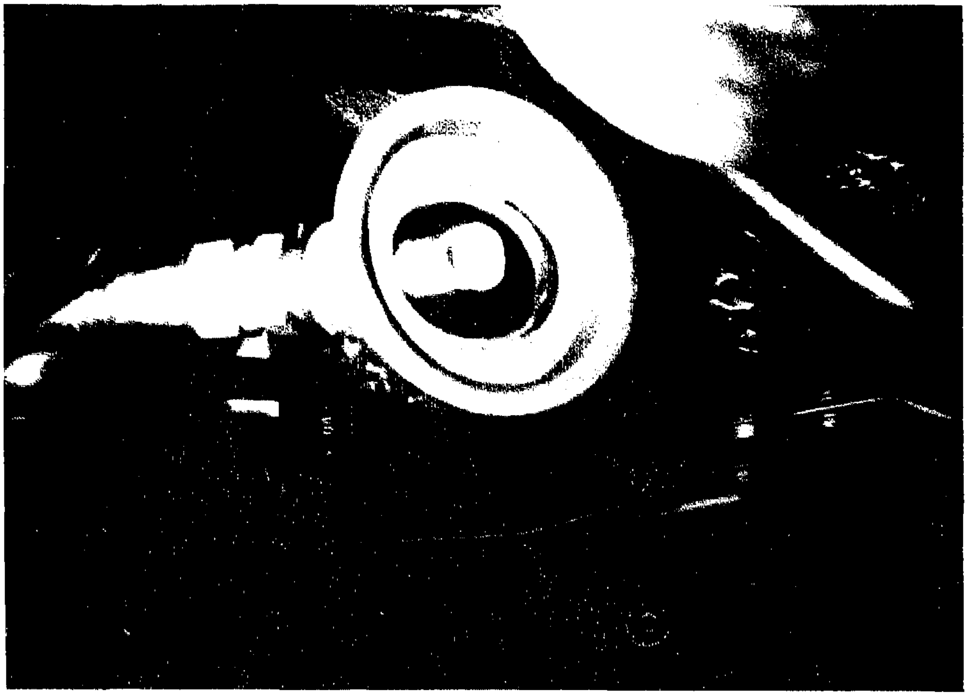


Buick LeSabre



Toyota Celica

FIGURE 10. AIR INJECTED UPSTREAM OF THE ELECTRICALLY-HEATED CATALYST



Toyota Celica

FIGURE 11. AIR INJECTION INSIDE EXHAUST PIPE

The entire air path is open during the injection periods. There are no significant restrictions in the fittings or the solenoid-controlled valve. This was done to permit the greatest amount of flow from the air pump. As will be discussed later, both vehicles actually needed more air injection than the originally installed air pump could provide. At the time the vehicles were originally converted, only the lower volume air electric air pump was available. High-volume air pumps with a nominal flowrate of 300 L/min were incorporated on the Buick and Toyota after the vehicles were delivered to the ARB.

G. Verification of Function

All components used on the electrically-heated catalyst systems on the LeSabre and Celica were checked for proper operation during the build-up stage. Inspections included air injection solenoid control valve operation at reduced battery voltages (such as during catalyst heating), exhaust system integrity, and air pump flowrates. A minor exhaust leak was found and repaired early in the demonstration. Many parameters were monitored to provide proper verification that the entire heated catalyst system was functioning properly.

H. Catalyst Power Consumption

Catalyst preheating temperatures and power consumption were monitored during all emission tests at SwRI. Temperature was measured with a thermocouple placed in the bed of the electrically-heated catalyst. Voltage (drop) was measured directly across the external leads (positive and ground) of the catalyst. Catalyst current was measured with a shunt placed in line between the heating controller and the electrically-heated catalyst. Typical values for these parameters, along with the preheating times and power consumptions, are given in Table 26.

TABLE 26. TYPICAL COLD-START CATALYST POWER CONSUMPTION

Vehicle	Preheat Time, Seconds	Preheat Temperature, °C	Voltage Drop, Volts	Current, Amperes	Power, Watts
Buick LeSabre	30	520	5.4	575	3110
Toyota Celica	30	675	6.3	720	4540
Conducted at SwRI, 1/0 cable, automotive battery					

1. Buick LeSabre

The Buick LeSabre catalyst was typically preheated for 30 seconds before engine cranking. Post-start catalyst electrical heating times were typically 5 to 10 seconds at very low power levels (almost zero). Catalyst preheating times were reduced to 25 seconds following a cable reconfiguration by the ARB. Previous cable changes on the LeSabre showed heating improvements at SwRI.

2. Toyota Celica

The cold-start catalyst power parameters given for the Toyota Celica (Table 26) are for the final catalyst configuration. A smaller catalyst previously tested on this vehicle typically consumed 3850 watts as compared to the 4540 watts of the final configuration. Initial post-start heating on the Celica typically lasted for as long as 60 seconds, putting a considerable drain on the battery. Subsequent heating strategies limited catalyst post-start heating times to 20 seconds, thus minimizing the energy drain on the battery while maintaining catalyst temperature and activity.

The close-coupled production (unheated) catalyst on this vehicle apparently delayed the temperature rise of the downstream electrically-heated catalyst and, therefore, contributed to long 60-second post-start heating times (recall that the catalyst heating times are controlled by the heating controller and are based on catalyst temperature). More detail on the electrically-heated catalyst conversion on the Toyota Celica will be presented in Section IX.

I. Emission Test Procedures

The Buick LeSabre and the Toyota Celica with the electrically-heated catalysts were evaluated using the Federal Test Procedure (FTP) (23). The FTP is an emission certification test procedure used for light-duty vehicles. It uses the Urban Dynamometer Driving Schedule (UDDS), which is 1372 seconds in duration. The UDDS is divided into two segments; the first consisting of 505 seconds and the second consisting of 867 seconds. An FTP is composed of a cold transient 505 and a cold stabilized 867 portion followed by a ten-minute soak and then a hot transient 505. A summary of the duration, driving distance, and average speeds for the FTP segments is given in Table 27.

TABLE 27. FTP DRIVING SCHEDULE SUMMARY

Segment	**Duration, seconds**	**Distance, miles**	**Average Speed, miles/hr**
Transient Phase	505	3.60	25.7
Stabilized Phase	867	3.90	16.2
UDDS	**1372**	**7.50**	**19.7**

For use in studying cold-start exhaust emissions, the first segment (Bag 1) of the UDDS was divided into two parts. Bag 1A was defined as the first 140 seconds of the cold-transient portion of the UDDS. This segment contains the majority of the cold-start emissions produced by the test vehicle. The remainder of the cold-transient segment is designated as Bag 1B (140-505 seconds). The sum of the mass emissions produced in Bags 1A and 1B is equal to the emissions generated during a conventional FTP Bag 1. The FTP driving schedule with the cold and hot transient test segments identified is given in Figure 12.

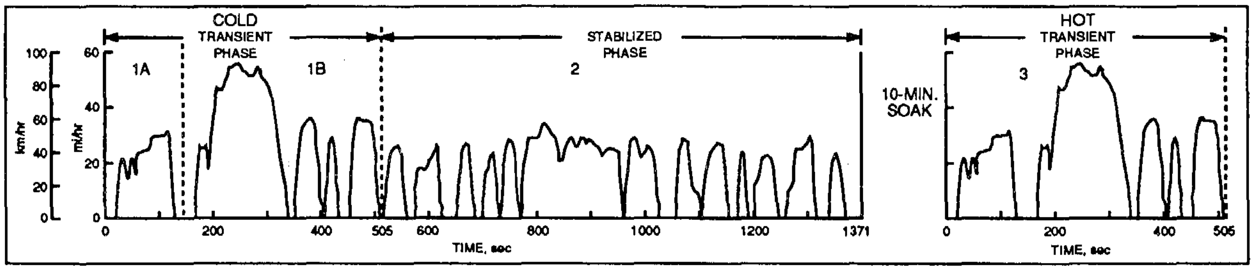


FIGURE 12. FTP DRIVING SCHEDULE SHOWING TEST SEGMENTS

VIII. BUICK LESABRE CONVERSION AND EMISSION ANALYSIS

The 1990 Buick LeSabre was originally equipped with an underbody catalytic converter. A photograph of the original equipment catalyst configuration is shown in Figure 13. The electrically-heated catalytic converter was mounted just in front of the original converter, which had to be moved back approximately two centimeters to accommodate the installation. This configuration allows the heat generated within the electrically-heated catalyst to assist light-off of the main converter. The air pump was mounted under the hood in the engine compartment. An aftermarket battery was used to replace the original battery with one of more cranking capacity. While at SwRI, all LeSabre emission tests were performed with a single underhood battery. The catalyst power controller was originally located behind the front passenger seat. The battery and controller were eventually relocated to the trunk by the ARB.

A total of 16 FTP emission tests were performed on the LeSabre while at SwRI, most of which involved determining an optimum air injection flowrate. Hydrocarbon exhaust speciation data for some of the FTP tests are presented in Section X. Spreadsheets of the catalyst configurations, FTP emission results, and the emissions by test segment (bags) for the Buick LeSabre are located in Appendix J. Vehicle emission test results for each FTP performed on the LeSabre are located in Appendix K.

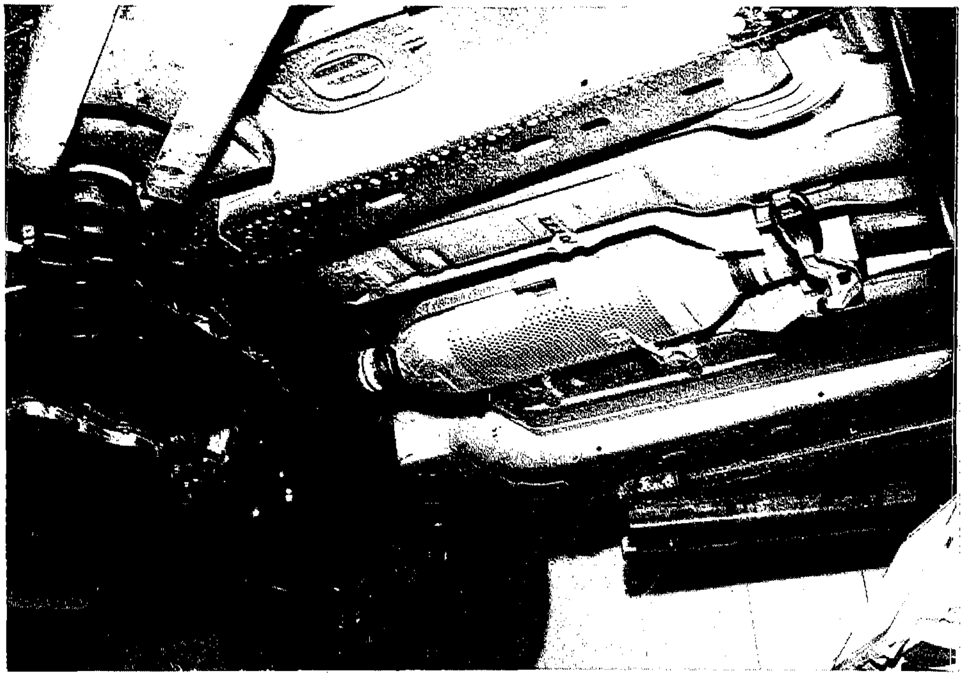
A. FTP Air Injection Calibration

Optimization was performed on the Buick LeSabre to determine the air injection flowrate that provided the best overall emissions. Cold-start and hot-start air injection flowrates were investigated. Flowrates of 170, 300, and 370 L/min (5.9, 10.7, and 13.0 CFM) were compared to the no-flow condition. For these experiments, air was injected ahead of the electrically-heated catalyst with a laboratory air injection pump. A photograph of the laboratory air injection pump is given in Figure 14. This was a production automotive air pump driven by an alternating current (AC) electric motor. All air injection comparison FTP tests were performed with the electrically-heated catalyst in place and heated prior to the engine start. (Note: The air injection output from the laboratory air pump assembly may not be fully representative of an actual on-vehicle pump because the flowrate versus backpressure relationships could be different).

The Buick LeSabre (weighted composite) FTP air injection analysis is given in Table 28. FTP emissions are given for HC, CO, and NO_X with different air injection flowrates. Air was injected ahead of the preheated catalyst for 75 seconds following the cold-start and for 30 seconds following the hot-start.

These selected injection times were based on the periods the fuel system was in open-loop control following engine starting. (Open-loop fuel control typically lasted 100 seconds following cold-starts and 30 seconds following hot-starts.) Air injection began at the time the engine cranked and stopped at 75 or 30 seconds into the FTP. It is concluded that air injection, even a small amount, assists catalytic control of HC and CO.

Oxides of nitrogen emissions increased only slightly, if at all, due to the selected air injection duration (75 seconds for cold-start and 30 seconds for hot-starts). The air injection flowrate had no apparent effect on the NO_X conversion efficiency during these periods. Longer air injection duration would be expected to cause an increase in NO_X emissions.



Single Full-Size Underbody Catalytic Converter

Original Exhaust Pipe Configuration

FIGURE 13. BUICK LESABRE STOCK CATALYST CONFIGURATION

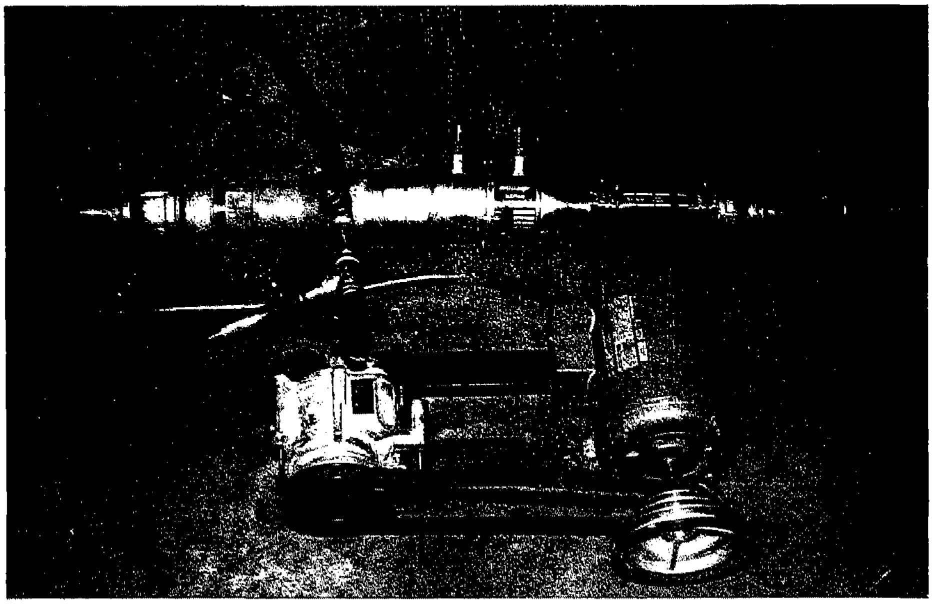


FIGURE 14. LABORATORY PUMP FOR AIR INJECTION FLOWRATE EXPERIMENTS

1. Cold-Start

Table 29 gives the same flowrate analysis for the cold-start portion (Bag 1A) of the FTP. This bag was measured separately to study the cold-start emissions separately from the remainder of Bag 1. Observe that the Bag 1A HC and CO emissions sharply decrease with the addition of air. Carbon monoxide emissions are lowest with the use of 300 L/min (10.7 CFM) air injection. Carbon monoxide emissions then increase slightly with the highest air injection rate. This increase is most likely caused by excess air cooling the catalyst and decreasing catalyst activity.

From the data obtained during the air injection flowrate analysis on the LeSabre, the CO conversion was more responsive to air injection than the HC conversion. Bag 1A CO emissions dropped about 90 percent with air injection (to the preheated catalyst), as compared to a 70 percent HC emission reduction, at an air injection flowrate of 300 L/min (10.7 CFM).

Oxides of nitrogen emissions during cold-start Bag 1A increased roughly 20 percent due to the air injection at 300 L/min (10.7 CFM). The data were scattered, however, and at 370 L/min (13.0 CFM), NO_X emissions were unexpectedly lower, which is presumed to be an anomaly. More research is needed to accurately assess any possible NO_X penalty of cold-start air injection.

2. Hot-Start

Hot-start NO_X emissions (Bag 3) are given in Table 30. Buick LeSabre HC and CO emissions were reduced 50 and 70 percent, respectively, with air injection to the preheated catalyst during the hot-start. The air injection NO_X emission penalty ranged from

TABLE 28. BUICK LESABRE FTP EMISSIONS WITH PREHEATED CATALYST AND AIR INJECTION

FTP Emissions	Air Injection Flowrate, L/min			
	No Air[a]	170	300	370
HC, g/mi	0.08	0.03	0.04, 0.04	0.03
CO, g/mi	0.63	0.26	0.21, 0.18	0.22
NO_x, g/mi	0.18	0.21	0.19, 0.21	0.18

[a]Heat only.
Air Injection: Cold-Start 75 sec.; hot-start 30 sec.
Repeat tests at 300 L/min.

TABLE 29. BUICK LESABRE COLD-START EMISSIONS WITH PREHEATED CATALYST AND AIR INJECTION

Bag 1A Emissions	Air Injection Flowrate, L/min			
	No Air[a]	170	300	370
HC, g/mi	1.50	0.36	0.50, 0.29	0.42
CO, g/mi	9.68	1.96	1.22, 1.09	2.92
NO_x, g/mi	2.24	2.80	2.69, 2.53	1.80

[a]Heat only.
Air Injection for 75 seconds.
Repeat tests at 300 L/min.

TABLE 30. BUICK LESABRE HOT-START EMISSIONS WITH PREHEATED CATALYST AND AIR INJECTION

Bag 3 Emissions	Air Injection Flowrate, L/min			
	No Air[a]	170	300	370
HC, g/mi	0.06	0.03	0.03, 0.03	0.02
CO, g/mi	0.50	0.19	0.28, 0.13	0.11
NO_x, g/mi	0.32	0.36	0.31, 0.40	0.40

[a]Heat only.
Air injection for 30 seconds.
Repeat tests at 300 L/min.

zero to 25 percent during the hot-start. There was some scatter among the data, but they were repeatable enough and sufficiently directional to conclude that there was an optimal air injection flowrate. Although NO_X emissions can increase, catalyst systems and engine calibrations can be optimized to eliminate or minimize this increase (as will be shown).

3. LeSabre Air Injection Rate and Duration

It was decided, with input and approval from the ARB, that the air injection flowrates for cold-start and hot-start emission testing would be 300 L/min (10.7 CFM). The air injection times would be 75 seconds for cold-starts and 30 seconds for hot-starts, based on the open-loop fuel system control times. This air injection flowrate and duration strategy was used for the remainder of the LeSabre emission tests.

B. Comparison to Stock Catalyst Configuration

Tables 31 and 32 summarize the stock catalyst configuration and the electrically-heated catalyst tests with 300 L/min (10.7 CFM) air injection flowrate. For these tests, the engine and fuel system calibrations were original. The electrically-heated catalyst was superior in HC and CO emission control for the FTP. The cold-start NO_X emissions for the (stock) LeSabre could probably be improved by eliminating an extended period of lean operation observed with the original open-loop fuel calibration. When compared to the original equipment catalyst configuration, the heated catalyst system with air injection displayed slightly higher NO_X emissions. A fuel economy penalty, which may be expected with the heated catalyst tests, was not measurable on the LeSabre.

The Buick LeSabre original configuration emissions were improved by the electrically-heated catalyst configuration chosen for this application. The heated catalyst was followed by a full-size catalytic converter, allowing for maximum utilization of the electrical energy expended. The electrically-heated catalyst was located reasonably close to the exhaust manifold. This location allows for quick heating and minimal post-start electrical heating time. Baseline emissions were such that enough HC and CO were present at the cold-start for the electrically-heated catalyst system to have a noticeable effect. This type of vehicle was a good candidate for electrically-heated catalyst emission benefits.

TABLE 31. BUICK LESABRE EMISSIONS WITH STOCK CATALYST CONFIGURATION

Test No.	FTP Emissions, g/mi			Fuel Economy, mi/gal
	NMHC	CO	NO_X	
L-OE-0	0.15	1.36	0.18	19.1
L-OE-00	0.13	1.08	0.19	18.9
L-OE-01	0.16	1.53	0.15	19.9
LS-OE-13	0.13	1.10	0.15	20.2

Conducted at ARB and SwRI.

TABLE 32. BUICK LESABRE EMISSIONS WITH PREHEATED CATALYST AND AIR INJECTION

Test No.	FTP Emissions, g/mi			Fuel Economy, mi/gal
	NMHC	CO	NO_X	
L-AH-06	0.02	0.18	0.21	20.0
L-AH-10	0.02	0.21	0.19	19.8
LS-AH-11	0.04	0.41	0.23	19.9
LS-AH-12	0.03	0.41	0.21	19.6

Air Injection: 300 L/sec; 75 sec. for cold-start, 30 sec. for hot-start.
Conducted at ARB and SwRI.