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Demonstration of Lean NOx Catalytic Converter Technology on a Heavy-Duty Diesel Engine

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

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DEMONSTRATION OF LEAN NOx CATALYTIC CONVERTER TECHNOLOGY ON A HEAVY-DUTY DIESEL ENGINE

Final Report 92-310

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DISCLAIMER

FOREWORD

This project was conducted for the State of California Air Resources Board (ARB) by the Department of Emissions Research, Southwest Research Institute (SwRI). This report is submitted in fulfillment of ARB Contract Number 92-310, "Demonstration of a Non-Additive Lean NO_x Catalytic Converter for Heavy-Duty Diesel Vehicles," by Southwest Research Institute, 6220 Culebra Road, San Antonio, Texas. This program was initiated June 21, 1993, and completed May 25, 1996. It was identified within Southwest Research Institute as Project 08-5744. The ARB Contract Manager for the program was Mr. Hector Maldonado of the Research Division, Sacramento, California. The ARB Project Technical Monitor was initially Mr. Bill Lovelace and finally Ms. Renee R. Kemena, both of the Mobile Source Division, Sacramento, California. SwRI Project Manager and Principal Investigator was Mr. Martin J. Heimrich, Senior Research Engineer, Department of Emissions Research.

Several catalyst manufacturers were contacted and asked to supply prototype diesel NO_x catalysts for this study. Manufacturers submitting catalysts were Allied Signal, Degussa, Engelhard, Johnson-Matthey, and Nippon Shokubai. Caterpillar contributed a model 3116 diesel engine for use in this program. Southwest Research Institute and the California Air Resources Board recognize and appreciate the support these companies gave to this research effort. This report also incorporates the findings of several lean NO_x catalyst studies. The author recognizes those researchers whose published data is referenced in this report.

ABSTRACT

Experimental catalysts for the reduction of oxides of nitrogen (NO_x) were evaluated on a 258-horsepower (192 kW) direct-injection heavy-duty diesel engine. An experimental reductant delivery system provided supplementary hydrocarbons for the reduction of NO_x. Initially, diesel fuel was used as the supplementary reductant. Early experiments resulted in a 10 to 17 percent reduction in NO_x emissions when tested using the heavy-duty engine transient Federal Test Procedure (FTP), and a 30 to 40 percent reduction at selected steady-state catalyst inlet temperatures. A fuel economy penalty of five percent was measured for initial FTP experiments. Emissions of total hydrocarbons (HC), carbon monoxide (CO), and particulate matter (PM) tended to increase during initial experiments with the addition of the supplemental reductant, but these emissions decreased with the incorporation of improved catalyst formulations and reductant fuel spray calibrations. Additional experiments were performed with ethanol and toluene as supplemental NO_x reducing agents. Emissions of nitrous oxide (N_2O) were measured and found to increase when NO_x emissions were reduced with the diesel NO_x catalysts tested. Steady-state emissions tests revealed a very narrow temperature window for NO_x reduction. Initial project results are encouraging, but further catalyst and system development is required to meet future emissions and durability requirements.

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EXECUTIVE SUMMARY

The State of California is considering adopting regulations for low-emission heavy-duty motor vehicles. The heavy-duty vehicle (HDV) category includes mostly diesel-powered vehicles. For diesel vehicles, emissions of oxides of nitrogen (NO_x) are the most critical of the smog precursors and are the most difficult to control with conventional technology. Heavy-duty diesel vehicles are currently estimated to account for 33 percent of the total on-road vehicle NO_x emissions. In the year 2010, with no additional emission controls, it is projected that the heavy-duty diesel vehicle will emit over 41 percent of the total on-road vehicle NO_x emissions.(1) Substantial reductions in NO_x emissions from heavy-duty diesel vehicles are needed.

For gasoline-powered vehicles, the most significant advancement in NO_x control technology has been the three-way catalyst. The three-way catalyst simultaneously controls hydrocarbon (HC), carbon monoxide (CO), and NO_x emissions from gasoline-powered automobiles. These catalyst systems, which operate at a stoichiometric (chemically balanced) fuel-to-air ratio, are able to reduce up to 90 percent of the engine-out NO_x emissions from current-technology gasoline vehicles.

Diesel engines, however, operate at a lean (oxygen-rich) fuel-to-air ratio and do not benefit from conventional catalytic NO_x control technology. Excess oxygen in raw diesel exhaust inhibits the NO_x reduction reaction from occurring on a conventional automotive catalyst. A catalytic converter that can control NO_x in a lean environment is needed to obtain significant reductions in diesel NO_x emissions.

To investigate catalytic NO_x emission controls for heavy-duty diesel vehicles, a research project was conducted at Southwest Research Institute (SwRI) for the California Air Resources Board (ARB). The scope of this project was to focus only on catalytic NO_x emission control approaches for diesel engines. This final report first examines some of the early publications on lean NO_x catalyst systems that were evaluated using actual diesel engine exhaust gas. Following a review of lean NO_x catalyst literature, laboratory development and demonstration of a catalytic NO_x emission control system for diesel engines is described.

At the start of this project, literature was screened for practical and relevant applications of diesel NO_x catalysts, and these references were reviewed. Literature that contained practical diesel NO_x catalyst applications included documented studies that incorporated actual diesel engine exhaust or lean NO_x catalysts supported on automotive-type substrates. Diesel engine and catalyst manufacturers were contacted to obtain current research trends. The objective of this task was to identify leading catalytic NO_x emission control strategies for diesel engines.

Prior to this study, very little research was published that used actual diesel engines and diesel NO_x catalytic converters. Some promising studies had investigated the performance of copper ion-exchanged zeolite catalyst formulations using synthetic exhaust gases and catalyst core reactors. Platinum and non-zeolite catalyst formulations were also identified in the literature. Diesel NO_x catalyst literature is reviewed in Section II of this report.

Catalyst and engine manufacturers were surveyed to learn what catalytic NO_x control approaches were being investigated. This survey found that many engine manufacturers were experimenting with copper and platinum zeolite NO_x catalysts on diesel engines. Most of the major catalyst companies had programs for the development of a diesel NO_x catalyst. Information regarding the formulation of experimental diesel NO_x catalysts, however, was not disclosed by the catalyst manufacturers. Nevertheless, all of the major automotive catalyst companies were asked to supply diesel NO_x catalysts for this program, and several companies did supply catalysts for evaluation under non-disclosure agreements.

As described in the literature review section of this report, the then current-technology diesel NO_x catalyst required a supplementary reductant in order to chemically reduce NO_x. Literature identified ammonia, urea, and hydrocarbons as the most effective NO_x reductants. Hydrocarbon, in the form of diesel fuel, was chosen as the NO_x reductant for this laboratory investigation because it was available as an on-board fuel and did not present the safety problems associated with ammonia.

As a result, a diesel fuel reductant delivery apparatus was developed in this project to test catalysts on a diesel engine. A supplementary hydrocarbon delivery system was required for NO_x reduction because the diesel engine does not emit enough hydrocarbons for the chemical reduction of emitted NO_x.

Diesel NO_x catalysts were evaluated on a Caterpillar 3116 diesel engine with an experimental diesel fuel spray apparatus providing supplemental hydrocarbon. Many technical difficulties were encountered. The catalysts were found to have a very narrow temperature window of NO_x reduction, resulting in low NO_x conversion efficiencies when tested over the heavy-duty engine transient Federal Test Procedure (FTP). Initially, the supplemental fuel delivery system failed to operate properly, particularly at high temperatures. These difficulties prompted a change in technical direction for the remainder of the project. At the direction of the California Air Resources Board, the on-road NO_x catalyst demonstration was canceled, and the remainder of the project redirected to an expanded laboratory effort. The objective of the remainder of the project was to better understand the operational performance of the diesel NO_x catalyst system, including the supplemental reductant delivery system.

The redirected project effort began with the solicitation of improved diesel NO_x catalysts and the redesign of the supplementary reductant delivery system. Catalyst companies were provided with the previous diesel NO_x catalyst test results and the exhaust gas temperature range of the test engine. These data allowed the catalyst companies the opportunity to select more appropriate catalyst formulations for the demonstration.

Additional catalysts were obtained and tested with a redesigned reductant spray system. In general, the new catalysts performed better than the previously tested catalysts during steady-state operation. The improvement in catalytic conversion efficiency was primarily the result of the catalysts being evaluated at their experimental optimum NO_x reduction temperature. In addition, the redesigned reductant fuel spray system allowed more control over the HC-to-NO_x ratio of the exhaust gas, resulting in improved catalytic reduction efficiencies. Steady-state catalytic NO_x reduction efficiencies were measured as high as 24 to 30 percent (at selected temperatures) with some of the catalysts tested. Two very active catalyst formulations evaluated together (in a parallel configuration) resulted in a 30 to 40 percent NO_x reduction efficiency. A summary of selected diesel NO_x catalyst steady-state test results is given in Executive Summary Table 1.

Transient emission test NO_x reduction results were similar between the first and second group of catalysts. Typical NO_x reduction efficiencies with the addition of a supplementary reductant (diesel fuel) were approximately 14 percent. Higher FTP transient test NO_x reduction efficiencies, as high as 24 percent, were achieved with an excessively large catalyst volume. A summary of transient emission test results is provided in Executive Summary Table 2.

Emissions of nitrous oxide (N_2O) were studied because N_2O is an intermediate product of the chemical reduction of NO_x. Emissions of N_2O were found to increase as NO_x was (partially) reduced. The second group of catalysts tested produced an average of 0.3 gram of N_2O for every 1.0 gram of NO_x reduced. These tests were performed at the temperature of maximum measured NO_x removal. This report covers the current status of diesel NO_x catalytic converter performance, and concludes with general requirements for the successful development of a catalytic NO_x emission control system for mobile diesel engines.

EXECUTIVE SUMMARY TABLE 1. SELECTED DIESEL NO_x CATALYST STEADY-STATE EMISSION TEST RESULTS

Catalyst	Catalyst Inlet Temperature,°C	Supplemental Reductant	Feedgas HC/NO_x Ratio [a]	Exhaust Gas Space Velocity, h^{-1}	Maximum NO_x Reduction Efficiency, %
DG-2	210	Diesel Fuel	11	40,000	30
DG-2	220	Diesel Fuel	13	40,000	30
PS-1	220	Diesel Fuel	11	40,000	24
PS-1	220	Diesel Fuel	8	40,000	22
ORP	220	Diesel Fuel	11	40,000	19
JM2	210	Diesel Fuel	7	20,000	30
JM1+JM2(P) [b]	180	Diesel Fuel	8	10,000	30-44
JM1+JM2(P) [b]	180	Ethanol	---[c]	10,000	30
220+221(S) [d]	260	Diesel Fuel	8	20,000	17

[a] Feedgas HC/NO_x ratio measured as C_1/NO_x by volume at catalyst inlet temperature specified.

[b] (P) - Catalysts configured in parallel.

[c] See footnotes, Table 37, page 73.

[d] (S) - Catalysts configured in series

EXECUTIVE SUMMARY TABLE 2. SELECTED DIESEL NO_x CATALYST FTP TEST RESULTS

Catalyst	Total Volume of Catalyst, L	Supplemental Reductant	Caterpillar 3116 Engine Hot-Start Heavy-Duty Transient Emissions, g/bhp-hr				Maximum NO_x Reduction,[a] %
			HC	CO	NO_x	PM	
DG-2	7.0	Diesel Fuel	7.68	0.51	3.80	1.26	14
DG-2	7.0	Diesel Fuel	5.58	0.39	4.09	0.79	---
DG-2	7.0	Diesel Fuel/ Ethanol	1.49	0.28	4.12	0.23	---
PS-1	7.0	Diesel Fuel	8.05	0.66	3.86	1.39	13
PS-1	7.0	Diesel Fuel	0.51	0.53	4.02	0.32	---
PS-1	7.0	Ethanol	3.67	0.32	4.41	0.18	---
ORP	7.0	Diesel Fuel	4.31	0.49	3.83	0.56	14
ORP	7.0	Ethanol	1.32	0.21	4.23	0.17	---
JM1+JM2(P) [b]	28.0	Diesel Fuel	0.69	0.26	3.38	0.24	24
JM2	14.0	Diesel Fuel	0.23	0.39	3.87	0.21	---
JM1+JM2(P) [b]	28.0	Ethanol	0.99	0.11	3.72	0.16	---
220	7.0	Diesel Fuel	4.53	0.77	4.28	0.53	5

[a] Maximum NO_x reduction compared to baseline

[b] (P) catalysts configured in parallel

I. INTRODUCTION

Emissions of oxides of nitrogen (NO_x) are produced by internal combustion engines, and are known to contribute to the formation of smog and ground-level ozone by reaction with hydrocarbons in the presence of sunlight. Motor vehicles produce a significant percentage of the atmospheric NO_x emissions. In particular, heavy-duty diesel vehicles are currently estimated to produce 33 percent of the total on-road vehicle NO_x emissions.(1) To improve air quality in urban areas, the California Air Resources Board (ARB) and the United States Environmental Protection Agency (US EPA) continue to establish increasingly stringent emission standards for new passenger cars and heavy-duty vehicles.

This report first examines some of the early publications on lean NO_x catalyst systems tested using diesel engine exhaust. Following a review of the early lean NO_x catalyst literature, a description of the laboratory evaluation and analyses of catalytic NO_x emission control systems for heavy-duty diesel engines is presented. The scope of this project was to focus only on catalytic NO_x emission control approaches for diesel engines. A flow chart of the major activities of this project is given in Figure 1.

A. Project Objective

The objective of this study was to develop and test a lean NO_x catalyst system on a heavy-duty diesel engine. Data obtained from this study will be used to determine the feasibility of application of lean NO_x catalyst systems to heavy-duty diesel vehicles, and the associated emissions reduction potential of these systems. This information will provide insight into the long-range potential of lean NO_x catalyst-equipped engines to meet low NO_x emission standards.

B. Test Engine and Fuel

A 1993 model year Caterpillar 3116 heavy-duty diesel engine was used to evaluate candidate lean NO_x catalyst formulations. This four-cycle diesel engine was certified to the 1991 emission standards and equipped with a turbocharger and an intercooler. Low-sulfur diesel fuel meeting the 1993 California diesel fuel specifications was used for all emissions tests.

C. Emissions Test Procedures

Catalyst evaluations were performed on the Caterpillar 3116 diesel engine using the Federal Test Procedure (FTP) heavy-duty transient test cycle. Hot-start transient tests were used to compare the performance of different catalyst systems. Steady-state emissions tests were used to compare catalyst performance at specific inlet exhaust gas temperatures or engine operating conditions. Regulated emissions of hydrocarbons (HC), carbon monoxide (CO), NO_x, and total particulate matter (PM) were measured according to the procedures given in the Code of Federal Regulations (CFR). Nitrous oxide (N_2O) emissions were measured using dilute exhaust gas sampling and gas chromatography procedures.

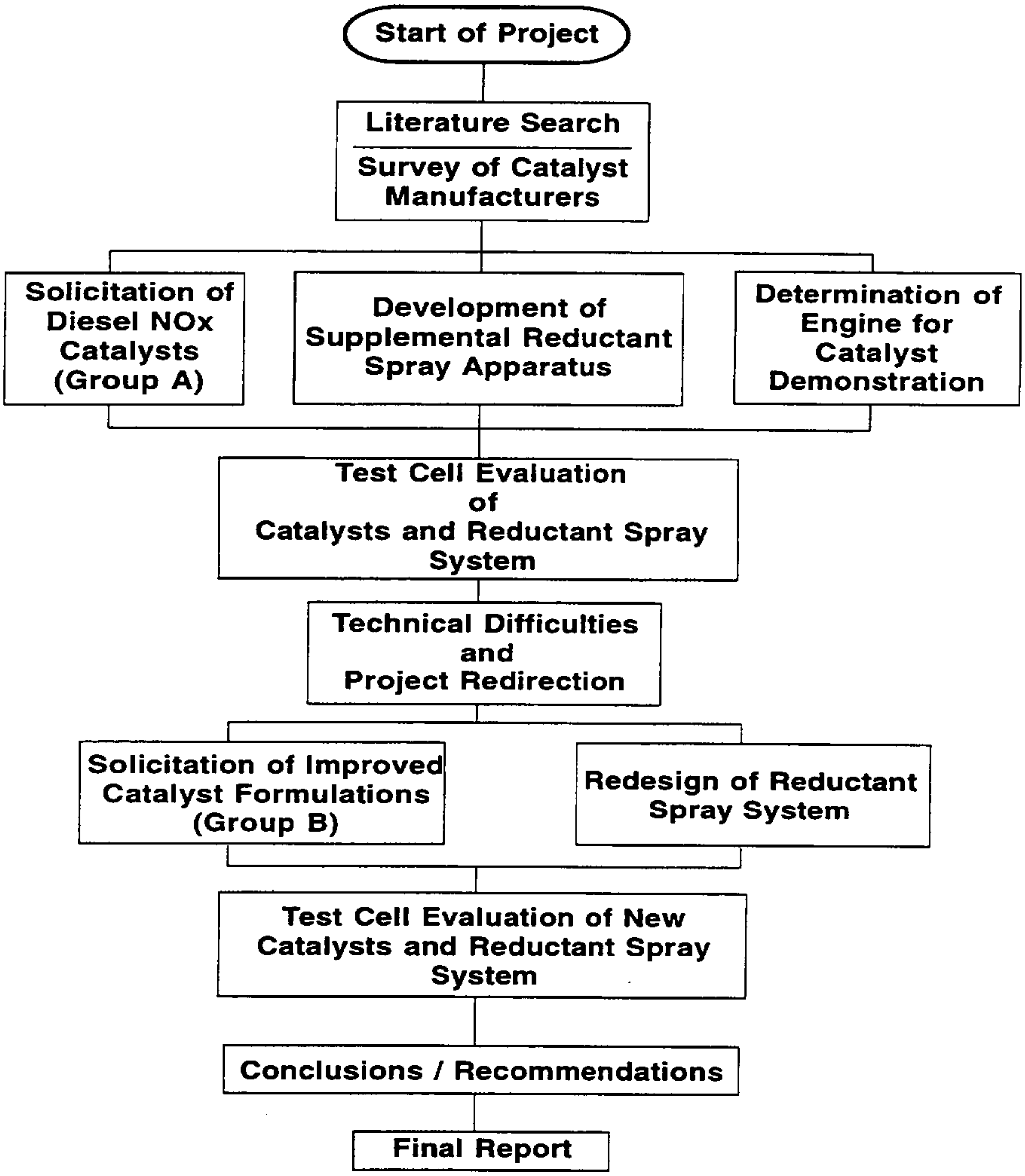


FIGURE 1. PROJECT OVERVIEW

D. Diesel NO_x Catalyst Suppliers

Diesel NO_x catalysts were obtained for use in this project from automotive catalyst manufacturers. Companies submitting catalysts were Allied-Signal, Degussa, Engelhard, Johnson-Matthey, and Nippon Shokubai. Generally, the compositions of the submitted catalysts were not disclosed by the catalyst companies. A total of 22 catalyst test pieces were obtained for this project.

E. Supplementary Reductant Spray System

A supplementary reductant spray system was developed for use with the diesel NO_x reduction catalysts. Diesel engine exhaust gas typically contains too few NO_x reductants (such as hydrocarbons, CO, and hydrogen) for sufficient reduction of NO_x emissions. Supplemental reductants, such as hydrocarbons and hydrocarbon intermediates at the catalyst site, react with NO_x over the catalyst. Hydrocarbon diesel fuel was the primary NO_x reductant investigated in this study, but ethanol, toluene, and combinations of these substances (with diesel fuel) also were tested. High-temperature spray nozzles were incorporated in the exhaust system of the demonstration engine to deliver these reductants.

II. LITERATURE SEARCH SUMMARY OF DIESEL NO_x CATALYTIC CONVERTER TECHNOLOGY

A. Overview

This literature search summarizes the findings of several of the earlier technical articles on diesel NO_x catalytic converter technology. The purpose of this review is to allow the reader with limited experience in lean NO_x catalyst technology an opportunity to become acquainted with the issues facing the catalyst researcher and the diesel engine designer. In the "Technical Background" section of this literature search, simplified chemical equations are used to define catalytic NO_x removal mechanisms for stoichiometric and lean-burn engine exhaust streams. The "Experiments with Diesel Engine Exhaust" section (Section II.C) provides an overview of studies that have applied experimental lean NO_x catalytic converter technology to diesel engines.

Currently, development of catalytic NO_x control technology for diesel engines is focused on systems that incorporate fuel hydrocarbons as the chemical reducing agent. Copper- and zeolite-based catalysts have been the predominant systems studied to date, but now catalysts containing precious metals are being investigated. Observed NO_x reduction efficiencies typically ranged from 10 to 30 percent on actual engine exhaust systems when exhaust hydrocarbon enrichment strategies were used. Effects of carbon monoxide, sulfur dioxide, and water on NO_x reduction efficiencies are reviewed.

B. Technical Background

Catalytic removal of NO_x in engine exhaust can be accomplished by non-selective reduction, selective reduction, and decomposition. An example of non-selective reduction is the three-way catalytic converter used in current-technology gasoline-powered automobiles. Three-way catalytic converters simultaneously control emissions of HC, CO, and NO_x. Engine-out NO_x emissions can be reduced by up to 90 percent in stoichiometric exhaust, because there is essentially no excess oxygen (O_2) following combustion. In this environment, NO_x emissions are chemically reduced using exhaust CO, HC, hydrogen (H_2) and other combustion products as shown in Equations 1 through 3.(2) In these equations, "CH_2" is used to represent exhaust hydrocarbons. This process is termed "non-selective" catalytic reduction because hydrocarbons, CO, or H_2 can all be NO_x reducing agents.

NO_x Reduction in Stoichiometric Exhaust
(Non-Selective Catalytic Reduction)

$$2\,NO + 2\,CO \rightarrow 2\,CO_2 + N_2 \qquad [1]$$
$$6\,NO + 2\,CH_2 \rightarrow 2\,CO_2 + 2\,H_2O + 3\,N_2 \qquad [2]$$
$$2\,NO + 2\,H_2 \rightarrow N_2 + 2\,H_2O \qquad [3]$$

Traditional three-way catalytic converters, however, do not control NO_x emissions in oxygen-rich exhaust at normal exhaust system temperatures. Historically, catalytic reduction of NO_x emissions in lean exhaust has been accomplished using ammonia (NH_3) or some other reducing agent injected into the exhaust, often into the catalyst bed.(3,4) This process of using a specific reducing agent is referred to as "selective" catalytic reduction (SCR) and is commonly used to control NO_x emissions from stationary sources. With SCR, reducing agents, such as ammonia, preferentially react with NO_x in lean exhaust. Ideally, NO_x emissions are chemically reduced to form nitrogen and water, as represented in Equation 4.(5)

Selective Catalytic Reduction with NH_3

$$4\ NO + 4\ NH_3 + O_2 \rightarrow 4\ N_2 + 6\ H_2O \qquad [4]$$

Ammonia injection, however, does not appear to be practical for controlling NO_x emissions from mobile sources, because ammonia is not commonly accepted as a safe and practical on-board fuel. Furthermore, unless carefully metered, the ammonia itself can be emitted during transient operation as an undesirable pollutant. This emission of reductant is referred to as "ammonia slip" in stationary source parlance.

Reduction of NO_x emissions also can be accomplished using hydrocarbons as the reducing agent.(5,6,7) This process is also termed "selective" catalytic reduction when hydrocarbons, or their intermediate products produced through partial decomposition on the catalyst, preferentially react with the NO_x rather than the oxygen. In the case of diesel engines, exhaust hydrocarbons are not available in sufficient quantities for complete NO_x reduction. A possible source of additional hydrocarbon reductants is the fuel. There is now a growing body of literature describing concepts and techniques for delivering hydrocarbon fuel as a reductant to a lean NO_x catalyst (some of these concepts will be discussed later in this report). The chemical reduction of NO_x, using a hydrocarbon reductant, is given in Equation [5].(8)

Selective Catalytic Reduction with Hydrocarbon

$$2\ NO + CH_2 + \tfrac{1}{2}\ O_2 \rightarrow N_2 + CO_2 + H_2O \qquad [5]$$

In this equation, "CH_2" is used to represent exhaust gas hydrocarbons. Exhaust gas and engine fuel hydrocarbon constituencies are known to be very different; therefore, these chemical relationships may not adequately represent the real situation.

Chemical "decomposition" is the ideal mechanism to control NO_x emissions in oxygen-rich exhaust. The chemical decomposition of NO (nitric oxide), the principal constituent of NO_x in engine exhaust, to non-polluting compounds is given in Equation [6].

NO_x Decomposition

$$2\ NO \rightarrow N_2 + O_2 \qquad [6]$$

Decomposition of NO_x is thermodynamically favorable at temperatures below 900°C, but the activation energy required for this reaction in engine exhaust is too high without the use of a catalyst. Several catalysts promote this reaction at temperatures below 600°C, but none of these have sufficient activity or durability to be practical.(5,6) Catalytic removal of NO_x by decomposition is inherently simpler than by chemical reduction, because no reducing agent is required. The decomposition of NO_x suggests an emission control strategy that is independent of exhaust gas composition or reductant injection systems.

The focus of this report is to review catalyst technologies that reduce NO_x in diesel exhaust using added hydrocarbon as the reducing agent (selective catalytic reduction with hydrocarbon). Other reducing agents, such as ammonia or urea, are not discussed further because the use of these added compounds is beyond the scope of this study, as initially defined by the Air Resources Board. Two catalyst technologies that have been discussed in the literature are the copper ion exchanged ZSM-5 zeolite and the platinum impregnated zeolites. Other technologies identified in the literature include copper impregnated alumina. These technologies are covered in the following review.

C. Literature Survey -- Experiments with Diesel Engine Exhaust

In a study by Heimrich, et al(9), lean NO_x catalyst cores were prepared in the laboratory and evaluated in diesel engine exhaust. Experimental diesel NO_x catalysts were prepared by coating zeolite powders onto a ceramic catalyst support. Sodium cations (Na^+) in the zeolite were exchanged with copper cations (Cu^{2+}) to increase catalytic activity. The copper ion exchange procedure was developed by Iwamoto.(6) Three copper zeolite catalysts were investigated, with the primary difference in the formulations being the type of zeolite. A copper-mordenite zeolite catalyst demonstrated NO_x reduction efficiencies of 95 percent while previously-adsorbed diesel exhaust gas hydrocarbons were available on the zeolite. When the previously-adsorbed diesel exhaust gas hydrocarbons were consumed, NO_x reduction quickly decreased, as shown in Figure 2. A copper ZSM-5 zeolite catalyst demonstrated longer periods of NO_x reduction, albeit at a lower conversion efficiency of approximately 50 percent. A copper Y-type zeolite catalyst sustained a modest level of NO_x conversion activity for the periods tested. All experiments were conducted with an NO_x inlet concentration of 200-300 ppm. This reference shows that exhaust hydrocarbons are an effective NO_x reductant (when they are used efficiently, and are available in sufficient quantities).

A supplemental hydrocarbon (ethylene) was added to the exhaust stream in an attempt to improve NO_x conversion efficiency. Ethylene addition improved NO_x conversion efficiency from 10 to 50 percent on one formulation tested.(9,10) Remarkably, the catalyst-out hydrocarbon concentration did not exceed the engine-out hydrocarbon concentration for an extended range of ethylene addition. That is, hydrocarbon addition to the exhaust gas did not result in increased hydrocarbon emissions with the catalyst tested. This finding is extremely important if fuel addition is considered as a supplemental NO_x reductant.

Space velocity experiments showed decreasing NO_x conversion efficiency at space velocities greater than 30,000 per hour (h^{-1}).(10) These results suggest a proportionally larger catalyst volume than typically used for gasoline engines.

Initial catalyst characterization efforts identified a method to determine excess copper deposition on the surface of ion-exchanged zeolite catalysts. Scanning electron microscopy (SEM) using a backscattered electron imaging (BEI) detector and x-ray EDS (energy-dispersive spectroscopy) were used to study copper impregnation.(10)

Engler, et al(11), conducted a thorough investigation of lean NO_x catalyst performance under diesel exhaust gas conditions. Catalysts consisted of activated zeolites impregnated with the Groups IB and VIII elements of the Periodic Table. In this reference, the influences of exhaust hydrocarbon concentration, hydrocarbon species, carbon monoxide, sulfur dioxide, and water on catalytic NO_x reduction were reported. Thermal stability and catalyst poisoning were also studied. Some of these test results are discussed in the following paragraphs.

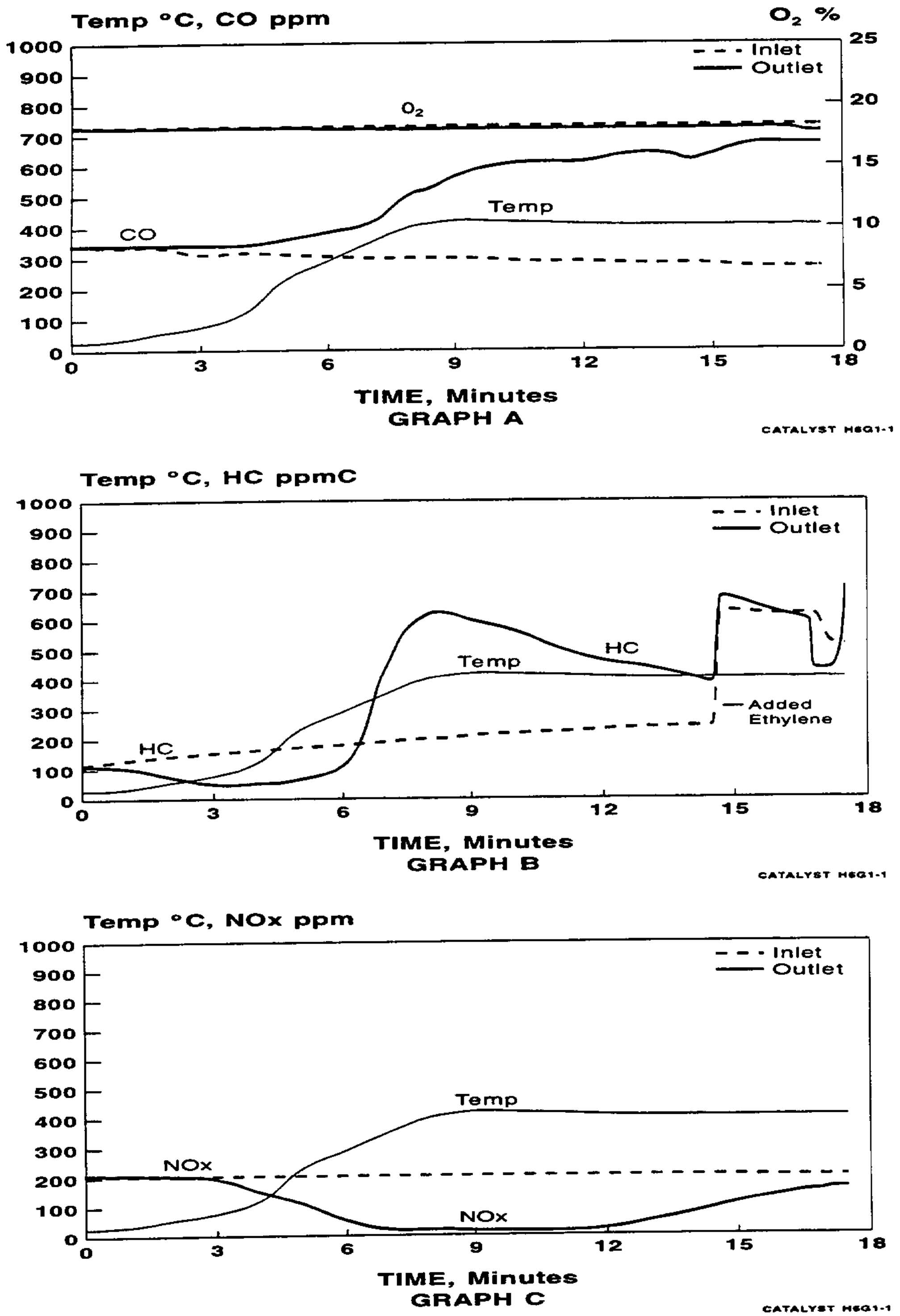


FIGURE 2. EMISSIONS RESPONSE FOR A CU-MORDENITE CATALYST ON A BENCH REACTOR USING DIESEL ENGINE EXHAUST

Calculated equilibrium constants show that several NO_x decomposition and NO_x reduction reactions are thermodynamically possible.(11) Diesel engines, however, seldom provide enough gaseous hydrocarbons for the reduction of NO_x. By assuming a stoichiometric reaction of NO_x with available hydrocarbons, it would appear that for a diesel engine, it would be necessary to increase the concentration of exhaust hydrocarbons to obtain maximum NO_x conversion. This increase can be accomplished with a diesel engine fuel injector system modified to produce higher engine-out HC emissions.(11,12) An alternate approach is the injection of diesel fuel, upstream of the NO_x converter.(11,13) Reaction mechanisms for NO_x reduction proposed by Inui, et al(14) and Iwamoto, et al(15) are summarized again by Engler.(11)

Experimental catalysts were prepared by coating cordierite honeycombs, followed by impregnation with salts of the active metals. Reported catalyst formulations were prepared with copper (Cu), palladium (Pd), platinum (Pt), rhodium (Rh), gold (Au), silver (Ag), and iridium (Ir). Catalysts were aged both in an oven and on an engine.

Catalyst bench test performance results clearly show that the metals used for impregnation have a significant influence on the NO_x reduction efficiency. Peak catalyst performance (adapted from data reported in Reference 11) is summarized in Table 1. Notice that after laboratory oven aging, only the platinum sample showed stable NO_x reduction. The platinum impregnated zeolite catalyst was shown to simultaneously control emissions of HC, CO, and NO_x.(11)

TABLE 1. CATALYTIC NO_X REDUCTION EFFICIENCY

Zeolite Catalyst Element	Fresh Catalyst		Aged Catalyst	
	Temperature, °C	Conversion Efficiency, %	Temperature, °C	Conversion Efficiency, %
Cu	375	85[a]	425	55
Pt	225	55[b]	225	50
Rh	225	40[b]	---	0
Ir	350	25	400	20
Ag	375	35[a]	400	10
Au	375	30[a]	400	10
Pd	225	20	275	10

[a] Negative CO-conversion rate (CO was produced)
[b] Simultaneously controlled NO_x, HC, and CO
Adapted from Engler(11)

The influence of exhaust gas space velocity on the platinum impregnated catalyst(11) is compared with that of previous NO_x catalysts in an unsupported (powder) form.(16,17) These early catalyst investigations concluded that NO_x reduction decreased dramatically with increasing space velocities. Engler estimates his catalysts, in the monolithic form, were evaluated at a space velocity 15 times greater than the unsupported catalysts in previous studies. Data suggest that a good compromise between high reduction efficiencies and high space velocity can be obtained at space velocities between 40,000 h^{-1} and 60,000 h^{-1}.

The Engler and other studies demonstrated that exhaust gas HC concentration and constituency influenced NO_x reduction efficiency. Increased HC concentrations tended to increase the NO_x reduction efficiency while shifting the maximum NO_x conversion point to slightly higher temperatures. Reduction of NO_x was shown to be more efficient with olefinic hydrocarbons than paraffinic hydrocarbons.(5,6,7,10,11)

Carbon monoxide was shown not to be effective as an NO_x reductant in lean exhaust. An experiment was performed to determine the influence of exhaust CO content on NO_x reduction. Results from a synthetic gas reactor show that while the CO concentration increased from 0 to 700 ppm, NO_x (with an exhaust HC concentration of 30 ppm) decreased only slightly. Thus, carbon monoxide had a negligible effect on NO_x reduction.(11)

Additionally, it was shown that in the absence of oxygen, almost no NO_x reduction was achieved with a platinum-containing zeolite catalyst. This suggests that the partial oxidation of hydrocarbons has an important influence on NO_x reduction.(11) Water was shown to decrease NO_x reduction, but unaged catalysts in a test reactor still exhibited NO_x reduction of 55 percent in exhaust containing 10 volume-percent water (actual diesel exhaust typically contains 5 to 10 volume-percent water). Sulfur dioxide does not directly hinder the reaction, however, synthetic gas tests reveal that the overall catalyst activity decreased due to the adsorption of the poisoning elements sulfur and phosphorus.(11)

A lean NO_x catalyst evaluation was performed using two diesel vehicles and the European ECE vehicle test cycle.(11) During these tests, a constant level of 800 ppm of gaseous hydrocarbons ($C_4H_8/C_4H_{10} = 2/1$) was added to the engine exhaust. The platinum-zeolite catalyst was evaluated following 50 hours of engine bench aging. Significant NO_x reduction was observed for only one of the vehicles.

Vehicle "A" demonstrated a significant NO_x conversion of approximately 23 percent with an unaged catalyst and approximately 19 percent conversion after 50 hours of diesel catalyst aging. In addition to the observed NO_x reduction, particulate and CO emissions were also reduced by 50 percent. The hydrocarbon emission for this ECE test increased by a factor of two because of the addition of fuel in the exhaust system.(11) This increased hydrocarbon emission, or "slip," can be easily corrected with the proper catalyst formulation, as demonstrated by other catalysts tested.

In a paper by Herzog, et al,(12) a summary of NO_x reduction strategies for heavy-duty direct-injection engines was presented. Herzog presented data showing catalytic NO_x control increasing from approximately 17 percent to 30 percent with the use of a modified fuel delivery system. The modified fuel system increased fuel-specific organic soluble particulate emissions and decreased carbonaceous (insoluble) fuel-specific particulate emissions. Although engine fuel injection modifications increased engine-out organic soluble particulate emissions, the catalyst reduced catalyst-out soluble particulate to the same level seen prior to injection modifications. It was not clear what effect the modifications had on engine performance or fuel economy. Temperature at maximum NO_x reduction efficiency shifted from 250°C to approximately 350°C with the modified fuel injection system. Data presented suggest that hydrocarbons and soluble particulates can be used to reduce NO_x emissions, thereby controlling multiple undesirable emissions simultaneously. Modifying the diesel engine fuel system to increase gaseous HC or organic particulate emissions is a possible approach for improved catalytic NO_x reduction.

In February of 1992, Herzog concluded that in spite of very promising initial results, there is a large amount of development work remaining to be done prior to commercialization. Herzog's recommended goals included:

- Expanding the temperature window of high NO_x conversion rates
- Achieving NO_x conversion rates of 50 to 60 percent
- Improving catalyst activity in the presence of sulfur dioxide
- Avoiding the formation of sulfates at higher exhaust temperatures
- Assuring high conversion rates over the lifetime of the engine.

Another method for introducing hydrocarbons to the NO_x catalyst is to use an exhaust auxiliary fuel spray system. Such an approach was taken by Sumiya, et al, and was described in a paper on catalytic reduction of NO_x in diesel engine exhaust.(13) Diesel fuel spray experiments were conducted on a laboratory fixed-bed flow reactor and on an actual diesel engine. Copper-containing catalysts were prepared by impregnating gamma-alumina (γ-Al_2O_3) with aqueous solutions of copper salts. In this paper, laboratory studies of the fundamental interaction between NO_x, oxygen, and hydrocarbons over a copper-containing catalyst was reported, and the mechanism of NO_x reduction by the addition of diesel fuel ahead of the catalyst discussed.

Maximum NO_x reduction efficiencies, from Reference 13, using copper-based catalysts and an experimental fuel spray system on a bench flow reactor are given in Table 2. In the absence of water vapor in the exhaust, a 30 percent NO_x reduction was realized at 400°C with propene (C_3H_6) as the reductant. Reduction of NO_x dropped to 10 percent when water was added to the exhaust stream. Note that the point of maximum NO_x reduction also shifted toward higher temperatures with the addition of water. Using diesel fuel as the reductant, NO_x reduction efficiency increased from 10 percent to 30 percent in exhaust gas containing 10 percent water vapor. Reduction of NO_x improved to 50 percent with higher fuel-to-NO_x ratios.

TABLE 2. FUEL INJECTION EXPERIMENTS ON A BENCH REACTOR

	No Water		Water - 10%	
Reductant	Maximum NO_x Reduction, %	Temperature, °C	Maximum NO_x Reduction, %	Temperature, °C
Propene	30	400	10	450
Diesel Fuel	---	---	30	450
Diesel Fuel	---	---	50[a]	450

[a] Higher fuel-to-NO_x ratio
Adapted from Reference 13

Sumiya studied the NO_x reduction reactivity of individual hydrocarbons and diesel fuel. He ranks the NO_x reduction reactivities of alkanes, alkenes, alkynes, and diesel fuel at 450°C as follows:

NO_x Reduction Reactivity

In the absence of water vapor:

alkynes > diesel fuel > alkenes > alkanes

In the presence of water vapor:

diesel fuel > alkynes > alkenes > alkanes

Note that diesel fuel was the best NO_x reductant in the presence of water vapor. Sumiya suggests that heavy saturated hydrocarbons in diesel fuel are converted to more active hydrocarbons through carbon-carbon bond breaking over the catalyst.(13) These active hydrocarbons react with NO_x with higher selectivity at lower temperature, even in the presence of water vapor.(13) Sumiya states that these results suggest that a further-developed fuel addition technique should result in greater NO_x reduction at lower fuel-to-NO_x ratios at lower temperatures. Sumiya further states improvements in fuel spray technology may possibly result in an effective aftertreatment technology for diesel engines.(12)

Sumiya also studied the removal of NO_x from the exhaust of an actual diesel engine utilizing an exhaust fuel injection scheme. His engine-exhaust catalyst was prepared by coating a ceramic foam substrate with copper containing γ-Al_2O_3.(13) The foam substrate acted as a low-efficiency particulate trap, as well as an NO_x reduction catalyst. Sumiya's engine was run at a constant speed and load. As seen with the catalyst reactor experiments, NO_x reduction efficiency increased with the fuel-to-NO_x ratio. An NO_x reduction of 30 percent at 450°C was achieved with fuel spray in the exhaust system. Sumiya states in his paper that the fuel spray system was subsequently improved to achieve greater NO_x reduction in engine testing at temperatures of approximately 400°C. He attributes the improvements to more effective diesel fuel vaporization. This paper concludes with a proposed system for controlling NO_x and particulates. Advanced NO_x control is suggested by using a microprocessor-controlled diesel fuel spray system that introduces fuel only under high NO_x conditions.

Catalytic reduction of NO_x in diesel engine exhaust was studied on a bench reactor by Konno, et al, and published in 1991.(18) Catalyst formulations prepared in this study were copper-ion exchanged ZSM-5 zeolites (Cu-ZSM-5). Without the use of supplemental hydrocarbons, Cu-ZSM-5 catalysts reduced NO_x by 25 percent at 400°C. When exhaust hydrocarbons were increased, NO_x reduction efficiency increased to 80 percent. Water in the exhaust gas decreased the NO_x reduction efficiency. Oxygen and sulfur appeared to have only a small effect on catalytic NO_x reduction activity. Maximum NO_x reduction was observed at 400°C and did not decrease with space velocities up to 20,000 h^{-1}. These tests were performed using actual diesel engine exhaust with the particulate and water removed.

D. Performance Summary

A summary of the lean NO_x catalyst literature reviewed for this report is given in Table 3. Catalytic reduction of NO_x (by hydrocarbon) has been observed as high as 50 percent on a continuous basis, and as high as 95 percent on a temporary basis (using previously adsorbed hydrocarbon reductants on the catalyst). Supplemental hydrocarbon reductants were required to chemically reduce NO_x. Fuel spray systems were used to deliver hydrocarbon reductants to the catalyst. Detailed information was not available on the fuel spray systems employed.

Many different metals and zeolite structures have been investigated for NO_x reduction in lean exhaust. Initially, the Cu-ZSM-5 zeolite received most of the attention (in the literature) because of its superior performance compared to other early lean NO_x catalyst formulations. Another promising catalyst formulation uses cobalt (Co) as the active metal, but this catalyst needs a higher temperature to operate than the copper-based catalysts. Recently, attention has been focused on developing silica aluminum phosphate-based zeolites that have improved pore structures and better hydrothermal durability.(8,19) Test results on these catalysts, unfortunately, were not available.

TABLE 3. SUMMARY OF DIESEL NO_x CATALYST LITERATURE -- EXPERIMENTAL RESULTS USING ACTUAL EXHAUST

Author	Ref.	NO_x Reduction, %	Catalyst	Space Velocity, h^{-1}	Engine	Reductant	Delivery	Comments
Heimrich (Southwest Research Institute) 1993	9	95	Cu-Mordenite	20,000	Diesel	Adsorbed Exhaust HC	None	Exhaust HCs can be used as Reductants
	9	50	Cu-ZSM-5	20,000	Diesel	Adsorbed Exhaust HC	None	No increased total HC emission
	9	50	Cu-Zeolite	Up to 30,000	Diesel	Ethylene plus Exhaust HC	Bottle	Particulate removed
Engler (Degussa) 1993	11	10-85 (unaged) 10-55 (aged)	Zeolites impregnated with Group IB and VIII elements	40,000 (estimated from unsupported catalysts)	Synthetic Gas	C_3H_6/C_3H_8	None	HC/NO_x = 2400ppmC/ 270ppm
	11	23/19 (aged/unaged)	Pt-Zeolite	Transient Space Velocity	Diesel (IDI)	800ppm C_4H_8/C_4H_{10} (2/1) plus exhaust HC	Bottle	Vehicle test, 50-hour catalyst aging
Herzog (AVL-LIST) 1992	12	17-30	Zeolite	---	Diesel	Fuel	Engine Fuel System	Modified Fuel System, Fuel economy not given
Sumiya (Riken) 1992	13	30/10 (0% water/ 10% water)	Cu-Al_2O_3	15,000	Synthetic Gas	C_3H_6	Bottle	Bench test, HC/NO_x = 5100ppmC/ 800ppm
	13	30/50 (fuel/increased fuel)	Cu-Al_2O_3	15,000	Synthetic Gas	Diesel Fuel		Bench test 10% water, maximum Fuel/NO_x mass ratio = 5
	13	30	Cu-Al_2O_3	---	Diesel	Diesel Fuel	Spray System	Fuel/NO_x mass ratio = 5
Konno (Hokkaido University) 1992	18	25/50 (without/with ethylene)	Cu-ZSM-5	20,000	Diesel	Ethylene	Bottle	Water and particulate removed
	18	80	Cu-ZSM-5	20,000	Diesel	Light oil	Drip	

III. TEST ENGINE AND HEAVY-DUTY ENGINE EMISSIONS TEST PROCEDURE

In this section, descriptions of the test engine and the test cycles used in this study are provided. Engine test data obtained while conducting various experiments during the course of this project are also contained in this section for reference.

A. Test Engine and Fuel

A Caterpillar 3116 heavy-duty diesel engine was selected by the ARB. This engine was selected because it was used in the intended demonstration vehicle for this project, and was calibrated to meet model year 1991 emission standards, shown in Table 4. The Caterpillar 3116 is a turbocharged and intercooled in-line six-cylinder engine with a displacement of 6.6 liters. Table 5 provides a detailed description of the engine.

TABLE 4. HEAVY-DUTY DIESEL ENGINE EMISSION STANDARDS

Model Year (Truck)	Emission Standards, g/bhp-hr			
	NO_x	HC	CO	PM
1989	10.7	1.3	15.5	0.6
1990	6.0	1.3	15.5	0.6
1991	5.0	1.3	15.5	0.25
1994	5.0	1.3	15.5	0.10
1998	4.0	1.3	15.5	0.10

TABLE 5. DESCRIPTION OF TEST ENGINE

Engine Specifications	
Manufacturer	Caterpillar
Model	3116
Year	1993
Fuel	Diesel
Type	Direct Injection 4-cycle
Induction	Turbocharged
Fuel System	Unit injector
Injection Timing	9.6° BTDC
Displacement	6.6 liters
No. of Cylinders	6, In-line
Operating Range	750-2600 rpm
Power output	258 hp (192 KW)

In the test cell, an air-to-water intercooler was used to control intake manifold charge air temperature. Injection timing and valve lash were set to Caterpillar specifications prior to use in this project. Maximum engine torque produced was measured at 1600 rpm, and rated output was 258 bhp at 2600 rpm. Engine operation specifications for this engine were provided by Caterpillar and are given in Table 6. Engine installation in the test cell is shown in Figure 3.

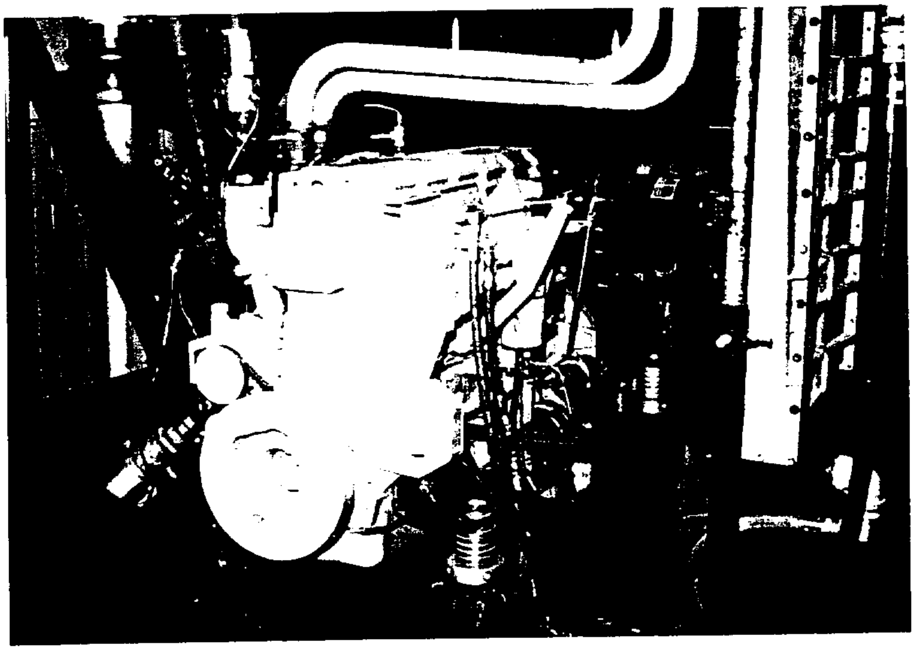


FIGURE 3. CATERPILLAR 3116 ENGINE INSTALLATION IN TEST CELL

Low-sulfur diesel fuels meeting the 1993 California diesel fuel specifications were used for all emission tests in this program. This fuel was purchased from Phillips in two batches, designated by SwRI as test fuels EM-1749-F and EM-1852-F. The sulfur content of these fuels was 0.035 percent by weight, as shown in Table 7. Other fuel properties are given in Appendix A.

B. Heavy-Duty Engine Transient Test

The heavy-duty transient cycle is described by means of percent of maximum torque and percent of rated speed for each one-second interval of a test cycle of 1199 seconds duration. To generate the transient cycle, a full power curve for the engine is obtained from an engine speed below idle to a maximum no-load speed. Data from this "power curve," or engine map, are used with the specified speed and load percentages to produce the transient cycle for the engine. A graphic presentation of the speed and torque commands which constitute a transient cycle is given in Figure 4 for illustration purposes.

TABLE 6. ENGINE TEST SPECIFICATION SHEET

Engine Manufacturer: Caterpillar	Serial No. 2BK30968
Model No.: 3116	AR. No. 612481
Displacement: 6.6 liter	

Item No.	Test Parameter	Baseline	
1	Intake restriction (Transient Cycle)	24	in. H_2O
2	Exhaust restriction (Transient Cycle)	40	in. H_2O
3	Intake restriction (Federal Smoke)	24	in. H_2O
4	Exhaust restriction (Federal Smoke)	40	in. H_2O
5	Rated engine speed	2595	rpm
6	Rated engine power	min. 243 max. 258	hp
7	Fuel rate at rated speed and power	95	lb/hr
8	Fuel temperature at rated speed and power	min. 100 max. 108	°F
9	Rated torque speed [a]	1656	rpm
10	Rated torque [a]	min. 621 max. 687	lb-ft
11	Fuel rate at rated torque speed and torque [a]	69	lb/hr
12	High idle (governed)	min. 2785 max. 2865	rpm
13	Low idle (curb idle)	min. 720 max. 780	rpm
14	Water outlet temperature	185	°F
15	Cranking speed	100	rpm
16	Pressure drop across intercooler	4±2	in. H_2O
17	Air temperature after intercooler	110±5	°F
18	Engine oil, SAE rating	10W40	
19	Engine coolant type	H_2O/Glycol (50/50)	

[a] Factory measures these parameters at 100 rpm over peak torque speed so these values are not peak torque values. They are, however, a speed and torque that were achieved in the factory.

Data provided by Caterpillar, Inc.

TABLE 7. CERTIFICATION DIESEL FUEL ANALYSIS

Item	Analysis
Cetane Number	45.8
Total Sulfur, %	0.035
Hydrocarbon Composition:	
Aromatics, %	31.4
Paraffins, Naphthenes, Olefins	68.6

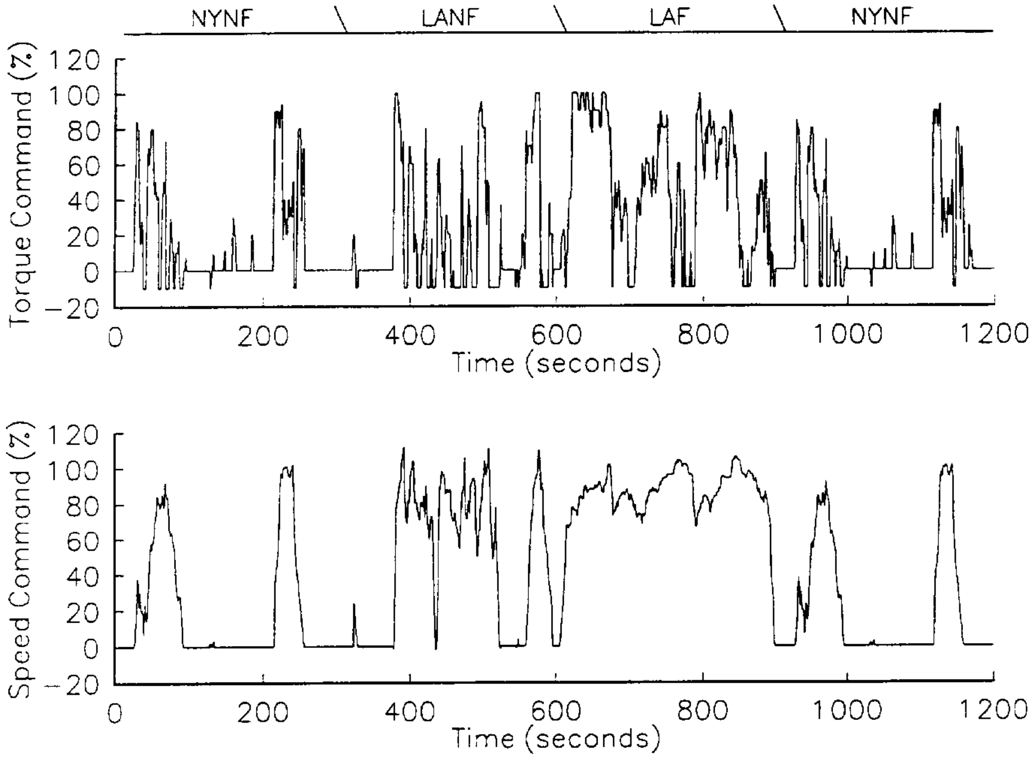


FIGURE 4. GRAPHIC REPRESENTATION OF TORQUE AND SPEED COMMANDS FOR THE TRANSIENT CYCLE FOR HEAVY-DUTY ENGINES

The transient test cycle is made up of distinct and separate segments. These segments are the New York Non-Freeway (NYNF), the Los Angeles Non-Freeway (LANF), and the Los Angeles Freeway (LAF) portions. A complete transient cycle is composed of the sequence of four segments in the following order; NYNF - LANF - LAF - NYNF. A transient test consists of a cold-start transient cycle and a hot-start transient cycle. The same engine command cycle is used in both cases. For the cold-start, the diesel engine is operated over a "prep" cycle, then allowed to stand overnight in an ambient soak temperature of 68°F to 86°F. The cold-start transient cycle begins when the engine is cranked. Upon completion of the cold-start transient cycle, the engine is shut down and allowed to stand for 20 minutes. After this hot-soak period, the hot-start cycle begins with engine cranking.

In order to determine how well the engine followed the transient cycle command, the engine responses are compared to engine commands and several statistics are computed. These computed statistics must be within tolerances specified in the Code of Federal Regulations (CFR). In addition to the statistical parameters, the actual cycle work produced must not be more than 5 percent above, or 15 percent below the work requested by the command cycle. After completion of the cold-start and the hot-start transient cycles, transient composite emissions results can be computed by the following:

$$\text{Transient Test Composite} = \frac{1/7\ (\text{Mass Emissions, Cold}) + 6/7\ (\text{Mass Emissions, Hot})}{1/7\ (\text{Cycle Work, Cold}) + 6/7\ (\text{Cycle Work, Hot})} \quad [7]$$

In this diesel NO_x catalyst test program, only hot-start transient emission tests were performed. Hot-start tests were selected because of the developmental nature of this project. The variety of potential catalyst system configurations required that maximum schedule flexibility be maintained. Hot-start transient tests provided meaningful test results on a wide variety of catalyst configurations. Brake-specific hot-start emissions were calculated as follows:

$$\text{Hot-Start Emissions} = \frac{\text{Mass Emissions, Hot}}{\text{Cycle Work, Hot}} \quad [8]$$

Regulated emissions of HC, CO, NO_x, and total particulate matter were also measured during transient operation according to the procedures given in CFR 40, Subpart N for heavy-duty diesel engine emissions measurement. All instruments were maintained, calibrated and operated as specified in CFR 40. Nitrous oxide (N_2O) emissions were measured using dilute exhaust gas sampling and gas chromatography procedures.

C. Engine Exhaust Temperatures

Engine exhaust temperatures are extremely important to catalytic converters, particularly current-technology diesel NO_x catalytic converters. Diesel NO_x catalysts, unlike conventional catalysts, have a very narrow temperature window of maximum NO_x reduction. A summary of catalyst inlet temperatures for the Caterpillar 3116 engine operating over the heavy-duty engine transient test cycle is given in Table 8. Temperature ranges are separately provided for the non-freeway and freeway portions of the test. The catalyst inlet exhaust gas temperature was actually less than 125°C at the start of the hot test. It stabilized, however, at 125°C during the extended idle period of the initial NYNF segment of the test. The final NYNF segment of the test had an increased catalyst inlet temperature (compared to the initial NYNF cycle) because it followed the more-heavily loaded LAF portion of the heavy-duty transient test.

TABLE 8. CATALYST INLET TEMPERATURES FOR A CATERPILLAR 3116 ENGINE

FTP Heavy-Duty Transient Test	Temperature Range	Suggested Catalyst Design Temperature
Non-Freeway Portions	125°C - 250°C	220°C
Freeway Portion[a]	210°C - 375°C	300°C
Entire Test	125°C - 375°C	--

[a] First New York Non-Freeway portion of the hot-start heavy-duty transient cycle.

Catalysts that performed well in this study were those catalysts designed for maximum NO_x conversion at relatively low temperature (as compared to conventional automotive catalysts). A catalyst system with high NO_x conversion efficiency at 220°C and 300°C was suggested to the catalyst suppliers. A dual-technology catalyst (possibly a dual-bed catalyst design to accommodate different exhaust temperature ranges) may be advantageous to accommodate the exhaust temperature range of transient engine operation.

D. Steady-State Modes and Emissions

Two sets of steady-state modes were selected for the evaluation of diesel NO_x catalysts. The first set of modes was based on the percentage of engine torque at rated speed (2600 rpm) and maximum torque speed (1600 rpm). These steady-state test modes are given in Table 9. These modes, however, resulted in a wide range of catalyst inlet temperatures. Current diesel NO_x catalysts perform best in a narrow temperature window of exhaust gas temperature. To properly study the performance of the diesel NO_x catalyst, a second set of steady-state test modes (determined by catalyst inlet temperature) was established. The temperature-based test modes are given in Table 10. Torque-based test modes were used initially, during the evaluation of Catalyst Group "A." The temperature-based test modes were used for Catalyst Group "B."

E. Inlet Air Flowrates

Inlet air flowrate to the Caterpillar 3116 engine is important in estimating catalyst space velocity. Engine inlet air flowrates are provided for each of the steady-state modes tested. Flowrates for the 11 torque-based modes used with the Group "A" catalysts are given in Figure 5. Flowrates for the 1250 rpm temperature-based modes used with the Group "B" catalysts are given in Figure 6. Engine parameters for the intake air flowrate measurements are provided in Appendix B.

F. Caterpillar 3116 Engine Emissions

Baseline engine emissions for the Caterpillar 3116 engine were determined early in the program. Heavy-duty transient test results are given in Table 11. These baseline test results represent engine-out emission levels, because tests were conducted with an uncoated (inactive) catalyst substrate in the exhaust system. Exhaust system backpressure was set to manufacturer specifications.

Steady-state raw exhaust concentration measurements were made and are given by mode in Table 12. Brake-specific mass emissions were measured for the three steady-state modes that provided (the relatively low) catalyst inlet temperatures of 200°C, 220°C, and 240°C. Steady-state mass emissions are given in Table 13. Both these sets of steady-state emission measurements represent engine-out emission levels. A catalytically inactive substrate was placed in the exhaust to provide engine backpressure simulation.

TABLE 9. STEADY-STATE TEST MODES BASED ON ENGINE TORQUE

Mode Number	Description		Caterpillar 3116 Engine	
	Engine Speed	Percentage of Maximum Torque at Specified Speed	Engine Speed, rpm	Torque, lb-ft
1	Rated Speed	100	2600	535 [a]
2		75	2600	401
3		50	2600	268
4		25	2600	134
5		10	2600	54
6	Peak Torque Speed	100	1600	685 [a]
7		75	1600	514
8		50	1600	343
9		25	1600	171
10		10	1600	69
11	Idle	0	750	0

[a] Approximate torque
Modes used with Group "A" Catalysts

TABLE 10. STEADY-STATE TEST MODES BASED ON CATALYST INLET TEMPERATURE

Mode No.	Catalyst Inlet Temperature, °C	Engine Speed, rpm	Torque, [a] lb-ft
M180	180	1250	104
M190	190	1250	121
M200	200	1250	131
M210	210	1250	145
M220	220	1250	158
M230	230	1250	173
M240	240	1250	186
M250	250	1250	200
M260	260	1250	213
M270	270	1250	227
M280	280	1250	241

[a] Approximate torque required to obtain catalyst inlet temperature
Modes used with Group "B" Catalysts

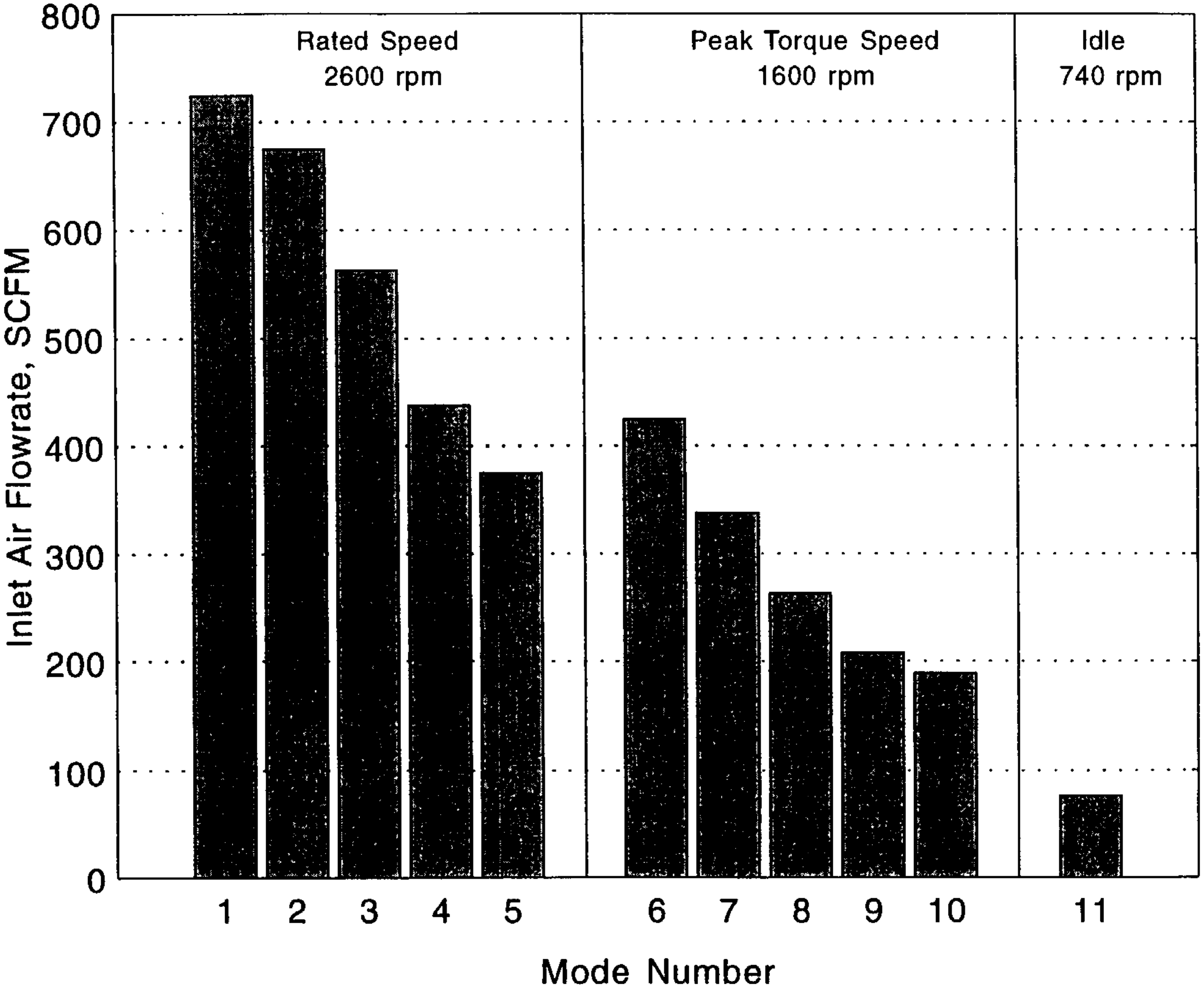


FIGURE 5. CATERPILLAR 3116 ENGINE INLET AIR FLOWRATE AT RATED AND PEAK-TORQUE SPEEDS

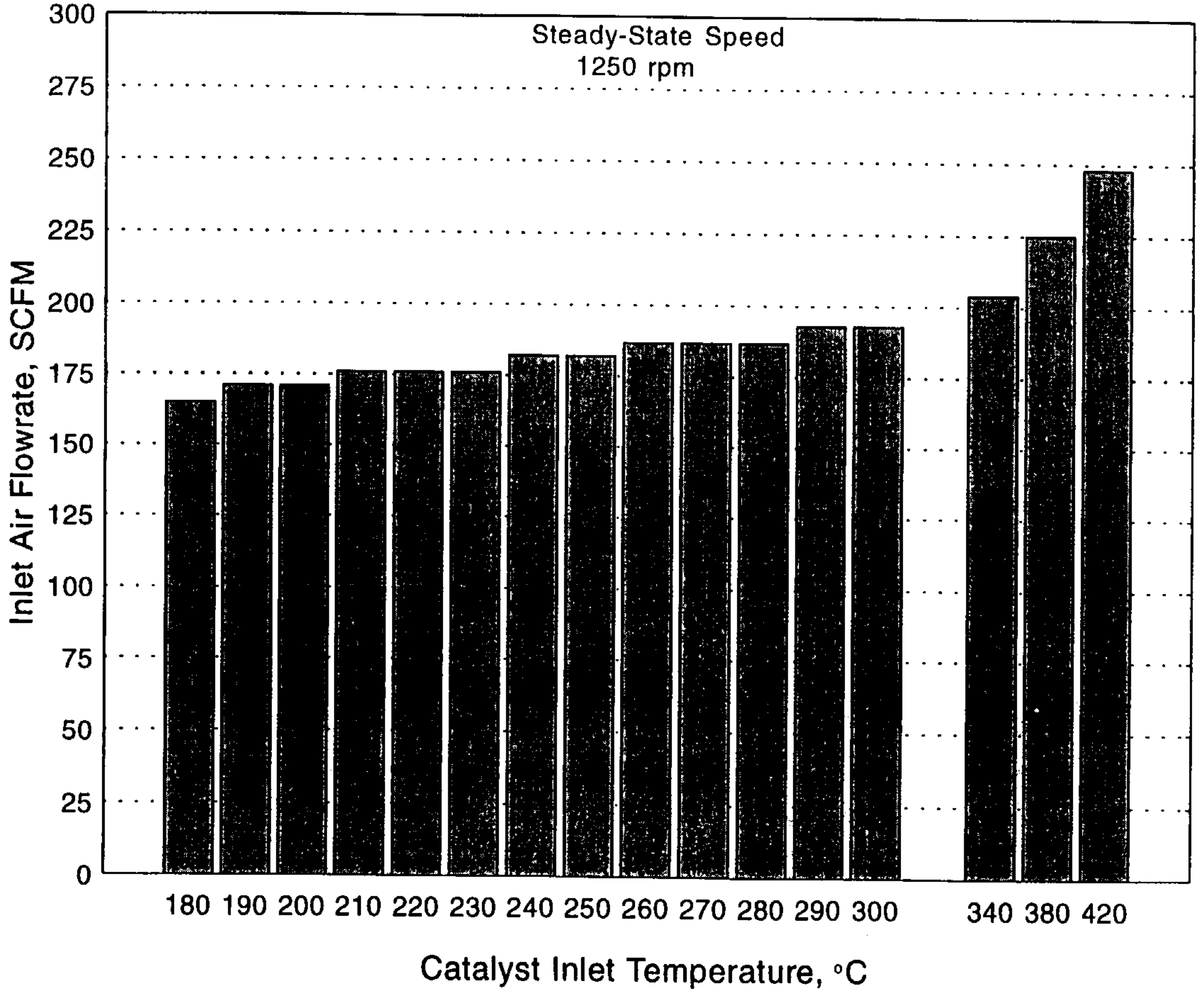


FIGURE 6. CATERPILLAR 3116 ENGINE INLET AIR FLOWRATE AT 1250 RPM

TABLE 11. HOT-START HEAVY-DUTY TRANSIENT BASELINE TEST RESULTS

Test No.	Emissions, g/bhp-h				Fuel Consumption, lb/hp-h
	HC	CO	NO_x	PM	
1	0.16	1.35	4.60	0.186	0.422
2	0.19	1.48	4.82	0.193	0.445
3	0.19	1.31	4.31	0.165	0.408
4	0.18	1.32	4.41	0.173	0.414

Tests conducted with engine backpressure set to US EPA certification specifications with a 300 cell/inch^2 uncoated (inactive) catalyst substrate in the exhaust system.

TABLE 12. STEADY-STATE CATALYST INLET TEMPERATURES AND EMISSION CONCENTRATIONS

Mode No.	Speed, rpm	Torque, lb-ft	Catalyst Inlet Temperature, °C	Emissions				
				HC, ppmC	CO, ppm	NO_x, ppm	O_2, %	CO_2, %
1	2600	535	460	25	220	462	10.6	7.6
2	2600	410	360	19	119	443	12.8	6.1
3	2600	265	285	50	107	405	14.4	4.8
4	2600	131	235	27	177	312	15.8	3.8
5	2600	54	191	40	850	248	17.1	2.8
6	1600	685	435	15	503	800	9.6	8.4
7	1600	520	414	20	417	810	10.2	7.9
8	1600	345	362	25	417	765	11.6	6.8
9	1600	175	262	31	480	562	14.4	4.8
10	1600	68	177	38	883	373	17.0	2.9
11	750	0	106	38	470	286	18.8	1.5

Tests conducted with engine backpressure set to US EPA certification specifications with a 300 cell/inch^2 uncoated (inactive) catalyst substrate in the exhaust system.

TABLE 13. SELECTED STEADY-STATE MASS EMISSIONS

Mode No.	Catalyst Inlet Temp., °C	Engine Torque, lb-ft	Steady-State Emissions, g/bhp-hr				Fuel Consumption, lb/hp-hr
			HC	CO	NO_x	CO_2	
M200	200	135	1.00	0.79	9.09	589	0.411
M220	220	160	1.07	0.71	8.80	555	0.387
M240	240	190	0.83	0.61	8.55	528	0.368

Test Nos. UNC-72-200, -220, -240
Steady-state engine speed: 1250 rpm
Tests conducted with engine backpressure set to US EPA certification specifications with a 300 cell/inch^2 uncoated (inactive) catalyst substrate in the exhaust system.

IV. LABORATORY EVALUATION OF DIESEL NO_x CATALYSTS - GROUP "A"

This section covers the laboratory evaluations of the first group of diesel NO_x catalysts (Group"A") obtained for this project. A supplemental reductant spray system was developed for use with diesel NO_x reduction catalysts. The catalysts and the reductant spray system were evaluated together in the laboratory using the Caterpillar 3116 diesel engine.

A. Description of Catalysts

The catalysts obtained and evaluated for this study are described in Table 14. Companies supplying diesel NO_x reduction catalysts for this part of the program included Engelhard, Johnson-Matthey, and International Catalyst Technology (ICT), a joint venture between Degussa and Nippon Shokubai. Most of the catalysts provided had a volume of seven liters, except Catalyst JM1 which had a volume of 14 liters. All the catalysts were designed to reduce NO_x with a supplemental reductant, namely diesel fuel, injected into the exhaust upstream of the catalyst. Information about the expected temperature window for maximum NO_x reduction was requested of the manufacturers. Catalysts D1 and D2 arrived late in this part of the program and were tested using only the heavy-duty transient test procedure. All the other Group "A" catalyst formulations were evaluated using steady-state and transient tests.

B. Initial Reductant Spray System Developments

A supplementary reductant delivery system was developed to add raw diesel fuel to the exhaust upstream of the diesel NO_x catalyst. Two different types of spray nozzles were tested in the systems shown schematically in Figure 7. Fuel delivery System "A" incorporated moderate pressure (15 psi to 75 psi) to atomize the liquid fuel to tiny droplets. Fuel delivery System "B" incorporated air at moderately low pressure to assist with the atomization of the fuel. A comparison of these two supplementary fuel delivery system designs is given in Table 15.

Supplementary reductant fuel delivery systems were tested in the laboratory prior to installation in an engine exhaust system. Figure 8 shows the fuel spray nozzle mounted in an exhaust pipe on a test bench. Figure 9 shows the air assisted fuel spray nozzle apparatus on the test bench. Pressure regulators were used to control the fuel and air (System B) pressures. The initial fuel spray operation is shown in Figure 10. The atomized fuel droplets were subjectively observed to be extremely small (like steam). Follow-up test bench spray experiments were performed with water (instead of fuel) for safety reasons. Both the moderate pressure (System "A") and the low pressure (System "B") designs performed well during bench tests. Spray droplet sizing measurements were not conducted during the early development of these spray systems, but are recommended for future spray system development.

The fuel spray nozzles were then tested in the exhaust system of the Caterpillar 3116 engine. The air assisted nozzle housing is shown installed in the exhaust system in Figure 11. Fuel spray distribution experiments were performed to determine if fuel was equally distributed at the front face of the catalyst. This test was performed by traversing a sample probe across the rear face of an uncatalyzed substrate and measuring the hydrocarbon concentration at 10 points while the engine was running. Experimental results

TABLE 14. DIESEL NO_x CATALYTIC CONVERTERS – GROUP "A"

Identification	Temperature Window for Maximum NO_x Conversion, °C	Supplemental Reductant System	Cell Density, Cells/in^2	Catalyst Volume, Liters
A-1	350-600	Fuel Spray	400	7
A-2	350-600	Fuel Spray	400	7
B	350-600	Fuel Spray	400	7
P	200-350	Fuel Spray	400	7
D1	Unknown	Fuel Spray	300	7
D2	Unknown	Fuel Spray	300	7
NB2	Unknown	Fuel Spray	300	7
NW3	Unknown	Fuel Spray	300	7
JM1	200-300°C	Fuel Spray	400	14

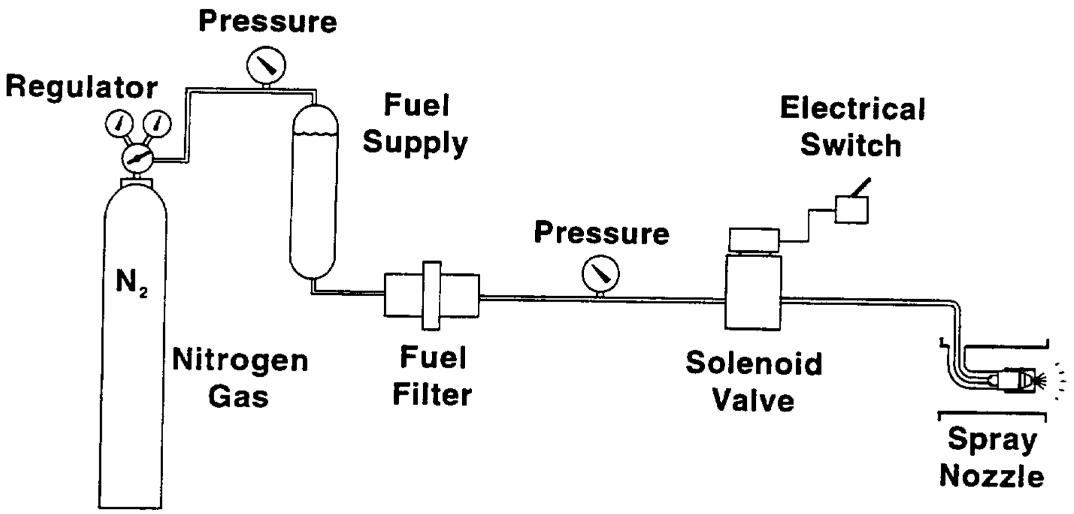
Catalysts A-1 and A-2 were duplicates of the same catalyst formulation.

TABLE 15. FUEL SPRAY APPROACHES FOR CARB DIESEL NO_x CATALYST DEMONSTRATION

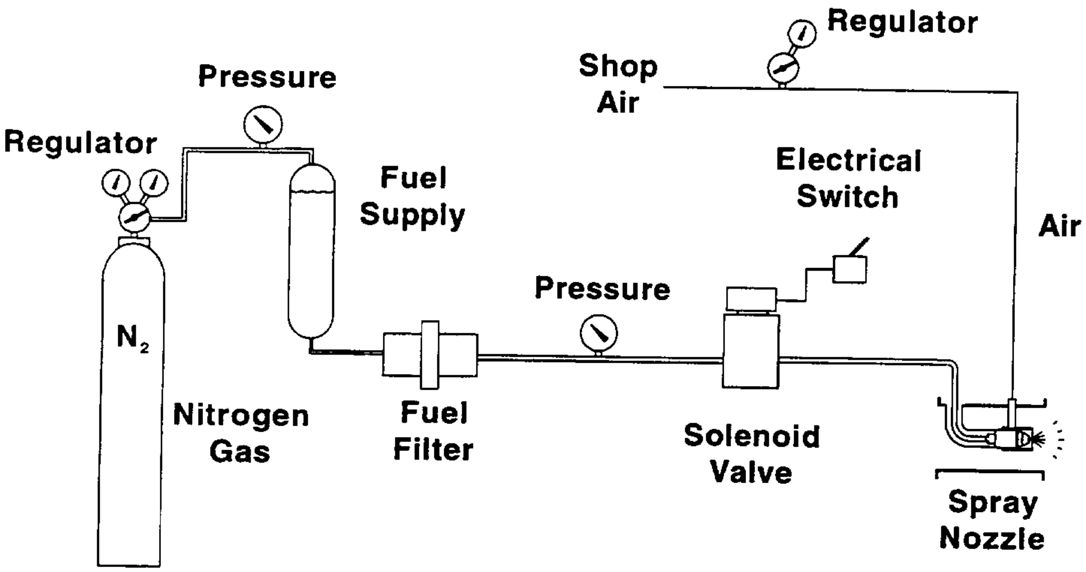
Fuel Delivery System	Delivery Technique	Vaporization	Fuel Pressure, psi	Air Pressure, psi
A	Moderate Pressure	Moderate fuel pressure is used to atomize the fuel	15-75[a]	N/A
B	Low Pressure with Air Assist	Air pressure is used to atomize the fuel	0-5[b]	0-15[a]

[a] Values given are estimates

[b] For most fuel flowrates of interest, fuel is drawn into the nozzle at a low pressure region created by the air flow.



a) Reductant Delivery System "A"



a) Reductant Delivery System "B" with Air Assist

FIGURE 7. SCHEMATIC OF SUPPLEMENTARY REDUCTANT SPRAY SYSTEMS

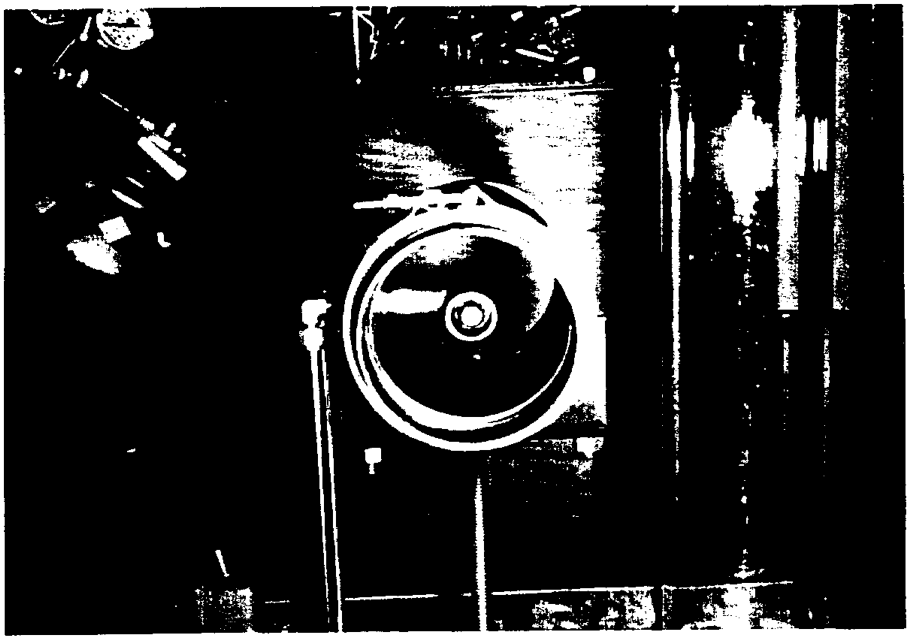


FIGURE 8. FUEL SPRAY NOZZLE IN AN EXHAUST PIPE

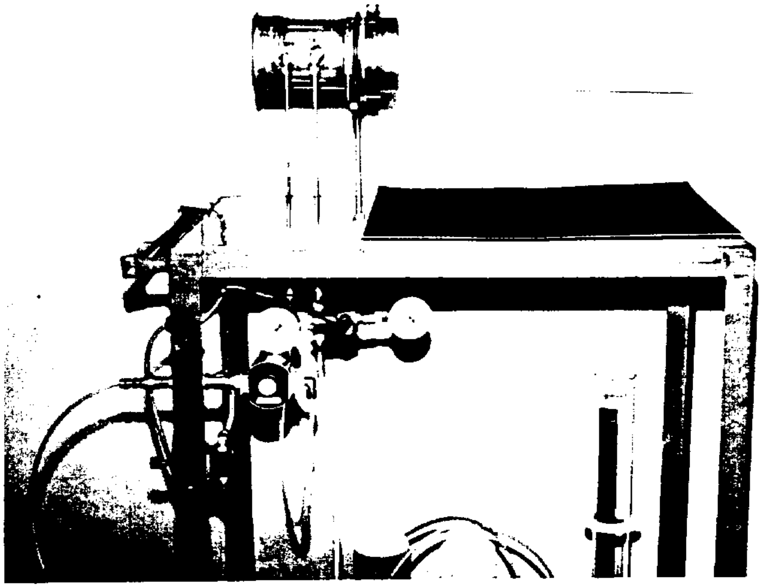


FIGURE 9. FUEL SPRAY NOZZLE APPARATUS ON THE TEST BENCH

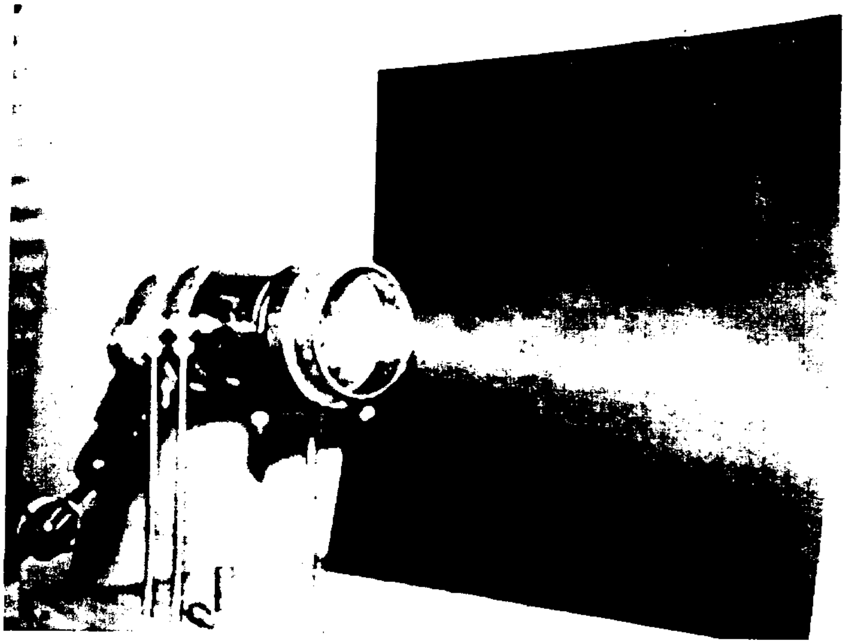


FIGURE 10. INITIAL FUEL SPRAY BENCH OPERATION

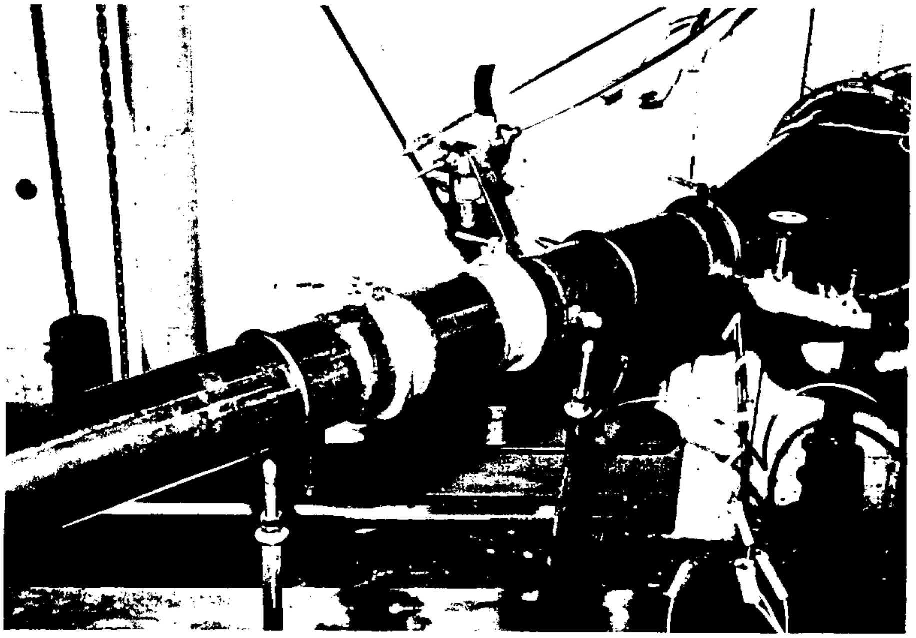


FIGURE 11. AIR ASSIST SPRAY NOZZLE INSTALLED IN EXHAUST SYSTEM

revealed that the most even distribution of supplemental hydrocarbon occurred when fuel was injected into the exhaust system in the opposite direction of the exhaust gas. The "counterflow" fuel spray direction provided an almost linear hydrocarbon distribution across the face of the catalyst, as tested in the SwRI exhaust system. The counterflow fuel spray direction is illustrated in Figure 12.

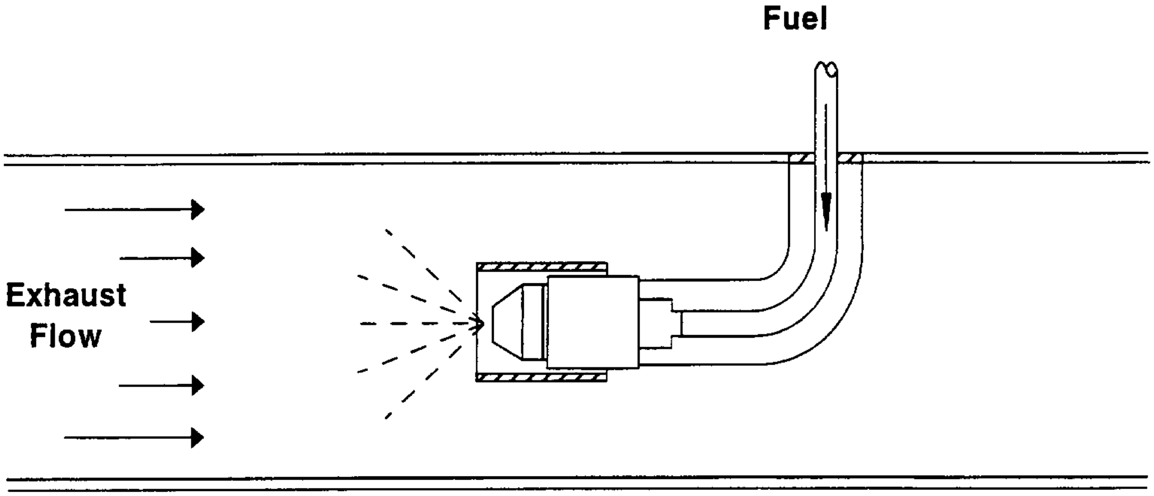


FIGURE 12. COUNTERFLOW REDUCTANT SPRAY DIRECTION

Steady-state emission tests were performed with both fuel spray systems. The air assisted spray nozzle could not provide enough fuel to establish a sufficient hydrocarbon level for maximum NO_x reduction. Therefore, the air-assisted nozzle was not pursued further.

Fuel nozzle design "A" was used for most of the testing of catalyst Group "A." This moderate pressure nozzle, however, operated erratically at higher temperatures. The fuel nozzle did not spray fuel in sufficient quantity at high exhaust temperatures. For this reason, only selected steady-state engine conditions (engine operation modes) were tested with the Group "A" catalysts. These fuel spray operation problems were corrected prior to the evaluation of the Group "B" catalysts (reported in Section VI).

C. Steady-State Experiments

Constant speed and load emission tests were initially performed on the catalysts as a quick screening prior to transient emission testing. Initially, eleven (11) modes were selected for study. The engine modes were based on a percentage of full torque at the rated and peak-torque speeds. Caterpillar rates the test engine at 2600 rpm. Maximum torque occurred at approximately 1600 rpm. The eleven modes are represented as a fraction of peak torque as described in Section III (Table 9). The speeds and torques used represent a wide range of engine operation.

Initially, all eleven modes were attempted, however, many modes were eliminated from the matrix because of spray nozzle problems and time constraints. Mode numbers 3 and 4 were selected to represent the remainder of steady-state tests to allow a quick screening of the remaining catalyst technologies available. Under the best conditions obtained, steady-state NO_x reduction efficiency ranged from 15 to 20 percent with diesel fuel addition to the exhaust gas, as shown in Table 16.

TABLE 16. SELECTED STEADY-STATE NO_x REDUCTION EFFICIENCIES – CATALYST GROUP "A"

Mode No.	Engine Speed, rpm	Torque, lb-ft	Catalyst Inlet Temp., °C	HC/NO_x Ratio	NO_x Inlet Concen. ppm	NO_x Reduction Efficiency, %
Catalyst JM1 (Volume: 14L)						
3	2600	269	290	4.16	348	5.7
4	2600	134	240	6.05	268	15.6
E1	2000	250	303	6.39	475	7.3
E2	2000	175	260	9.27	418	15.5
E3	2000	175	260	9.60	430	17.8
6	1600	685	452	8.48	776	1.9
8	1600	343	370	7.05	711	2.1
9	1600	171	250	4.66	517	16.3
Catalyst A-1 (Volume: 7L)						
3	2600	269	288	3.85	353	1.4
4	2600	136	234	5.02	268	2.2
6	1600	671	443	2.63	751	9.0
Catalyst P (Volume: 7L)						
3	2600	267	290	3.53	368	5.4
4	2600	134	238	5.67	277	9.7
E1	2000	250	295	6.63	484	6.7
E2	2000	175	256	9.50	408	19.0

Measurements made from raw exhaust analysis
Supplementary Reductant: Diesel Fuel
Inlet HC-to-NO_x Ratio: HC ppmC, NO_x ppm (HC and NO_x measured in raw exhaust)

The catalysts generally performed as expected, however, optimal catalyst temperatures and HC-to-NO_x ratios were seldom achieved. Exhaust temperatures obtained during the selected steady-state experiments often were not the temperatures required by the catalyst for maximum NO_x reduction. Exhaust gas temperature and the HC-to-NO_x ratio of the exhaust are critically important for maximum NO_x conversion. Occasionally, the fuel spray delivery system failed to supply the desired amount of fuel to the catalyst.

The steady-state results generated cannot be used to rank catalyst performance without careful consideration of the catalyst inlet temperatures and the HC-to-NO_x ratios. Each catalyst typically had a very narrow temperature window where the maximum NO_x conversion occurred. In addition, the maximum NO_x conversion strongly depended on the HC-to-NO_x ratio. Generally, higher HC-to-NO_x ratios resulted in higher NO_x reduction efficiencies at active catalyst temperatures. The greatest NO_x conversions took place when the HC-to-NO_x ratio was in the range of 6:1 or more. This HC-to-NO_x ratio is far more than the 0.5:1 ratio theoretically required.(22) The catalysts tested were not sufficiently selective toward the NO_x reduction reaction. Improvements in catalyst selectively toward the NO_x reduction reaction are needed.

D. Heavy-Duty Transient Emission Tests

Heavy-duty transient emission tests were performed to assess the NO_x reduction performance of the experimental catalysts. Tests were conducted with and without the supplemental fuel spray. Based on the results of the steady-state experiments, a sufficiently high (on average) HC-to-NO_x ratio was selected to determine the greatest possible NO_x reduction. The catalysts designed for low temperature (225°C) conversion worked better than those catalysts designed for higher temperatures (see Table 14) because of the low exhaust temperature of the diesel engine.

Catalytic NO_x reduction with the supplementary reductant fuel spray ranged from 5 to 17 percent with the low-temperature catalysts tested. The addition of fuel caused an increase in the particulate mass measured over the US EPA transient cycle. This particulate mass increase is most likely an increase in the organic fraction of the particulate matter due to the fuel spray. Hydrocarbon emissions also increased. Preliminary experiments with a "reduced-on-time" reductant fuel spray schedule immediately resulted in lower FTP hydrocarbon and particulate emission measurements without affecting NO_x conversion efficiency.

A summary of the heavy-duty transient test results for Catalyst Group "A" is given in Table 17, and complete FTP test result sheets are located in Appendix C. In Table 17, emission test results are given for uncoated catalyst substrates, catalysts without fuel assist, and catalysts with fuel assist. Catalyst temperatures are provided for reference. Emission tests using uncoated catalyst substrates provided baseline emission results with engine backpressure compensation. A test number code indicates the catalyst used and the fuel addition strategy used during the test. The test number description is given in Table 18.

E. Nitrous Oxide Emission Test Results

Nitrous oxide (N_2O) emission measurements were made for catalyst Tests -15 through -28 and are given in Table 19. In general, N_2O emissions were produced when NO_x was reduced. From a simple nitrogen balance analysis, it would appear that approximately 35 to 75 percent of the nitrogen in the NO_x is converted to N_2O, depending on the catalyst selected.

TABLE 17. HOT-START HEAVY-DUTY TRANSIENT TEST EMISSIONS AND CATALYST TEMPERATURES – CATALYST GROUP "A"

Test No.	Catalyst	Total Volume of Catalyst, L	Caterpillar 3116 Engine Emissions, g/hp-h				Catalyst Bed Temp., °C		Catalyst Inlet Temp., °C		Catalyst Outlet Temp., °C	
			HC	CO	NO_x	PM	Min.	Max.	Min.	Max.	Min.	Max.
1991 Emission Standards			1.3	15.5	5.0	0.25						
300-A-01	Uncoated	--	0.16	1.35	4.60	0.186	132	409	135	391	143	384
300-B-02	Uncoated	--	0.19	1.48	4.82	0.193	131	411	135	391	143	384
A1-A-03	A1	7	0.10	1.49	4.88	0.171	133	415	136	397	153	395
A1-B-04	A1	7	0.11	1.40	4.66	0.161	126	410	128	390	145	387
A1-A-05F	A1	7	19.25	1.81	4.04	1.020	122	400	126	377	136	384
NW3-A-06F	NW3	7	5.33	0.83	4.23	0.742	123	419	124	375	125	395
P-A-07	P	7	0.01	0.13	4.40	0.159	126	400	128	380	147	360
P-B-08F	P	7	3.51	0.45	4.07	0.514	123	410	125	380	148	380
JM-A-09	JM1	14	0.00	0.00	4.32	0.145	122	400	120	380	190	360
JM-B-10F	JM1	14	0.62	0.09	3.89	0.184	123	410	122	383	183	380
A1/P-A-11	A1/P	14	0.00	0.06	4.32	0.151	129	400	130	382	167	372
A1/P-B-12F	A1/P	14	3.12	0.28	3.91	0.409	130	410	130	386	184	405
P/A1-A-13	P/A1	14	0.00	0.21	4.49	0.153	--	--	130	394	170	383
P/A1-B-14F	P/A1	14	2.34	0.95	4.08	0.264	--	--	130	396	186	410
D1-A-15	D1	7	0.01	0.09	4.39	0.143	129	397	127	377	153	367
D1-B-16F	D1	7	3.66	0.27	4.07	0.473	129	412	128	381	165	388
D2-A-17	D2	7	0.00	0.13	4.54	0.159	130	413	133	390	154	384
D2-B-18F	D2	7	3.72	0.32	4.16	0.510	130	423	132	393	158	403
JM-A-19Fi	JM1	14	0.21	0.05	3.88	0.170	126	413	125	385	175	384
JM-B-20F	JM1	14	0.98	0.07	3.89	0.216	127	418	125	390	192	390
D2/D1-A-21	D2/D1	14	0.00	0.00	4.40	0.153	132	412	133	388	183	376
D2/D1-B-22Fi	D2/D1	14	0.32	0.01	3.96	0.167	130	418	131	386	195	397
300-A-23	Uncoated	--	0.20	1.41	4.48	0.180	130	412	133	393	145	385
JM-A-24Fi	JM1	14	0.18	0.03	4.16	0.201	130	428	130	405	197	400
JM-B-25Fi	JM1	14	0.17	0.03	4.15	0.221	130	430	130	406	205	402
JM-C-26Fi	JM1	14	0.42	0.07	3.85	0.171	125	410	125	383	196	385
300-A-27	Uncoated	--	0.19	1.31	4.31	0.165	124	400	128	376	138	370
300-B-28	Uncoated	--	0.18	1.32	4.41	0.173	128	401	130	378	140	371

TABLE 18. TEST NUMBER INTERPRETATION

Example: D2/D1-B-22Fi

Catalyst Identification	Order in Test Sequence	Index Number and Fuel Spray Code	
"300" is uncoated substrate "D2" is Catalyst D2 "D2/D1" is Catalyst D2 followed by Catalyst D1	A = first test B = second test C = third test in a back-to-back sequence	Index Number 1,2,3, etc. refers to number of the test in the order performed in the project	Fuel Spray Code "F" indicates fuel was added (no F indicates no fuel was added) "i" indicates an intermittent fuel schedule was used (i.e., fuel spray was off during engine idles)

TABLE 19. NITROUS OXIDE EMISSIONS MEASURED FOR SELECTED DIESEL NO_x CATALYST FTP TESTS – CATALYST GROUP "A"

Test Number	Catalyst	Total Volume of Catalyst, L	Fuel Spray	Caterpillar 3116 Engine Emissions, g/bhp-hr	
				NO_x	N_2O
D1-A-15	D1	7	no	4.39	0.016
D1-B-16F	D1	7	yes	4.07	0.179
D2-A-17	D2	7	no	4.54	0.003
D2-B-18F	D2	7	yes	4.16	0.152
JM-A-19Fi	JM1	14	yes	3.88	0.135
JM-B-20F	JM1	14	yes	3.89	0.182
D2/D1-A-21	D2+D1	14	no	4.40	ND
D2/D1-A-22Fi	D2+D1	14	yes	3.96	0.138
300-A-23	Uncoated	--	no	4.48	ND
JM-A-24Fi	JM1	14	yes	4.16	0.121
JM-B-25Fi	JM1	14	yes	4.15	0.118
JM-C-26Fi	JM1	14	yes	3.85	0.179
300-A-27	Uncoated	--	no	4.31	ND
300-B-28	Uncoated	--	no	4.41	ND

ND - Not Detected

F. Discussion

1. NO_x Reduction Analysis

A summary of the transient NO_x reduction performance for all catalysts tested is given in Table 20, where NO_x reduction is separated into two categories for the purpose of analysis. Catalytic NO_x reduction is tabulated (Table 18) as "estimated total NO_x reduction" and "NO_x reduction improvement due to fuel spray." Total NO_x reduction is estimated using the data available and the judgement of the investigator because engine-out (baseline) emissions seemed to trend downward during the course of these experiments. Since a consistent NO_x baseline was not available, engineering judgement was used to estimate total NO_x reduction performance. An engine-out NO_x emission of 4.7 g/hp-h was used to calculate NO_x reduction efficiency for Tests -01 through -20. Tests -20 through -28 used the uncoated catalyst test NO_x emission result of 4.48 g/hp-h (Test No. -23) as the baseline for calculating reduction efficiency, resulting in a estimated range of efficiency. Uncoated catalysts were assumed to have zero NO_x reduction efficiency. Any test that resulted in a NO_x emission rate at or above the assumed baseline was also assumed to have zero NO_x reduction efficiency. The NO_x reduction improvement due to fuel spray was calculated in a straightforward manner; NO_x reduction with fuel spray was calculated using results from the most recent no-fuel spray test as the baseline.

The described analysis clearly shows that the great majority of NO_x reduction occurs as a result of the added hydrocarbon reductant (the fuel spray). This conclusion is expected, based on an understanding of the theoretical aspects of NO_x reduction discussed in Section II of this report.

2. Diesel Fuel as a Supplementary Reductant

An additional problem has become evident with the use of diesel fuel as the supplemental NO_x reductant. Diesel fuel does not completely evaporate at the typical exhaust temperatures of the Caterpillar 3116 engine operating over the FTP Heavy-Duty Transient cycle. The boiling point distribution of typical No. 2 diesel fuel is from 180°C to 360°C. The exhaust gas temperature range of the Caterpillar 3116 engine is 125°C to 250°C for the non-freeway portions and 210°C to 375°C for the freeway portion of the FTP. Only a very small portion of the exhaust temperature operating range of the engine (over the FTP) extends to the highest temperature (360°C) in the boiling point distribution (or endpoint) of diesel fuel. A comparison of the catalyst inlet temperature for the demonstration engine and the boiling point distribution for typical No. 2 diesel fuel is illustrated in Figure 13.

This relatively large boiling point distribution means that the catalyst will often receive particles of liquid fuel when diesel fuel is injected. It is not fully understood, however, what effect this will have on catalyst performance and durability. Preliminary results of catalyst performance from this project showed that the low-temperature catalysts (generally those catalysts that contained platinum) oxidized most of the added hydrocarbon fuel. High-load steady-state engine operation produced catalyst inlet temperatures greater than the endpoint of No. 2 diesel fuel, as shown in Table 21. The topic of fuel injection to the catalyst is discussed further in Section VI.

TABLE 20. HOT-START HEAVY-DUTY TRANSIENT TEST EMISSIONS AND ESTIMATED NO$_x$ REDUCTION – CATALYST GROUP "A"

Test No.	Catalyst	Total Vol. of Cat., L	Caterpillar 3116 Engine Emissions, g/hp-h				Estimated Total NO$_x$ Reduction, %	NO$_x$ Reduction Improvement Due to Fuel Spray, %
			HC	CO	NO$_x$	PM		
1991 Emission Standards			1.3	15.5	5.0	0.25		
300-A-01	Uncoated	--	0.16	1.35	4.60	0.186	0.0	--
300-B-02	Uncoated	--	0.19	1.48	4.82	0.193	0.0	--
A1-A-03	A1	7	0.10	1.49	4.88	0.171	0.0	--
A1-B-04	A1	7	0.11	1.40	4.66	0.161	0.0	--
A1-A-05F	A1	7	19.25	1.81	4.04	1.020	14.0	13.3
NW3-A-06F	NW3	7	5.33	0.83	4.23	0.742	10.0	--
P-A-07	P	7	0.01	0.13	4.40	0.159	6.3	--
P-B-08F	P	7	3.51	0.45	4.07	0.514	13.4	7.5
JM-A-09	JM1	14	0.00	0.00	4.32	0.145	8.1	--
JM-B-10F	JM1	14	0.62	0.09	3.89	0.184	17.2	10.0
A1/P-A-11	A1/P	14	0.00	0.06	4.32	0.151	8.1	--
A1/P-B-12F	A1/P	14	3.12	0.28	3.91	0.409	16.8	9.5
P/A1-A-13	P/A1	14	0.00	0.21	4.49	0.153	4.5	--
P/A1-B-14F	P/A1	14	2.34	0.95	4.08	0.264	13.2	9.1
D1-A-15	D1	7	0.01	0.09	4.39	0.143	6.6	--
D1-B-16F	D1	7	3.66	0.27	4.07	0.473	13.4	7.3
D2-A-17	D2	7	0.00	0.13	4.54	0.159	3.4	--
D2-B-18F	D2	7	3.72	0.32	4.16	0.510	11.5	8.4
JM-A-19Fi	JM1	14	0.21	0.05	3.88	0.170	17.4	10.2
JM-B-20F	JM1	14	0.98	0.07	3.89	0.216	17.2	10.0
D2/D1-A-21	D2/D1	14	0.00	0.00	4.40	0.153	1.8-6.4	--
D2/D1-B-22Fi	D2/D1	14	0.32	0.01	3.96	0.167	11.6-15.7	10.0
300-A-23	Uncoated	--	0.20	1.41	4.48	0.180	0.0	--
JM-A-24Fi	JM1	14	0.18	0.03	4.16	0.201	7.1-11.4	3.7
JM-B-25Fi	JM1	14	0.17	0.03	4.15	0.221	7.4-11.7	3.9
JM-C-26Fi	JM1	14	0.42	0.07	3.85	0.171	14.1-18.1	10.9
300-A-27	Uncoated	--	0.19	1.31	4.31	0.165	0.0	--
300-B-28	Uncoated	--	0.18	1.32	4.41	0.173	0.0	--

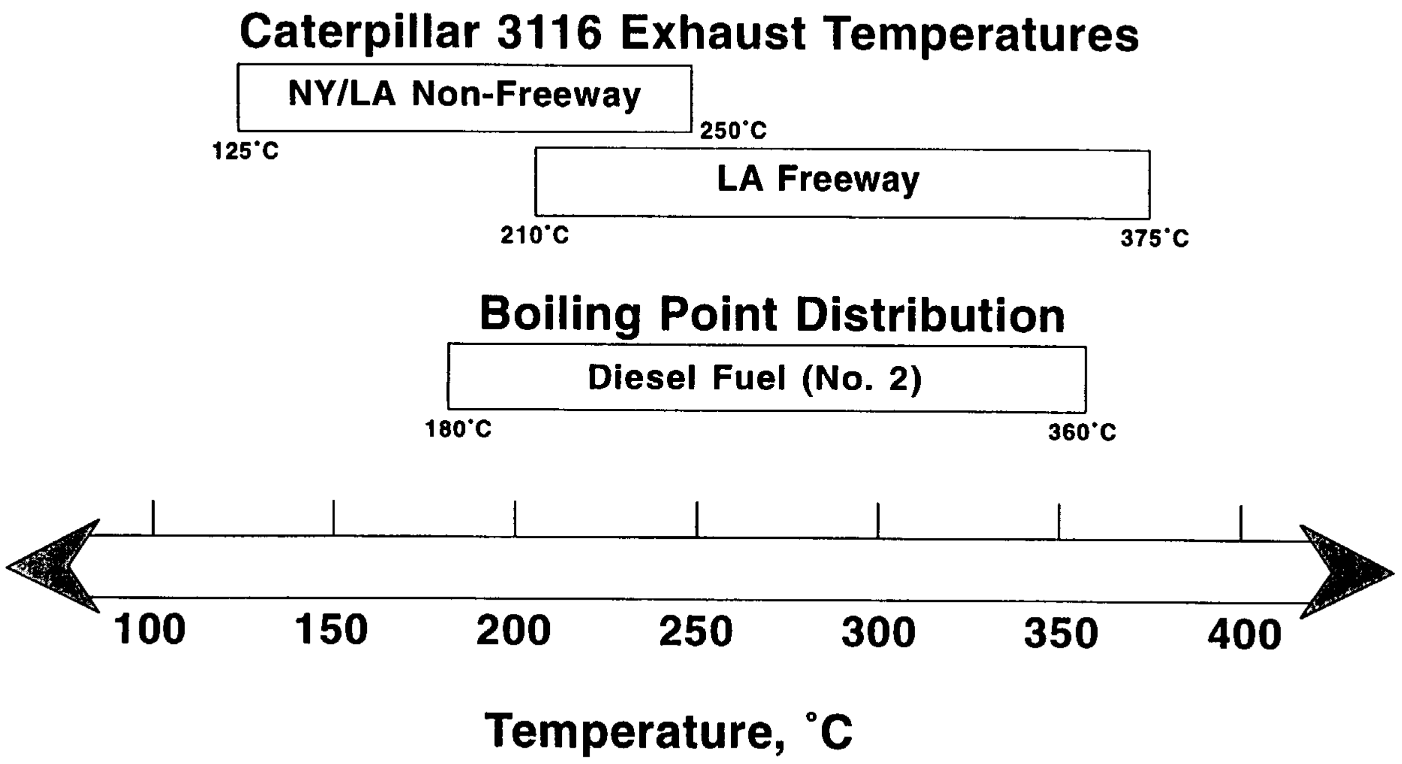


FIGURE 13. COMPARISON OF CATALYST INLET TEMPERATURE AND BOILING POINT DISTRIBUTION

TABLE 21. COMPARISON OF DIESEL FUEL ENDPOINT TEMPERATURE AND STEADY-STATE CATALYST INLET TEMPERATURE

Mode No.	Speed, rpm	Torque, lb-ft	Catalyst Inlet Temperature, °C	Catalyst Inlet Temperature at or above endpoint of Diesel Fuel
1	2600	535	460	yes
2	2600	410	360	yes
3	2600	265	285	no
4	2600	131	235	no
5	2600	54	191	no
6	1600	685	435	yes
7	1600	520	414	yes
8	1600	345	362	yes
9	1600	175	262	no
10	1600	68	177	no
11	750	0	106	no
Note: Boiling point (BP) distribution of typical No. 2 diesel fuel is 180°C to 360°C				

If liquid fuel is identified as a problem for catalyst durability and safety, one possible solution is to thermally "crack" diesel fuel components prior to injection into the exhaust. Fuel cracking can be achieved thermally at temperatures above approximately 500°C, or catalytically at lower temperatures. Cracking of diesel fuel hydrocarbons will result in lower-boiling-point olefins, which tend to be more reactive as NO_x reducing agents. Such an approach may possibly increase hydrocarbon selectivity toward reducing NO_x and result in more efficient fuel-spray hydrocarbon usage. The disadvantage of fuel cracking is that it adds another level of complexity to the diesel NO_x catalyst system. Also, cracking catalyst coking is a potential problem.

G. Summary

For convenience, a brief summary of the performance of the Group "A" catalysts is given in Table 22. This table further summarizes data presented previously in Tables 16 and 20. Only steady-state test results from selected catalysts are presented in Table 22. Note that the Group "A" catalysts were not necessarily evaluated at the optimal NO_x reduction temperatures.

TABLE 22. SUMMARY OF DIESEL NO_x CATALYST PERFORMANCE – CATALYST GROUP "A"

Catalyst	Total Volume of Catalyst, L	Caterpillar 3116 Diesel Engine				
		FTP	Steady-State			
		Maximum NO_x Reduction Efficiency, %	Catalyst Inlet Temp., °C	Feedgas HC/NO_x Ratio	Exhaust Space Velocity, hr^{-1}	Maximum NO_x Reduction Efficiency, %
A1	7	14	443	2.63	50,000	9.0
NW3	7	10				
P	7	13	256	9.50	70,000	19
A1+P(S)	14	17				
D1	7	13				
D2	7	12				
D2+D1(S)	14	14				
JM1	14	16	260	9.60	35,000	18

(S) - Catalysts tested in Series
Catalysts may not have been tested at their respective optimal NO_x reduction temperatures

V. REDIRECTION OF ORIGINAL PROJECT PLAN

A. Catalyst and Reductant Spray System Assessment

At this point in the project, SwRI had reviewed the results of previous studies of lean NO_x catalyst systems and determined the most promising technology for a heavy-duty diesel NO_x catalyst demonstration. An experimental NO_x emission control system was evaluated on a laboratory engine. Heavy-duty engine transient tests demonstrated NO_x emission reduction efficiencies as high as 17 percent, and steady-state tests demonstrated NO_x reduction as high as 19 percent.

After consultation with the technical project monitors from the Air Resources Board Research and Mobile Source Divisions, a 200-hour catalyst (and system) durability run was cancelled because of lowered-than-expected NO_x reduction efficiencies and early reductant fuel spray delivery system failures. The original project objectives were based on using further-developed diesel NO_x catalysts and emission control systems than could be obtained. The results of the testing described so far were disappointing, but did represent the state-of-the-art. Additionally, neither the ARB request for proposal nor the SwRI proposal addressed the need for the development of durable auxiliary equipment such as the supplemental reductant delivery system. Durability evaluations, while deemed not appropriate at this time, are recommended for future lean NO_x catalysts and systems that have undergone further improvements.

The original plan for the final working task of this project was to prepare a vehicle, then conduct a one-year on-road diesel NO_x catalyst demonstration. With direction from the ARB technical staff, the remainder of the program was redirected to a laboratory (only) diesel NO_x catalyst demonstration using more appropriate catalyst technology and an improved reductant fuel spray system. Administratively, the final task of the project was cancelled, and the remaining project budget and time were used to conduct additional laboratory development experiments.

B. Recommendations Made for the Continuation of Diesel NO_x Catalytic Converter System Analysis

After several discussions with the staff of the California Air Resources Board, it was concluded that research efforts would continue in order to better characterize diesel NO_x catalytic converter technology and system performance. An outline of the work that was recommended is given below:

- Develop an improved reductant fuel spray system. Early spray systems developed in this project had fuel flow or temperature problems.

- Obtain catalysts with an operating temperature range more suitable for Caterpillar 3116 diesel engine. Manufacturers of catalysts stated that they could select a more appropriate catalyst based on data (exhaust gas temperatures and composition) generated early in the program.

- Encourage catalyst companies to widen the temperature window of NO_x conversion and improve hydrocarbon selectivity toward NO_x reduction. Understand that this technology may not be available.
- Perform parametric experiments to be able to plot NO_x conversion vs temperature and reductant (hydrocarbon fuel) addition
- Measure N_2O emissions on selected catalyst tests
- Analyze NO_x emission reduction.
- Compile information and data in a final report.

The project outlined above would bring the NO_x catalyst technology to the point where an on-road vehicle demonstration could possibly be conducted.

VI. LABORATORY EVALUATION OF DIESEL NO_x CATALYSTS - GROUP "B"

This section covers the laboratory development and evaluations of a second group of diesel NO_x catalysts, designated as Group "B." Catalyst Group "B" primarily consisted of improved catalyst formulations that were obtained following the evaluation of the Group "A" catalysts. The supplemental reductant spray system described in Section IV was redesigned to improve operation at higher temperatures. The updated catalysts and the redesigned reductant spray system were evaluated together on the Caterpillar 3116 diesel engine in the test cell.

A. Description of Catalysts

The catalysts obtained and evaluated for this part of the study are described in Table 23. Companies supplying diesel NO_x reduction catalysts for this part of the program included Allied-Signal, Engelhard, Johnson-Matthey, and International Catalyst Technology (ICT), a joint venture between Degussa and Nippon Shokubai. Most of the catalysts provided had a volume of seven liters, except Catalysts JM1 and JM2 which had a volume of 14 liters each. Catalyst JM1 was evaluated as part of Catalyst Group "A;" all the other catalysts in Group "B" were new. These catalysts were designed to reduce NO_x with a supplemental reductant (diesel fuel) injected into the exhaust upstream of the catalyst and evaluated using steady-state and transient engine tests.

TABLE 23. DIESEL NO_x CATALYTIC CONVERTERS -- GROUP "B"

Identification	Supplemental Reductant System	Cell Density, cells/in^2	Catalyst Volume, liters
220	Fuel Spray	400	7.0
221	Fuel Spray	400	7.0
DG-1[a]	Fuel Spray	300	7.0
DG-2[a]	Fuel Spray	300	7.0
PS-1	Fuel Spray	400	7.0
JM1[b]	Fuel Spray	400	14.0
JM2	Fuel Spray	400	14.0
NP-3[a]	Fuel Spray	300	7.0
NP-6[a]	Fuel Spray	300	7.0
ORP	Fuel Spray	400	7.0

[a] Substrates provided to catalyst coater by SwRI.
[b] Catalyst JM1 evaluated as part of both Group "A" and Group "B."

B. Redesign of Reductant Spray System

The exhaust gas reductant spray system was redesigned prior to the evaluation of the Group "B" diesel NO_x catalytic converters. The new spray system incorporated a high-temperature stainless steel nozzle with a proven history in stationary source NO_x emissions control systems (systems that used ammonia as the supplementary reductant). This nozzle is shown removed from the exhaust pipe in Figure 14. For this project, the stainless steel nozzle was positioned 15 inches from the Caterpillar 3116 engine turbocharger outlet, such that it was protected from the direct flow of the hot exhaust gas. A photograph of the redesigned reductant spray system is shown in Figure 15. This reductant spray system was operated in a manner similar to system "A" shown previously in Figure 7.

A supplementary reductant flowrate measurement was performed on the redesigned nozzle assembly for the record. The flowrate of diesel fuel was measured with the nozzle and fuel at a temperature of 75°F (24°C). The flowrate of sprayed diesel fuel plotted against nozzle pressure is given in Figure 16. This plot shows that the flowrate of diesel fuel ranged from approximately 0.47 g/sec at 10 psi to 1.18 g/sec at 80 psi. At 40 psi, the measured flowrate of diesel fuel was 0.88 g/sec. Diesel fuel reductant flowrates were not measured at exhaust system operating temperatures.

C. Diesel NO_x Catalyst Test Results -- Catalysts DG-1 and DG-2

1. Transient Tests

Diesel NO_x Catalysts DG-1 and DG-2 were evaluated on a Caterpillar 3116 diesel engine using the heavy-duty engine FTP. Combinations of diesel fuel and ethanol were added to the exhaust as a supplementary reductant during these tests. Heavy-duty engine FTP emission test results are given in Table 24. Catalyst DG-2 reduced NO_x up to 14 percent on the Caterpillar 3116 engine over the heavy-duty FTP cycle with diesel fuel as a supplementary reductant. Federal Test Procedure result sheets for all the Group "B" catalyst evaluations are given in Appendix D.

2. Steady-State Tests

Catalyst DG-2 was evaluated at steady-state engine conditions at catalyst inlet temperatures ranging from 180°C to 280°C using diesel fuel and/or ethanol as a supplementary reductant, as shown in Figures 17 through 19. Additional NO_x conversion plots are given in Appendix E. Measured NO_x reduction efficiencies peaked at approximately 30 percent at 210°C to 220°C with diesel fuel as the supplementary reductant. The HC-to-NO_x ratio at the inlet of the catalyst was greater than 10-to-1 by volume for steady-state tests using diesel fuel as a supplementary reductant. Tests were conducted using an exhaust gas space velocity of approximately 40,000 h^{-1} to 44,000 h^{-1}. Two baseline steady-state emissions tests were performed on an uncoated substrate for comparison. Test results for the uncoated substrates are given in Figures 20 and 21. A summary of the maximum steady-state NO_x conversion efficiencies for Catalyst DG-2 is given in Table 25. Steady-state test dilution tunnel NO_x and HC concentrations with and without supplementary reductant addition for all the Group "B" catalysts tested (including the uncoated substrate) are provided in Appendix F. Steady-state emission test result sheets in brake specific units for all the catalysts and selected temperatures (typically 200°C, 220°C, 240°C) tested are given in Appendix G.

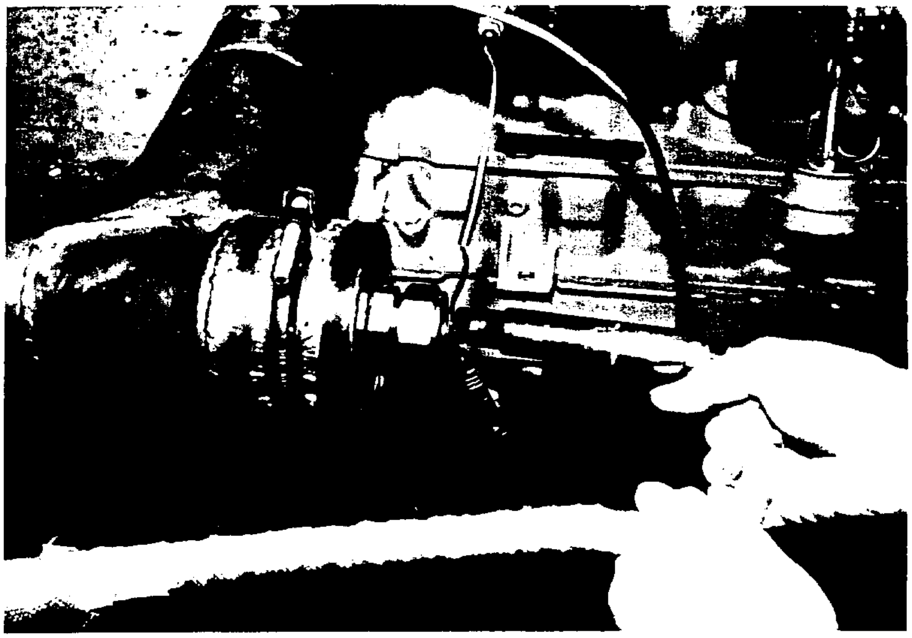


FIGURE 14. REDUCTANT SPRAY NOZZLE REMOVED FROM EXHAUST SYSTEM

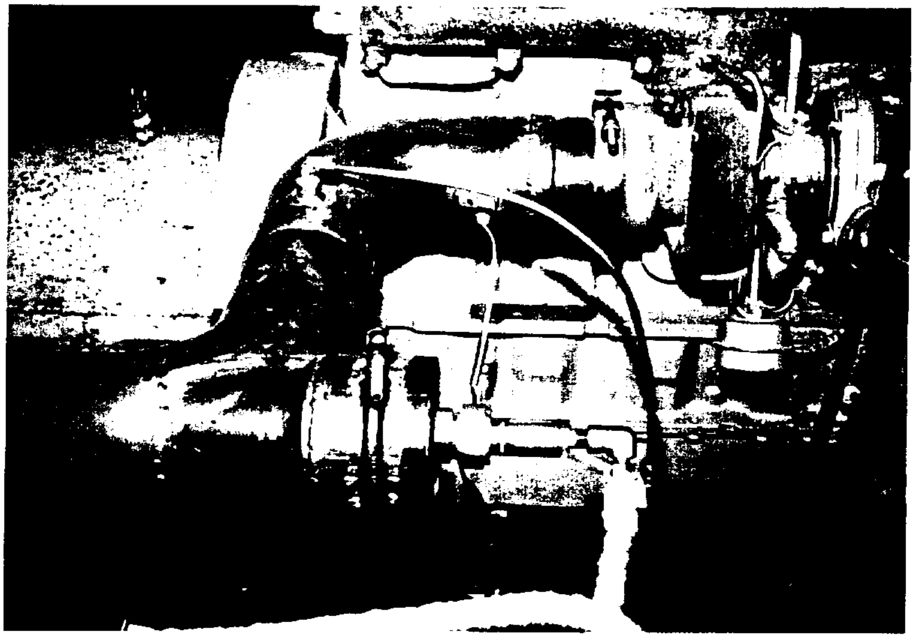


FIGURE 15. REDUCTANT SPRAY NOZZLE INSTALLATION ON ENGINE EXHAUST SYSTEM

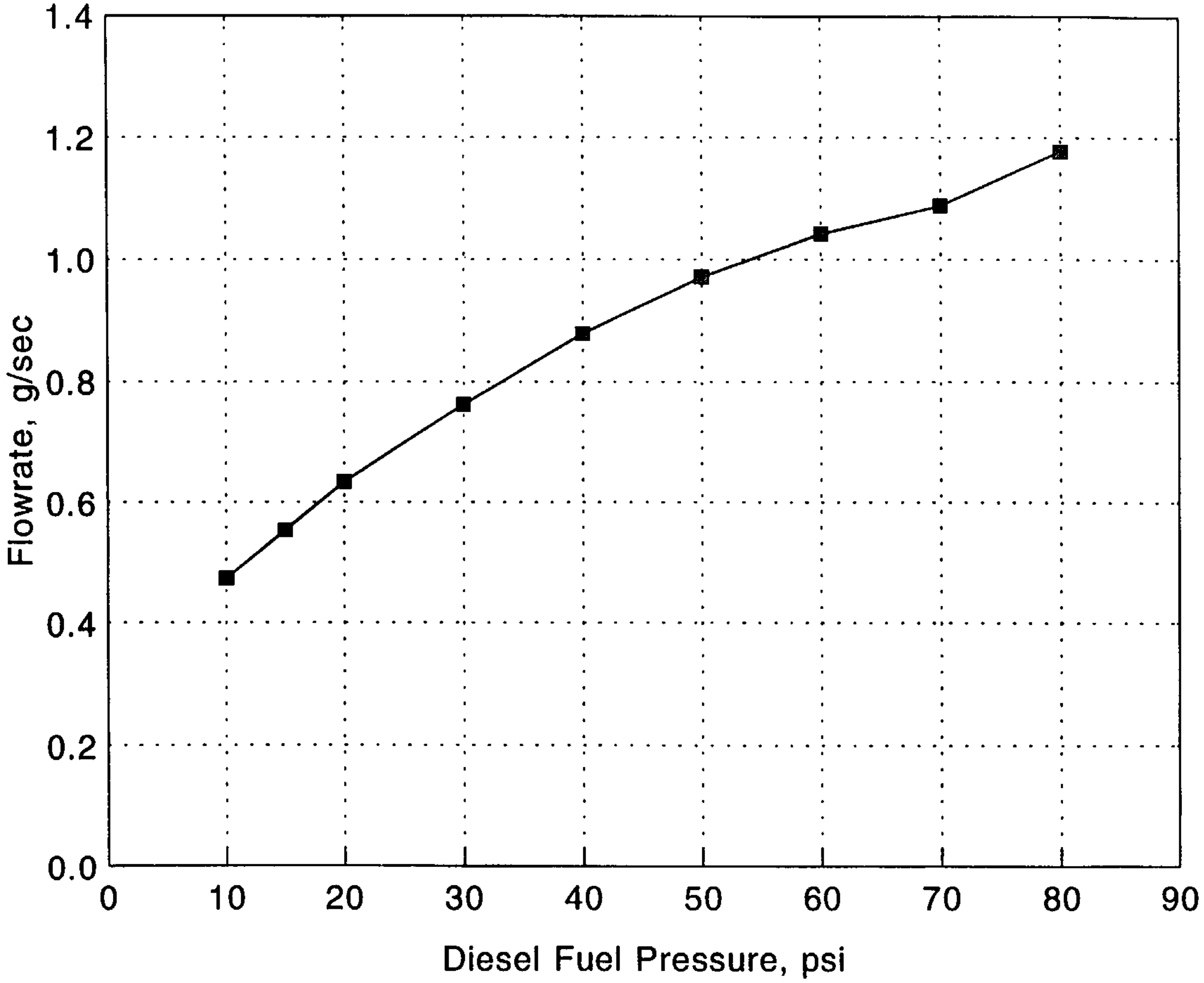


FIGURE 16. DIESEL FUEL REDUCTANT SPRAY FLOWRATE - CATALYST GROUP "B"

TABLE 24. DIESEL NO$_x$ CATALYST FTP TEST RESULTS – CATALYST DG-2

Test No.	Date	Catalyst	Reductant Spray	Caterpillar 3116 Engine Hot-Start Heavy-Duty Transient Emissions, g/bhp-hr			
				HC	CO	NO$_x$	PM
330-A-30 300-A-31	1/6/95 1/6/95	Uncoated Uncoated	None None	0.26 0.27	1.36 1.39	4.39 4.41	0.17 0.17
300-A-36	1/12/95	Uncoated	None	0.34	1.40	4.48	0.19
DG1-A-45Fi	1/18/95	DG-1	Diesel Fuel	7.61	1.76	4.47	1.01
DG2-A-46Fi	1/18/95	DG-2	Diesel Fuel	5.58	0.39	4.09	0.79
300-A-50	1/25/95	Uncoated	None	0.26	1.51	4.71	0.19
300-A-55 300-A-56Fi	2/15/95 2/15/95	Uncoated Uncoated	None Diesel Fuel	0.32 19.36	1.30 1.33	4.26 4.27	0.19 5.68
DG2-A-57 DG2-B-58Fi	2/16/95 2/16/95	DG-2 DG-2	None Diesel Fuel	0.03 7.68	0.13 0.51	4.31 3.80	0.18 1.26
DG2-A-67FEi	4/6/95	DG-2	Diesel Fuel/Ethanol	1.49	0.28	4.12	0.23
DG2-B-68	4/7/95	DG-2	None	0.02	0.14	4.23	0.22
DG2-A-69Ei DG2-B-70E	4/10/95 4/10/95	DG-2 DG-2	Ethanol Ethanol	0.97 1.60	0.25 0.20	4.22 4.15	0.23 0.30
300-A-71 300-B-72	4/11/95 4.11.95	Uncoated Uncoated	None None	0.20 0.20	1.37 1.37	4.46 4.42	0.19 0.18

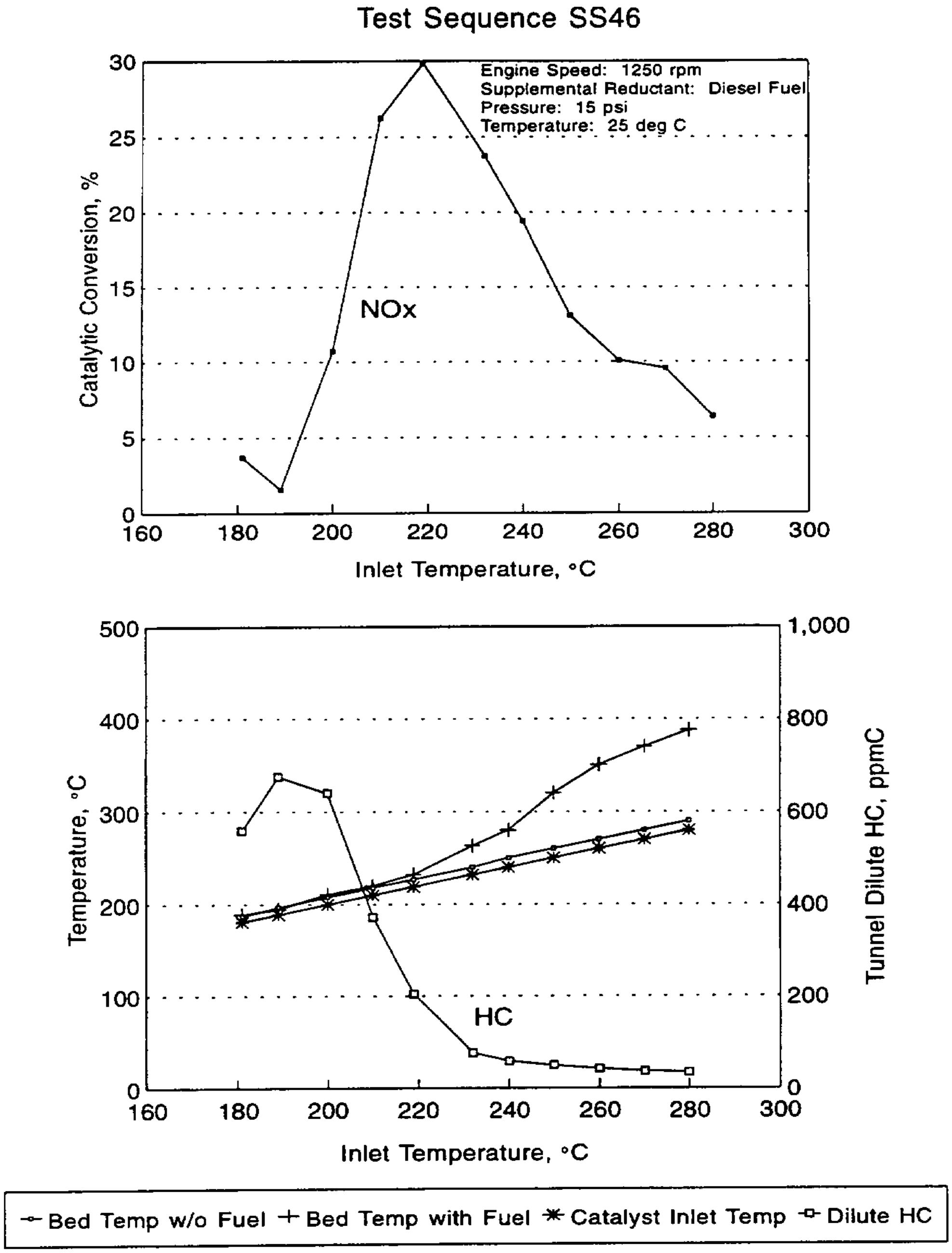


FIGURE 17. DIESEL NO_x CATALYTIC CONVERTER PERFORMANCE – CATALYST DG-2, TEST SEQUENCE SS46

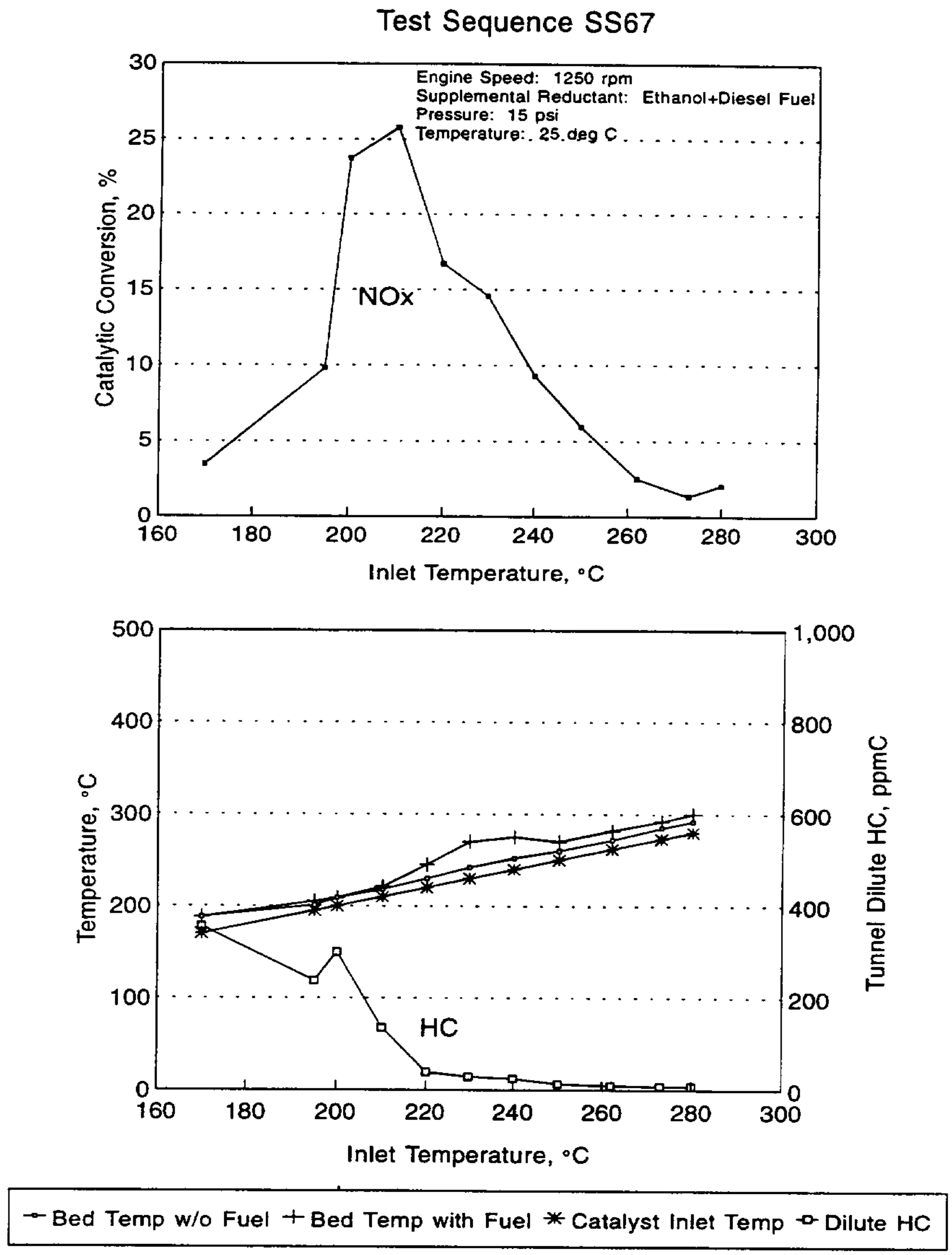


FIGURE 18. DIESEL NO$_x$ CATALYTIC CONVERTER PERFORMANCE – CATALYST DG-2, TEST SEQUENCE SS67

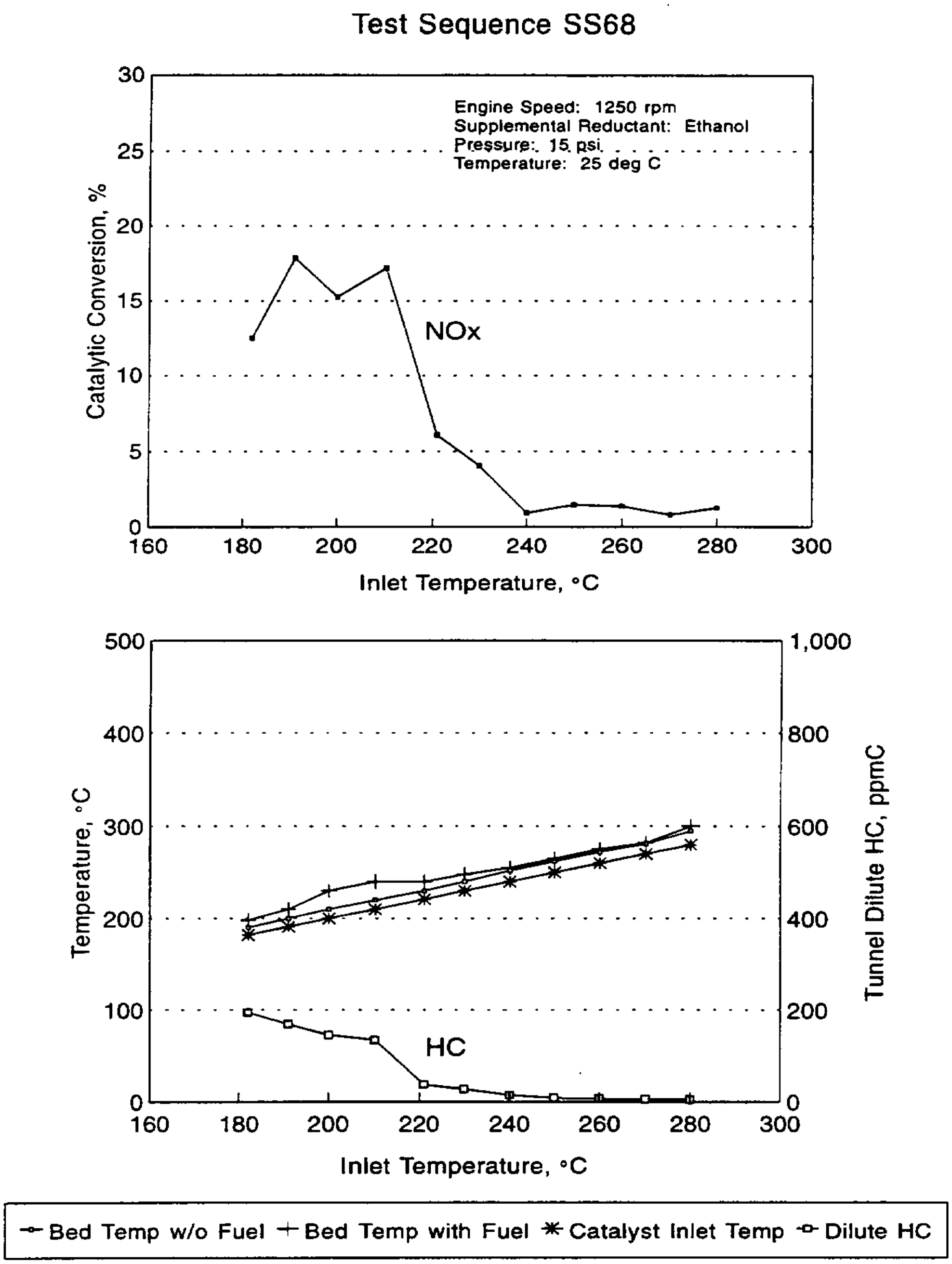


FIGURE 19. DIESEL NO$_x$ CATALYTIC CONVERTER PERFORMANCE – CATALYST DG-2, TEST SEQUENCE SS68

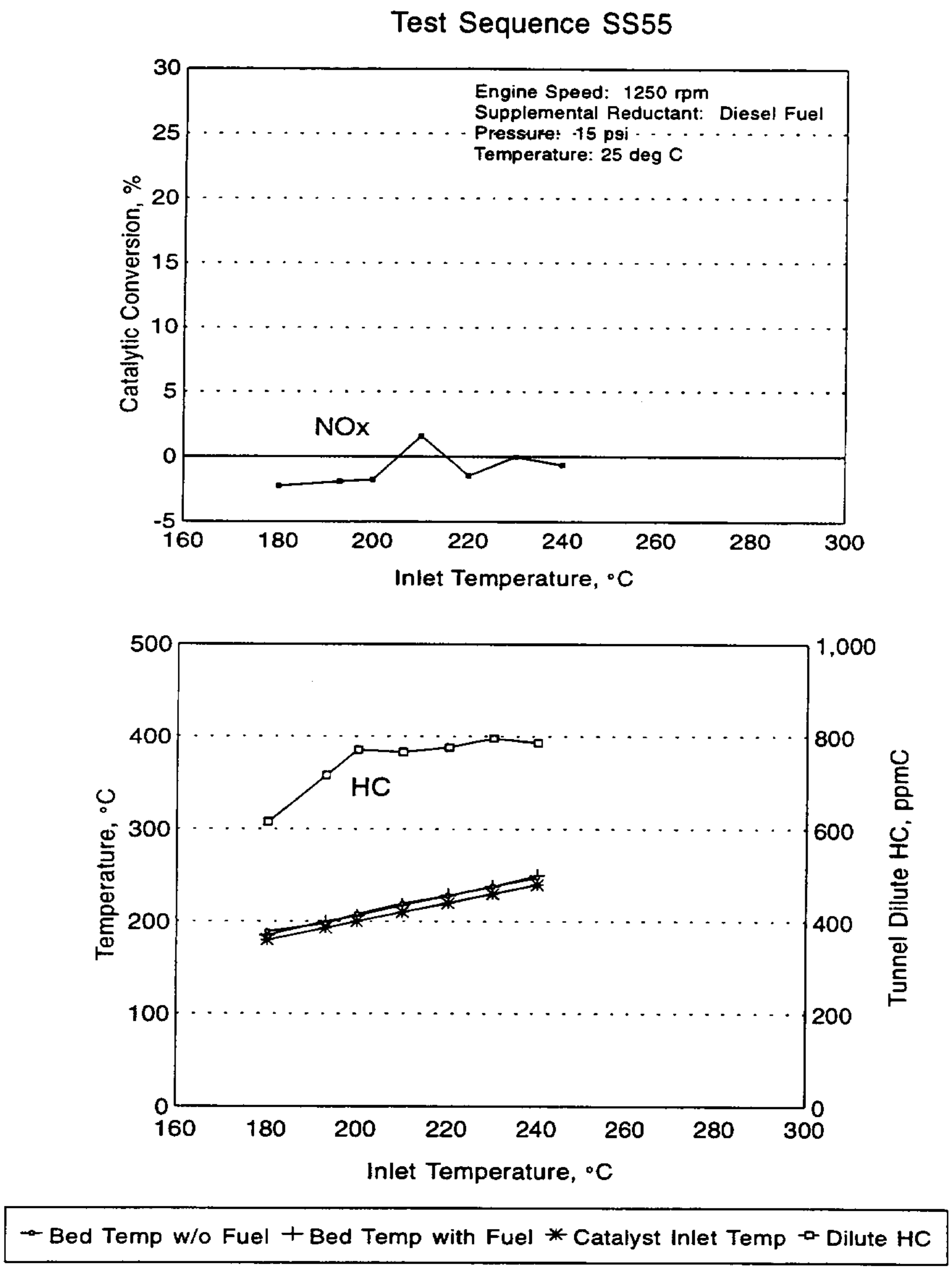


FIGURE 20. DIESEL NO_x CATALYTIC CONVERTER PERFORMANCE -- UNCOATED SUBSTRATE, TEST SEQUENCE SS55

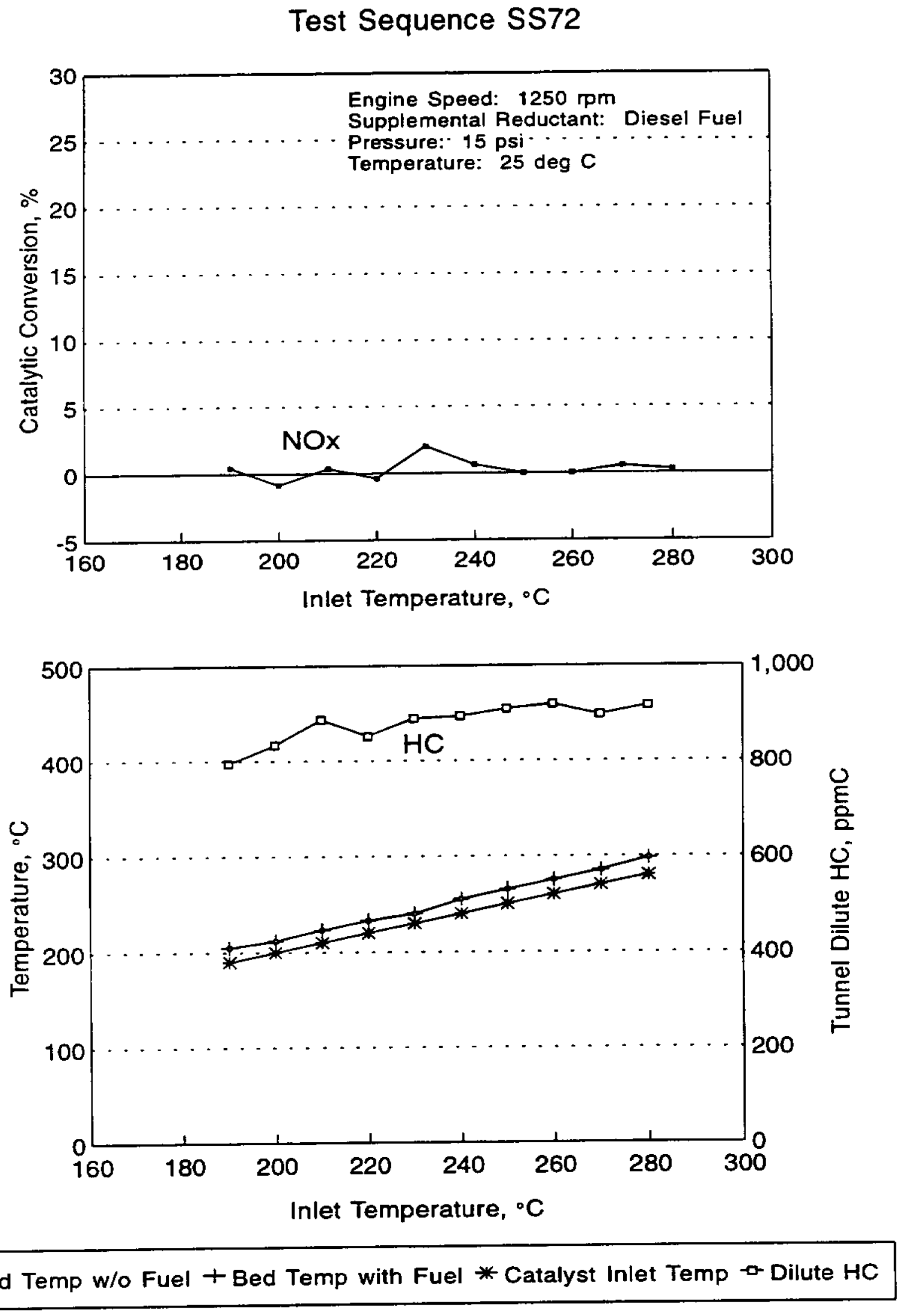


FIGURE 21. DIESEL NO_x CATALYTIC CONVERTER PERFORMANCE -- UNCOATED SUBSTRATE, TEST SEQUENCE SS72

TABLE 25. SUMMARY OF STEADY-STATE NO_x CATALYST TEST RESULTS – CATALYST DG-2

Test Sequence No.	Catalyst Inlet Temp, °C [a]	Supplementary Reductant			Feedgas HC/NO_x Ratio (typical) [b]	Maximum NO_x Reduction Efficiency, % [c]
		Material	Spray Pressure, psi	Spray Temp., °C		
SS46	220	Diesel Fuel	15	25	13	30
SS57	210	Diesel Fuel	10	25	11	30
SS58	230	Diesel Fuel	15	25	10	26
SS67	210	Diesel Fuel/ Ethanol	15	25	7.5 (8.4)[d]	26
SS68	190	Ethanol	15	25	4.5(5.6) [d]	18
SS68	210	Ethanol	15	25	3.7(4.6)[d]	17

[a] Catalyst inlet temperature at maximum measured NO_x reduction efficiency.
[b] Feedgas HC/NO_x ratio measured as C_1/NO_x by volume at catalyst inlet temperature specified.
[c] NO_x reduction efficiency calculated with respect to the no-added-reductant test performed with the catalyst in the exhaust system.
[d] HC/NO_x ratio assuming the FID response factor with ethanol is 0.8.

3. Nitrous Oxide Measurements

Measurements of nitrous oxide (N_2O) were made on selected FTP transient tests, and the results are given in Table 26. Similar data were taken for selected temperatures during steady-state temperature emission tests, and these data are provided in Table 27. The N_2O and NO_x measurements strongly suggest that N_2O is formed when NO_x is reduced. A plot of measured N_2O formation and NO_x reduction for the steady-state temperature emission tests is given in Figure 22. This plot shows that N_2O generally increases as NO_x is reduced, and that N_2O formation peaks (as NO_x reduction peaks) at a temperature of 220°C when diesel fuel is used as a supplementary reductant.

D. Diesel NO_x Catalyst Test Results -- Catalyst PS-1

1. Transient Tests

Diesel NO_x Catalyst PS-1 was evaluated on a Caterpillar 3116 diesel engine using the heavy-duty engine FTP. Combinations of diesel fuel, toluene, and ethanol were added to the exhaust as a supplementary reductant during these tests in an attempt to identify a superior reducing agent for NO_x. Heavy-duty engine FTP emission test results are given in Table 28. Catalyst PS-1 reduced NO_x from 5 to 13 percent on the Caterpillar 3116 engine over the heavy-duty FTP cycle with diesel fuel as a supplementary reductant.

TABLE 26. DIESEL NO_x CATALYST FTP NITROUS OXIDE EMISSIONS – CATALYST DG-2

Test Number	Date	Catalyst	Reductant Spray	Caterpillar 3116 Engine Hot-Start Heavy-Duty Transient Emissions, g/bhp-hr	
				NO_x	N_2O
DG2-A-57	2/16/95	DG-2	None	4.31	0.007
DG2-B-58Fi	2/16/95	DG-2	Diesel Fuel	3.80	0.115
DG2-A-67FEi	4/6/95	DG-2	Diesel Fuel/Ethanol	4.12	0.173
DG2-B-68	4/7/95	DG-2	None	4.23	0.052
DG2-A-69Fi	4/10/95	DG-2	Diesel Fuel	4.22	0.097
DG2-B-70E	4/10/95	DG-2	Ethanol	4.15	0.178
300-A-71	4/11/95	Uncoated	None	4.46	0.035
300-A-72	4/11/95	Uncoated	None	4.22	0.035

TABLE 27. DIESEL NO_x CATALYST STEADY-STATE NITROUS OXIDE EMISSIONS – CATALYST DG-2

Test Number	Date	Catalyst	Reductant Spray	Catalyst Inlet Temperature, °C	Caterpillar 3116 Engine Steady-State Emissions, g/bhp-hr		NO_x Reduced, g/bhp-hr	N_2O Formed, g/bhp-hr
					NO_x	N_2O		
DG2-58-SS200F	2/17/95	DG-2	Diesel Fuel	200	8.63	0.184	0.46	0.132
DG2-58-SS220F				220	6.92	0.658	1.88	0.615
DG2-58-SS240F				240	6.83	0.641	1.72	0.598
DG2-67-200FE	4/6/95	DG-2	Diesel Fuel/ Ethanol	200	7.02	0.780	2.07	0.728
DG2-67-220FE				220	6.67	0.805	2.13	0.762
DG2-67-240FE				240	7.68	0.406	0.87	0.363
DG2-68-200E	4/7/95	DG-2	Ethanol	200	7.61	0.750	1.48	0.698
DG2-68-220E				220	8.39	0.320	0.41	0.277
DG2-68-240E				240	8.32	0.153	0.23	0.110
UNC-72-200	4/11/95	Uncoated	None	200	9.09	0.052	Basis	Basis
UNC-72-220				220	8..80	0.043	Basis	Basis
UNC-72-240				240	8.55	0.043	Basis	Basis

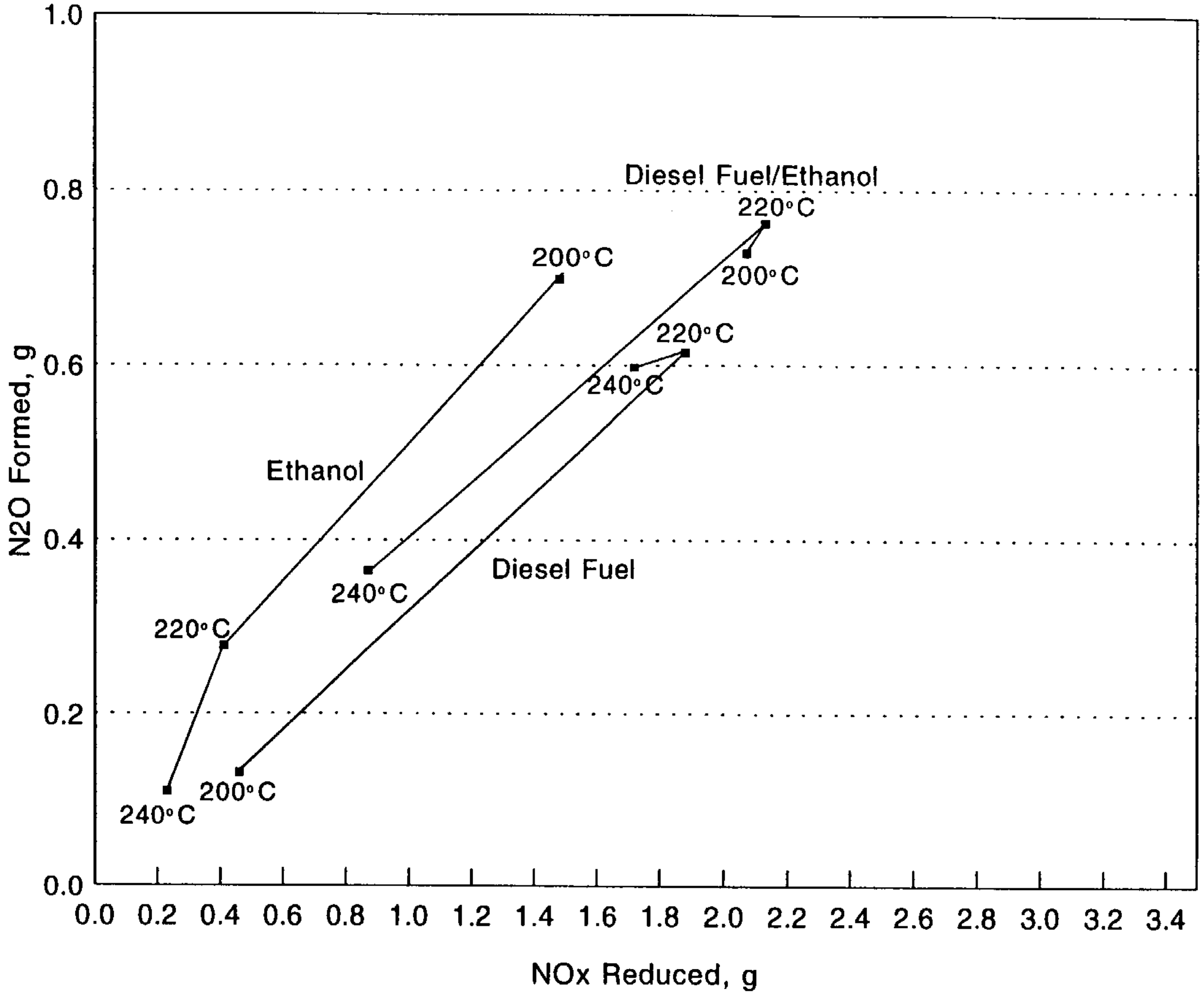


FIGURE 22. NITROUS OXIDE FORMATION AS A FUNCTION OF NO_x REDUCED -- CATALYST DG-2

TABLE 28. DIESEL NO_x CATALYST FTP TEST RESULTS – CATALYST PS-1

Test No.	Date	Catalyst	Reductant Spray	Caterpillar 3116 Engine Hot-Start Heavy-Duty Transient Emissions, g/bhp-hr			
				HC	CO	NO_x	PM
300-A-30 300-A-31	1/6/95 1/6/95	Uncoated Uncoated	None None	0.26 0.27	1.36 1.39	4.39 4.41	0.17 0.17
300-A-36	1/12/95	Uncoated	None	0.34	1.40	4.48	0.19
PS1-A-41-Fi PS1-B-42	1/17/95 1/17/95	PS-1 PS-1	Diesel Fuel None	2.47 0.06	0.36 0.13	4.03 4.45	-- --
300-A-43 300-B-44	1/17/95 1/17/95	Uncoated Uncoated	None None	0.34 0.30	1.18 1.35	4.50 4.53	-- --
300-A-50	1/25/95	Uncoated	None	0.26	1.51	4.71	0.19
300-A-55 300-A-56Fi	2/15/95 2/15/95	Uncoated Uncoated	None Diesel Fuel	0.32 19.36	1.30 1.33	4.26 4.27	0.19 5.68
PS1-A-59 PS1-B-60Fi	2/20/95 2/20/95	PS-1 PS-1	None Diesel Fuel	0.02 0.51	0.29 0.53	4.22 4.02	0.14 0.32
PS1-A-62FTi	2/22/95	PS-1	Diesel Fuel/ Toluene	6.40	0.66	3.85	0.31
PS1-A-62Fi PS1-B-63 PS1-C-64FTi	3/29/95 3/30/95 3/30/95	PS-1 PS-1 PS-1	Diesel Fuel None Diesel Fuel/ Toluene	8.47 0.04 7.33	0.63 0.29 0.59	3.87 4.24 3.97	1.52 0.19 0.53
PS1-D-65Ei	3/31/95	PS-1	Ethanol	3.67	0.32	4.41	0.18
PS1-A-66Fi	3/31/95	PS-1	Diesel Fuel	8.05	0.66	3.86	1.39
300-A-71 300-B-72	4/11/95 4/11/95	Uncoated Uncoated	None None	0.20 0.20	1.37 1.37	4.46 4.42	0.19 0.18

2. Steady-State Tests

Catalyst PS-1 was evaluated at steady-state engine conditions at catalyst inlet temperatures ranging from 180°C to 240°C (or 280°C), as shown in Figures 23 through 25. Additional NO_x conversion plots are given in Appendix E. The measured NO_x reduction efficiencies peaked at approximately 24 percent, with catalyst inlet temperature at 220°C and diesel fuel as the supplementary reductant. The HC-to-NO_x ratio at the inlet of the catalyst was greater than 10-to-1 by volume for steady-state tests using diesel fuel as a supplementary reductant. Tests were conducted using an exhaust gas space velocity of approximately 40,000 h^{-1} to 44,000 h^{-1}. A summary of the maximum steady-state NO_x conversion efficiencies is given in Table 29.

3. Nitrous Oxide Measurement

Measurements of nitrous oxide (N_2O) were made on selected FTP transient tests, and the results are given in Table 30. Similar data were taken for selected temperatures during steady-state temperature emission tests, and these data are provided in Table 31. The N_2O and NO_x measurements strongly suggest that N_2O is formed when NO_x is reduced. A plot of measured N_2O formation and NO_x reduction for the steady-state temperature emission tests is given in Figure 26. This plot shows that N_2O generally increases as NO_x is reduced, and that N_2O formation peaks (as NO_x reduction peaks) at a temperature of 220°C when diesel fuel is used as a supplementary reductant.

E. Diesel NO_x Catalyst Test Results -- Catalyst ORP

1. Transient Tests

Diesel NO_x Catalyst ORP was evaluated on a Caterpillar 3116 diesel engine using heavy-duty engine FTP tests and the temperature-based steady-state test conditions described in Section III. Combinations of diesel fuel and ethanol were added to the exhaust as a supplementary reductant during these tests. Heavy-duty engine FTP emission test results are given in Table 32. Catalyst ORP reduced NO_x up to 14 percent on the Caterpillar 3116 engine over the heavy-duty FTP cycle with diesel fuel as a supplementary reductant.

2. Steady-State Tests

Catalyst ORP was evaluated at steady-state engine conditions at catalyst inlet temperatures ranging from 180°C to 280°C, as shown in Figures 27 and 28. The measured NO_x reduction efficiencies peaked at approximately 19 percent at 220°C with diesel fuel as the supplementary reductant. The HC-to-NO_x ratio at the inlet of the catalyst was greater than 10-to-1 by volume for steady-state tests using diesel fuel as a supplementary reductant. Tests were conducted using an exhaust gas space velocity of approximately 40,000 h^{-1} to 44,000 h^{-1}. A summary of the maximum steady-state NO_x conversion efficiencies for Catalyst ORP is given in Table 33.

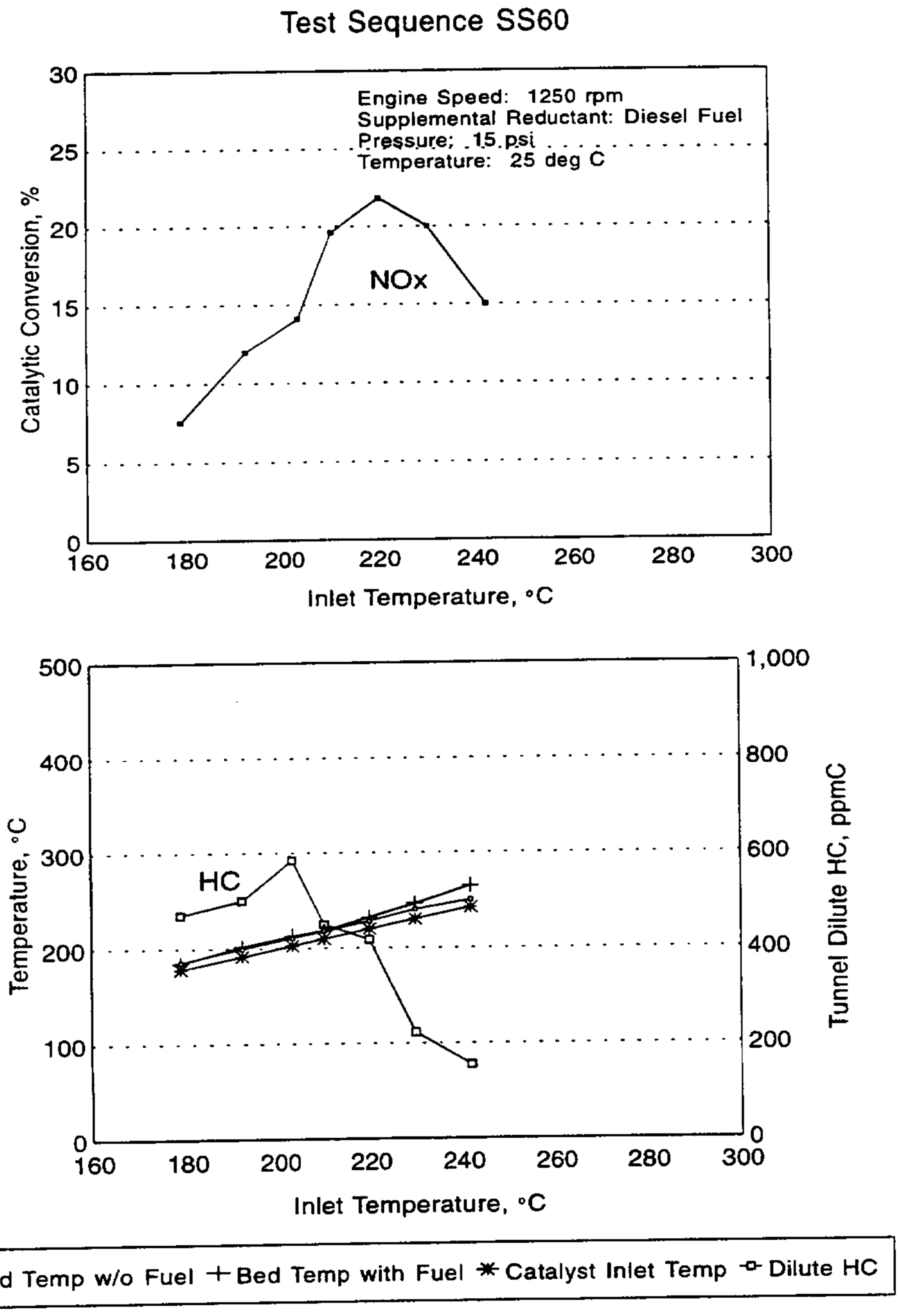


FIGURE 23. DIESEL NO_x CATALYTIC CONVERTER PERFORMANCE -- CATALYST PS-1, TEST SEQUENCE SS60

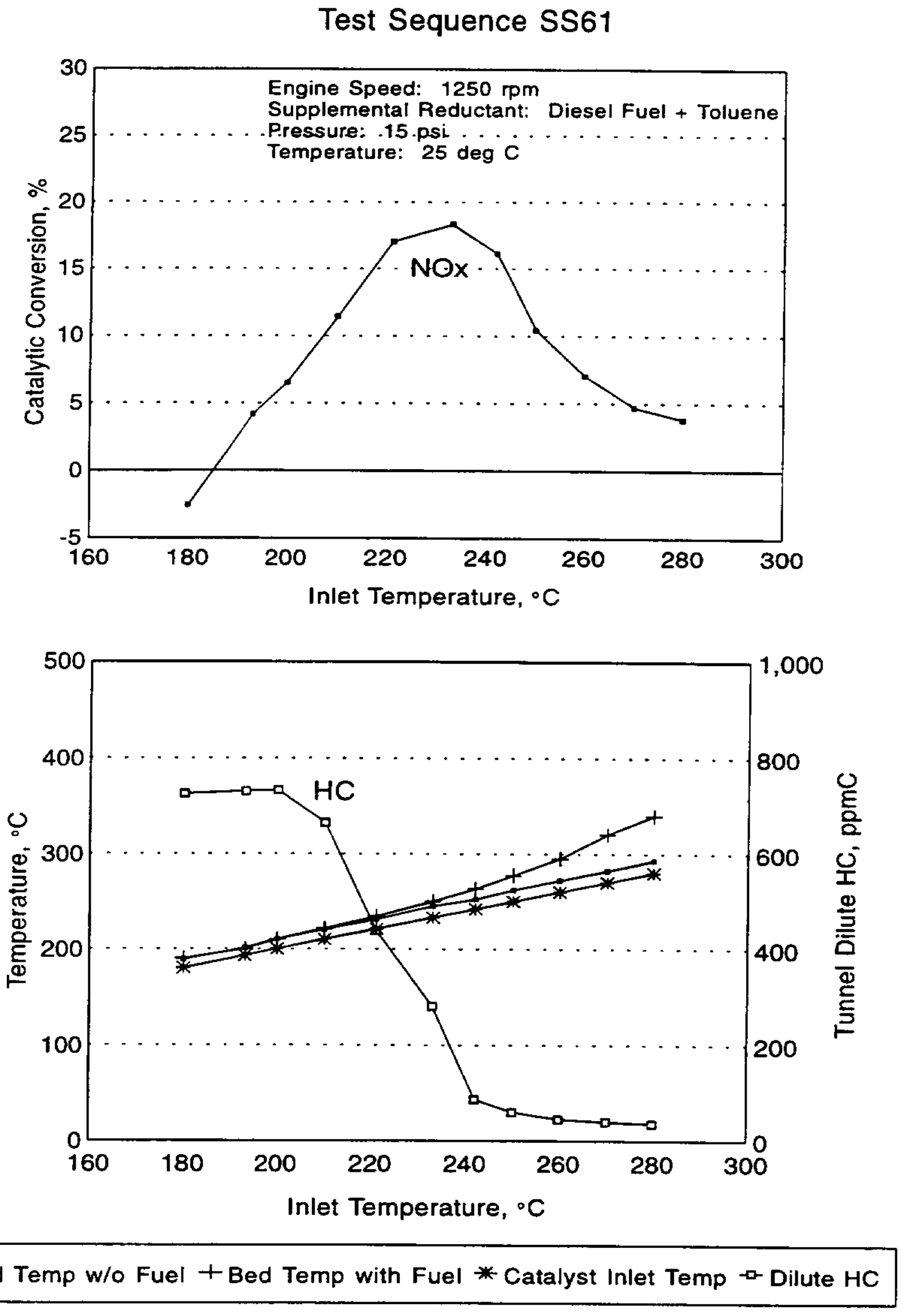


FIGURE 24. DIESEL NO_x CATALYTIC CONVERTER PERFORMANCE – CATALYST PS-1, TEST SEQUENCE SS61

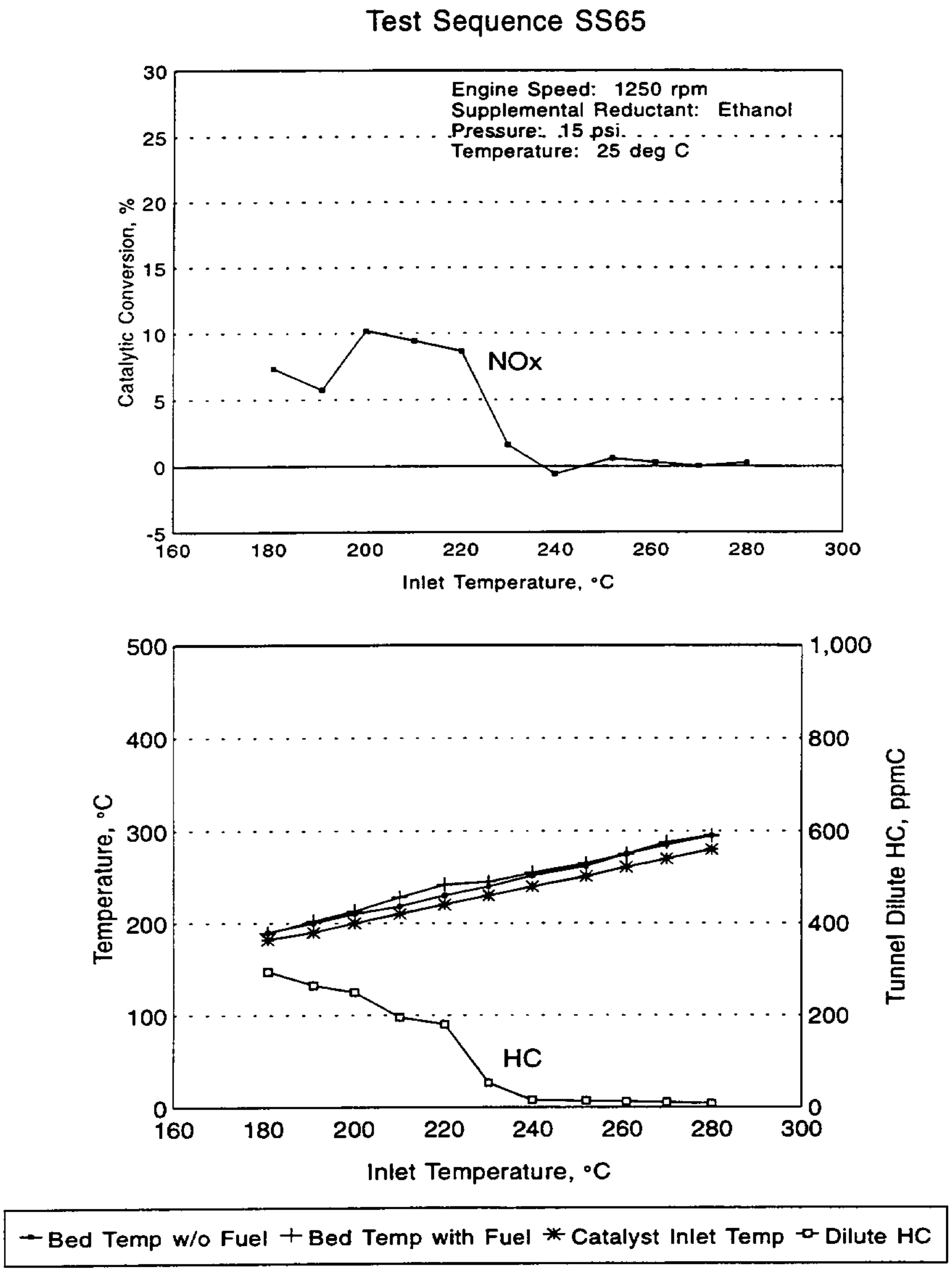


FIGURE 25. DIESEL NO_x CATALYTIC CONVERTER PERFORMANCE – CATALYST PS-1, TEST SEQUENCE SS65

TABLE 29. SUMMARY OF STEADY-STATE NO_x CATALYST TEST RESULTS – CATALYST PS-1

Test Sequence No.	Catalyst Inlet Temp, °C [a]	Supplementary Reductant			Feedgas HC/NO_x Ratio (typical) [b]	Maximum NO_x Reduction Efficiency, % [c]
		Material	Spray Pressure, psi	Spray Temp., °C		
SS41	220	Diesel Fuel	40	250	11	24
SS42	220	Diesel Fuel	25	250	8	19
SS60	220	Diesel Fuel	15	25	8	22
SS61	230	Diesel Fuel/ Toluene	15	25	11	18
SS65	200	Ethanol	15	25	4 (5) [d]	10
SS65A	220	Ethanol "Pulse" [e]	15	25	<1 [f]	1
SS65B	210	Diesel Fuel/ Ethanol	20	25	1	3
SS65C [g]	200	Diesel Fuel/ Ethanol	40	25	9	10

[a] Catalyst inlet temperature at maximum measured NO_x reduction efficiency.
[b] Feedgas HC/NO_x ratio measured as C_1/NO_x by volume at catalyst inlet temperature of 220°C.
[c] NO_x reduction efficiency calculated with respect to the no-added-reductant test performed with the catalyst in the exhaust system.
[d] HC/NO_x ratio assuming the FID response factor with ethanol is 0.8.
[e] "Pulse" - Supplementary reductant was cycled on and off at a frequency of approximately 0.25 Hz during the periods of reductant injection.
[f] "Pulse" experiment resulted in low HC content in the exhaust.
[g] Single-point experiment

TABLE 30. DIESEL NO_x CATALYST FTP NITROUS OXIDE EMISSIONS – CATALYST PS-1

Test Number	Date	Catalyst	Reductant Spray	Caterpillar 3116 Engine Hot-Start Heavy-Duty Transient Emissions, g/bhp-hr	
				NO_x	N_2O
PS1-A-62Fi	3/29/95	PS-1	Diesel Fuel	3.87	0.114
PS1-B-63	3/30/95	PS-1	None	4.24	0.004
PS1-C-64FTi	3/30/95	PS-1	Diesel Fuel/Toluene	3.97	0.100
PS1-D-65Ei	3/31/95	PS-1	Ethanol	4.41	0.032
PS1-A-66Fi	3/31/95	PS-1	Diesel Fuel	3.86	0.078
300-A-71	4/11/95	Uncoated	None	4.46	0.035
300-A-72	4/11/95	Uncoated	None	4.22	0.035

TABLE 31. DIESEL NO_x CATALYST STEADY-STATE NITROUS OXIDE EMISSIONS – CATALYST PS-1

Test Number	Date	Catalyst	Reductant Spray	Catalyst Inlet Temperature, °C	Caterpillar 3116 Engine Steady-State Emissions, g/bhp-hr		NO_x Reduced, g/bhp-hr	N_2O Formed, g/bhp-hr
					NO_x	N_2O		
PS1-60-SS200F	2/20/95	PS-1	Diesel Fuel	200	7.53	0.515	1.56	0.463
PS1-60-SS220F				220	6.64	0.743	2.16	0.700
PS1-60-SS240F				240	6.86	0.679	1.69	0.636
PS1-61-SS200FT	2/21/95	PS-1	Diesel Fuel/ Toluene	200	8.64	0.222	0.45	0.170
PS1-61-SS220FT				220	7.13	0.722	1.67	0.679
PS1-61-SS240FT				240	7.39	0.689	1.16	0.646
PS1-65-SS200E	4/5/95	PS-1	Ethanol	200	8.70	0.087	0.39	0.035
PS1-65-SS220E				220	8.75	0.059	0.05	0.016
PS1-65-SS240E				240	8.50	0.019	0.05	-0.024
UNC-72-200	4/11/95	Uncoated	None	200	9.09	0.052	Basis	Basis
UNC-72-220				220	8.80	0.043	Basis	Basis
UNC-72-240				240	8.55	0.043	Basis	Basis

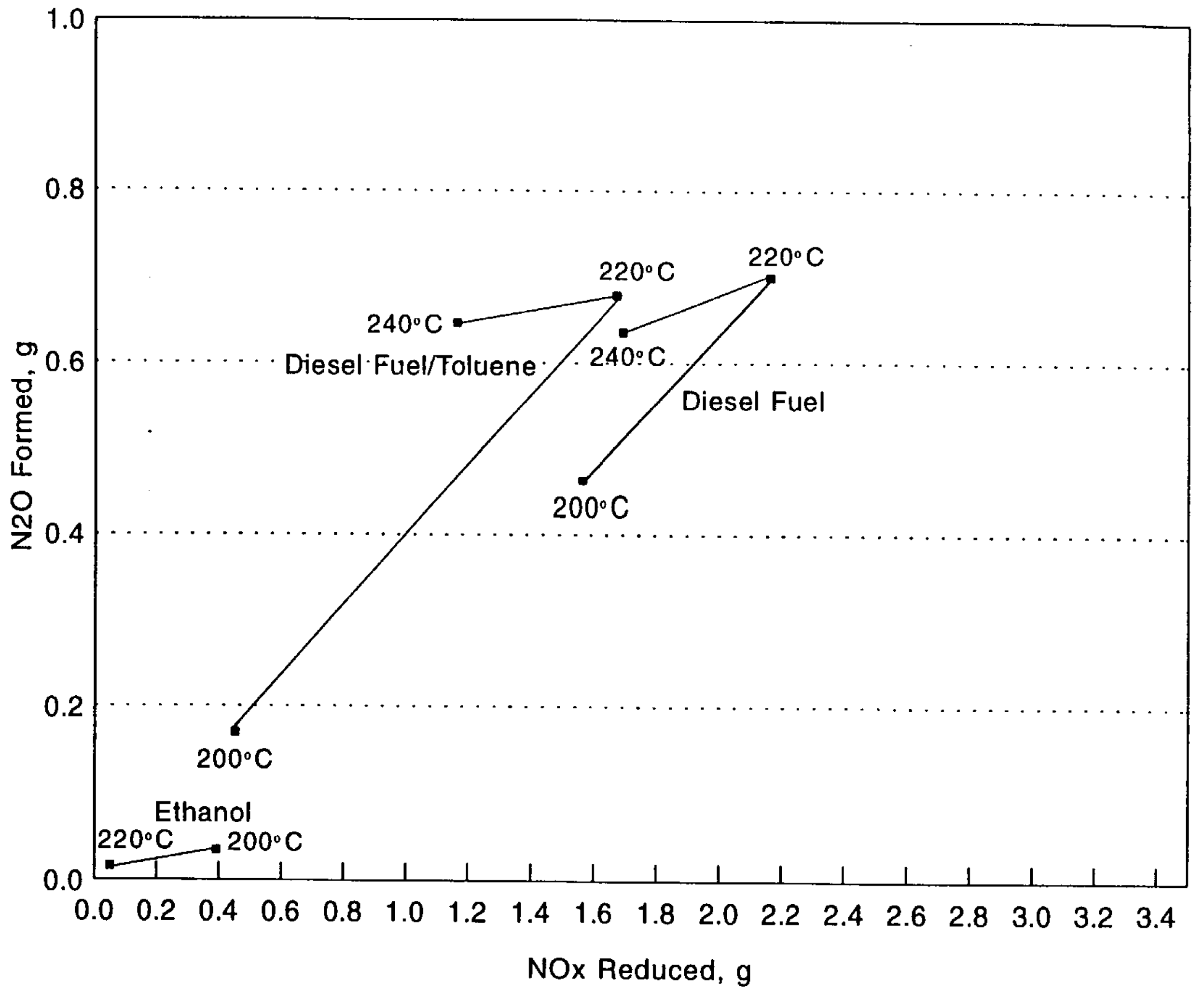


FIGURE 26. NITROUS OXIDE FORMATION AS A FUNCTION OF NO_x REDUCED -- CATALYST PS-1

TABLE 32. DIESEL NO_x CATALYST FTP TEST RESULTS – CATALYST ORP

Test No.	Date	Catalyst	Reductant Spray	Caterpillar 3116 Engine Hot-Start Heavy-Duty Transient Emissions, g/bhp-hr			
				HC	CO	NO_x	PM
300-A-55	2/15/95	Uncoated	None	0.32	1.30	4.26	0.19
300-A-56Fi	2/15/95	Uncoated	Diesel Fuel	19.36	1.33	4.27	5.68
300-A-71	4/11/95	Uncoated	None	0.20	1.37	4.46	0.19
300-B-72	4/11/95	Uncoated	None	0.20	1.37	4.42	0.18
ORP-A-79Ei	4/21/95	ORP	Ethanol	1.32	0.21	4.23	0.17
ORP-B-80Fi	4/24/95	ORP	Diesel Fuel	4.31	0.49	3.83	0.56
ORP-C-81	4/20/95	ORP	None	0.01	0.22	4.32	0.15

TABLE 33. SUMMARY OF STEADY-STATE NO_x CATALYST TEST RESULTS – CATALYST ORP

Test Sequence No.	Catalyst Inlet Temp, °C [a]	Supplementary Reductant			Feedgas HC/NO_x Ratio (typical) [b]	Maximum NO_x Reduction Efficiency, % [c]
		Material	Spray Pressure, psi	Spray Temp., °C		
SS79	200	Ethanol	15	25	3.4(4.3)[d]	13
SS79	220	Ethanol	15	25	3.1(3.9)[d]	12
SS80	220	Diesel Fuel	15	25	11	19

[a] Catalyst inlet temperature at maximum measured NO_x reduction efficiency.

[b] Feedgas HC/NO_x ratio measured as C_1/NO_x by volume at catalyst inlet temperature specified.

[c] NO_x reduction efficiency calculated with respect to the no-added-reductant test performed with the catalyst in the exhaust system.

[d] HC/NO_x ratio assuming the FID response factor with ethanol is 0.8.

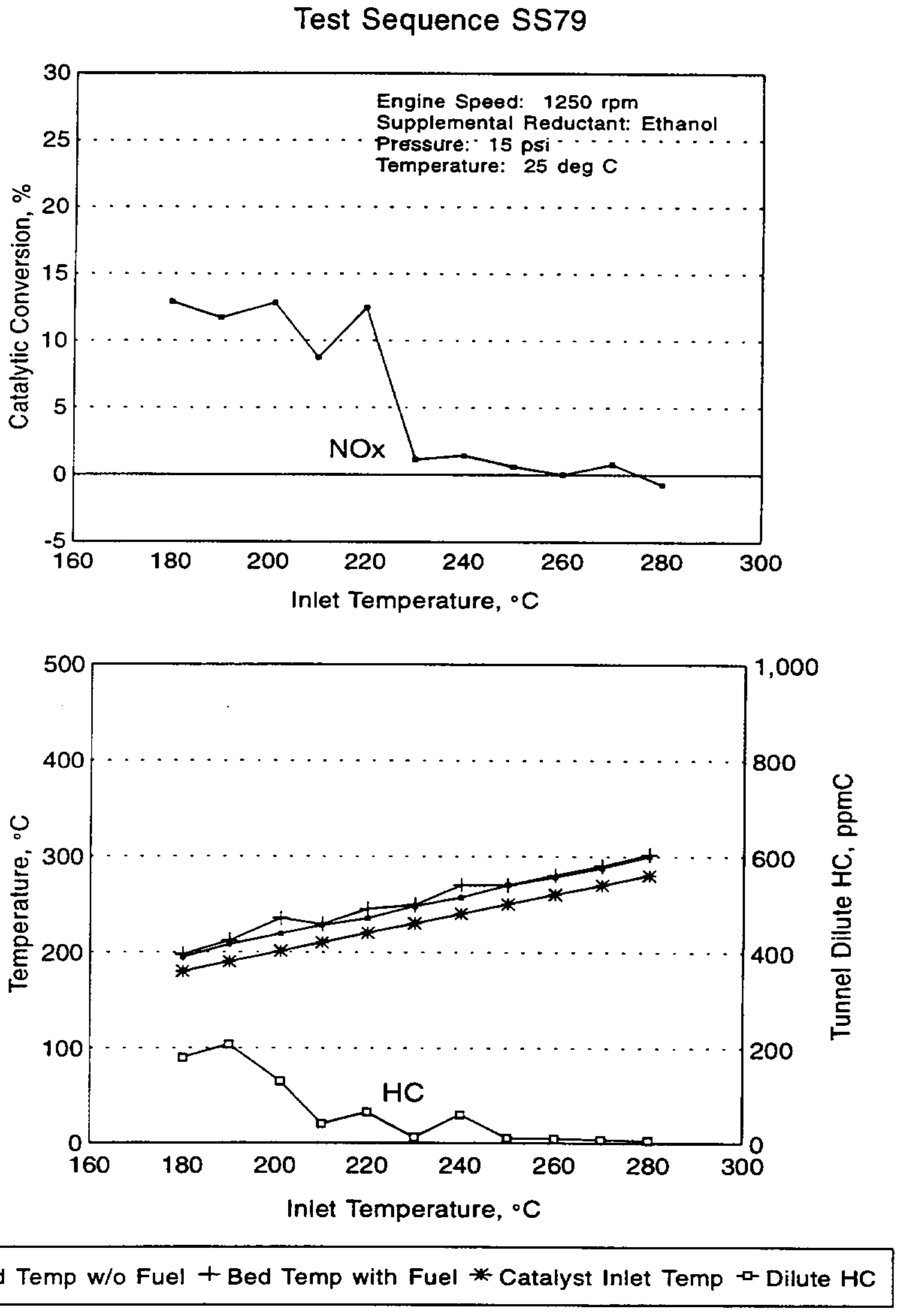


FIGURE 27. DIESEL NO$_x$ CATALYTIC CONVERTER PERFORMANCE — CATALYST ORP, TEST SEQUENCE SS79

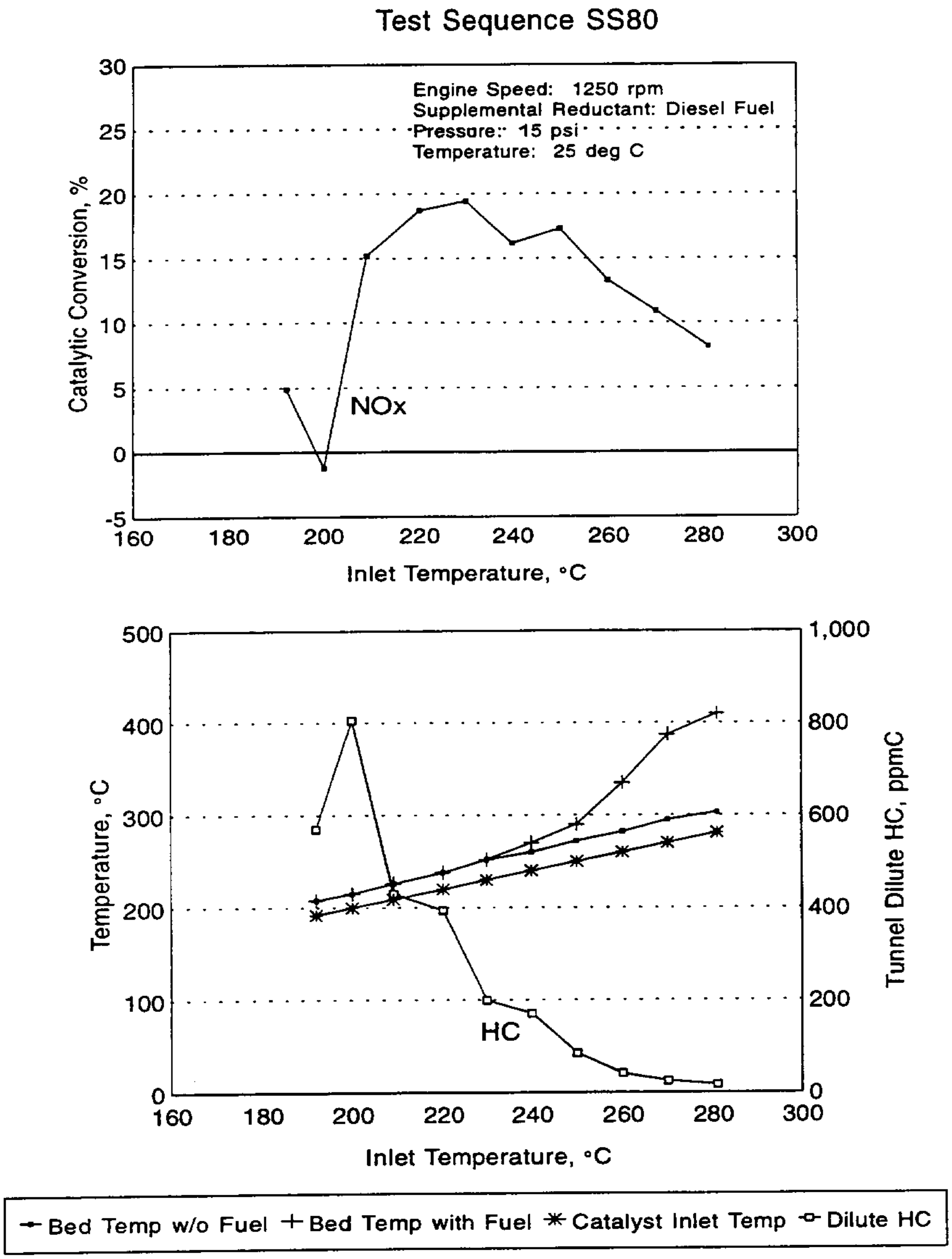


FIGURE 28. DIESEL NO$_x$ CATALYTIC CONVERTER PERFORMANCE – CATALYST ORP, TEST SEQUENCE SS80

3. Nitrous Oxide Measurements

Measurements of nitrous oxide (N_2O) were made on selected FTP transient tests, and the results are given in Table 34. Similar data were taken for selected temperatures during steady-state temperature emission tests, and these data are provided in Table 35. The N_2O and NO_x measurements strongly suggest that N_2O is formed when NO_x is reduced. A plot of measured N_2O formation and NO_x reduction for the steady-state temperature emission tests is given in Figure 29. This plot shows that N_2O generally increased as NO_x was reduced and that N_2O formation peaked (as NO_x reduction peaked) at a temperature of 220°C when diesel fuel was used as a supplementary reductant. With ethanol as a reductant, N_2O formation peaked below 200°C.

F. Diesel NO_x Catalyst Test Results -- Catalysts JM1 and JM2

1. Transient Tests

Diesel NO_x Catalysts JM1 and JM2 were evaluated on a Caterpillar 3116 diesel engine using the heavy-duty engine FTP. Combinations of diesel fuel, toluene, and ethanol were added to the exhaust as a supplementary reductant during these tests. Heavy-duty engine FTP emission test results are given in Table 36. Each of these catalysts reduced NO_x up to 13 percent on the Caterpillar 3116 engine over the heavy-duty FTP cycle with diesel fuel as a supplementary reductant. The volume of each of these catalysts was 14 liters. Catalysts JM1 and JM2 tested in parallel (total volume = 28 liters) resulted in up to 24 percent reduction in NO_x (compare Test Nos. -72 and -75F). A photograph of Catalysts JM1 and JM2 configured in parallel is given in Figure 30.

2. Steady-State Tests

Catalysts JM1 and JM2 were evaluated at steady-state engine conditions at catalyst inlet temperatures ranging from 180°C to 280°C, as shown in Figures 31 through 33. Additional NO_x conversion plots are given in Appendix E. The measured NO_x reduction efficiencies peaked at approximately 39 percent at 180°C with diesel fuel as the supplementary reductant. The HC-to-NO_x ratio at the inlet of the catalyst was at least 7-to-1 by volume for steady-state tests. Steady-state tests were conducted using an exhaust gas space velocity of approximately 20,000 h^{-1} for single catalyst tests (JM1 or JM2), and 10,000h^{-1} for double catalyst tests (JM1 + JM2). A summary of the maximum steady-state NO_x conversion efficiencies for Catalysts JM1 and JM2 is given in Table 37.

3. Nitrous Oxide Measurements

Measurements of nitrous oxide (N_2O) were made on selected FTP transients tests, and the results are given in Table 38. Similar data were taken for selected temperatures during steady-state temperature emission tests, and these data are provided in Table 39. The N_2O and NO_x measurements strongly suggest that N_2O is formed when NO_x is reduced. A plot of measured N_2O formation and NO_x reduction for the steady-state temperature emission tests is given in Figure 34. This plot shows that N_2O generally increased as NO_x was reduced and that N_2O formation apparently peaked (as NO_x reduction peaked) at a temperature of 200°C when diesel fuel or ethanol was used as a supplementary reductant.

TABLE 34. FTP HOT-START TRANSIENT NITROUS OXIDE EMISSIONS – CATALYST ORP

Test Number	Date	Catalyst	Reductant Spray	Caterpillar 3116 Engine Hot-Start Heavy-Duty Emissions, g/bhp-hr	
				NO_x	N_2O
300-A-71	4/11/95	Uncoated	None	4.46	0.035
300-A-72	4/11/95	Uncoated	None	4.22	0.035
ORP-C-81	4/20/95	ORP	None	4.32	0.021
ORP-A-79Ei	4/21/95	ORP	Ethanol	4.23	0.087
ORP-B-80Fi	4/24/95	ORP	Diesel Fuel	3.83	0.162

TABLE 35. STEADY-STATE NITROUS OXIDE EMISSIONS – CATALYST ORP

Test Number	Date	Catalyst	Reductant Spray	Catalyst Inlet Temperature, °C	Caterpillar 3116 Engine Steady-State Emissions, g/bhp-hr		NO_x Reduced, g/bhp-hr	N_2O Formed, g/bhp-hr
					NO_x	N_2O		
UNC-72-200	4/11/95	Uncoated	None	200	9.09	0.0518	Basis	Basis
UNC-72-220				220		0.0431	Basis	Basis
UNC-72-240				240		0.0426	Basis	Basis
ORP-79-200E	4/24/95	ORP	Ethanol	200	7.21	0.473	1.88	0.4212
ORP-79-220E				220		0.271		0.2279
ORP-79-240E				240		0.109		0.0664
ORP-80-200F	4/25/95	ORP	Diesel Fuel	200	7.54	0.294	1.55	0.2422
ORP-80-220F				220		0.871		0.8279
ORP-80-240F				240		0.807		0.7644

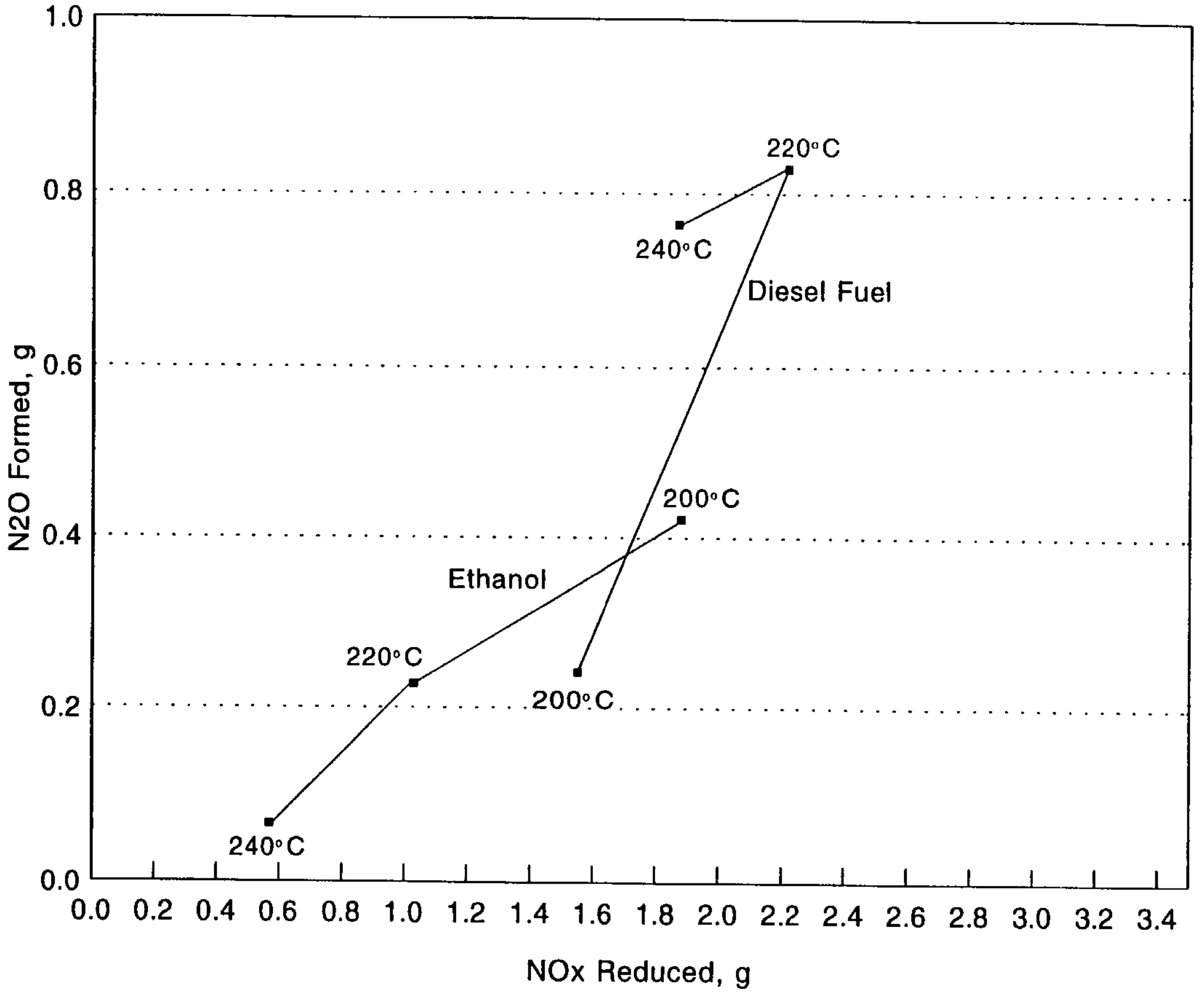


FIGURE 29. NITROUS OXIDE FORMATION AS A FUNCTION OF NO_x REDUCED -- CATALYST ORP

TABLE 36. DIESEL NO$_x$ CATALYST FTP TEST RESULTS -- CATALYSTS JM1 AND JM2

Test No.	Date	Catalyst	Reductant Spray	Caterpillar 3116 Engine Hot-Start Heavy-Duty Transient Emissions, g/bhp-hr			
				HC	CO	NO$_x$	PM
300-A-30	1/6/95	Uncoated	None	0.26	1.36	4.39	0.17
300-A-31	1/6/95	Uncoated	None	0.27	1.39	4.41	0.17
JM1-A-32-Fi	1/12/95	JM1	Diesel Fuel	0.70	0.18	3.85	0.17
JM1-B-33-FC	1/12/95	JM1	Diesel Fuel	0.59	0.17	3.91	0.18
JM1-C-34-FC	1/12/95	JM1	Diesel Fuel	0.48	0.16	3.92	0.19
JM1-D-35	1/12/95	JM1	None	0.00	0.04	4.32	0.15
300-A-36	1/12/95	Uncoated	None	0.34	1.40	4.48	0.19
300-A-43	1/17/95	Uncoated	None	0.34	1.18	4.50	--
300-B-44	1/17/95	Uncoated	None	0.30	1.35	4.53	--
JM2-A-48	1/23/95	JM2	None	0.00	0.17	4.42	0.14
JM2-B-49Fi	1/23/95	JM2	Diesel Fuel	0.23	0.39	3.87	0.21
300-A-50	1/25/95	Uncoated	None	0.26	1.51	4.71	0.19
JM12-A-52	2/10/95	JM1+JM2 (P)	None	0.00	0.10	4.21	0.14
JM12-B-53Fi	2/10/95	JM1+JM2 (P)	Diesel Fuel	1.04	0.29	3.58	0.18
JM12-A-54Ti	2/14/95	JM1+JM2 (P)	Toluene	0.60	0.32	3.58	0.61
300-A-55	2/15/95	Uncoated	None	0.32	1.30	4.26	0.19
300-A-56Fi	2/15/95	Uncoated	Diesel Fuel	19.36	1.33	4.27	5.68
300-A-71	4/11/95	Uncoated	None	0.20	1.37	4.46	0.19
300-B-72	4/11/95	Uncoated	None	0.20	1.37	4.42	0.18
JM12-A-73	4/12/95	JM1+JM2 (P)	None	0.00	0.02	4.17	0.15
JM12-B-74Fi	4/12/95	JM1+JM2 (P)	Diesel Fuel	0.34	0.20	3.60	0.17
JM12-C-75F	4/12/95	JM1+JM2 (P)	Diesel Fuel	0.69	0.26	3.38	0.24
JM12-A-76Ei	4/18/95	JM1+JM2 (P)	Ethanol	0.03	0.04	4.13	0.15
JM12-B-77	4/18/95	JM1+JM2 (P)	None	0.02	0.02	4.25	0.16
JM12-A-78Ei	4/18/95	JM1+JM2 (P)	Ethanol	0.99	0.11	3.72	0.16

Test Numbers:
Fi - Supplemental reductant (diesel fuel) spray. Intermittent spray controlled manually.
FC - Supplemental reductant (diesel fuel) spray. Intermittent spray controlled automatically by a computer controller.
Ti - Supplemental reductant (toluene) spray. Intermittent spray controlled manually.
Ei - Supplemental reductant (ethanol) spray. Intermittent spray controlled manually.

Catalyst Configuration:
(P) - Catalysts in parallel.

FIGURE 30. CATALYSTS JM1 AND JM2 CONFIGURED IN PARALLEL

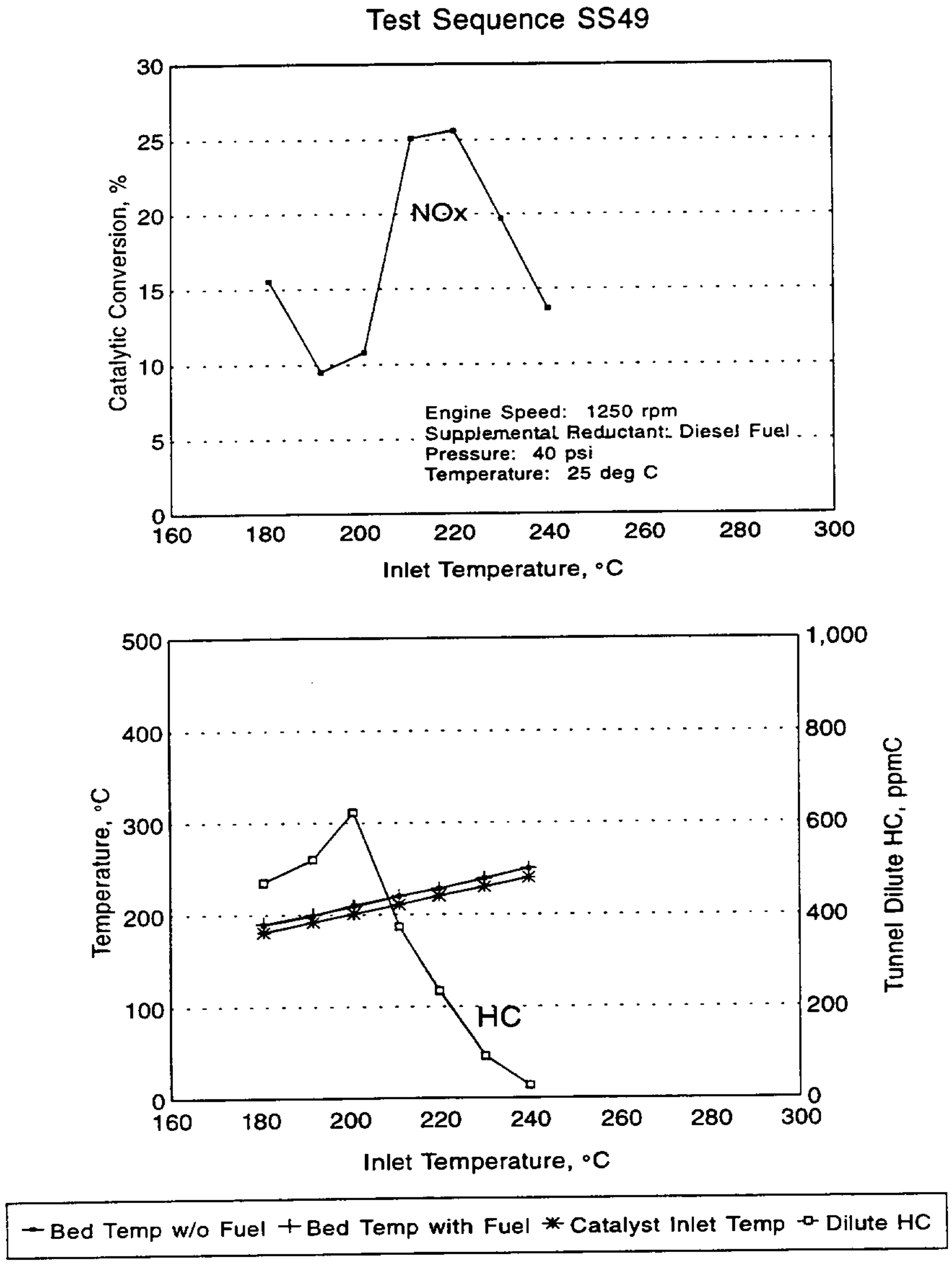


FIGURE 31. DIESEL NO$_x$ CATALYTIC CONVERTER PERFORMANCE -- CATALYST JM2, TEST SEQUENCE SS49

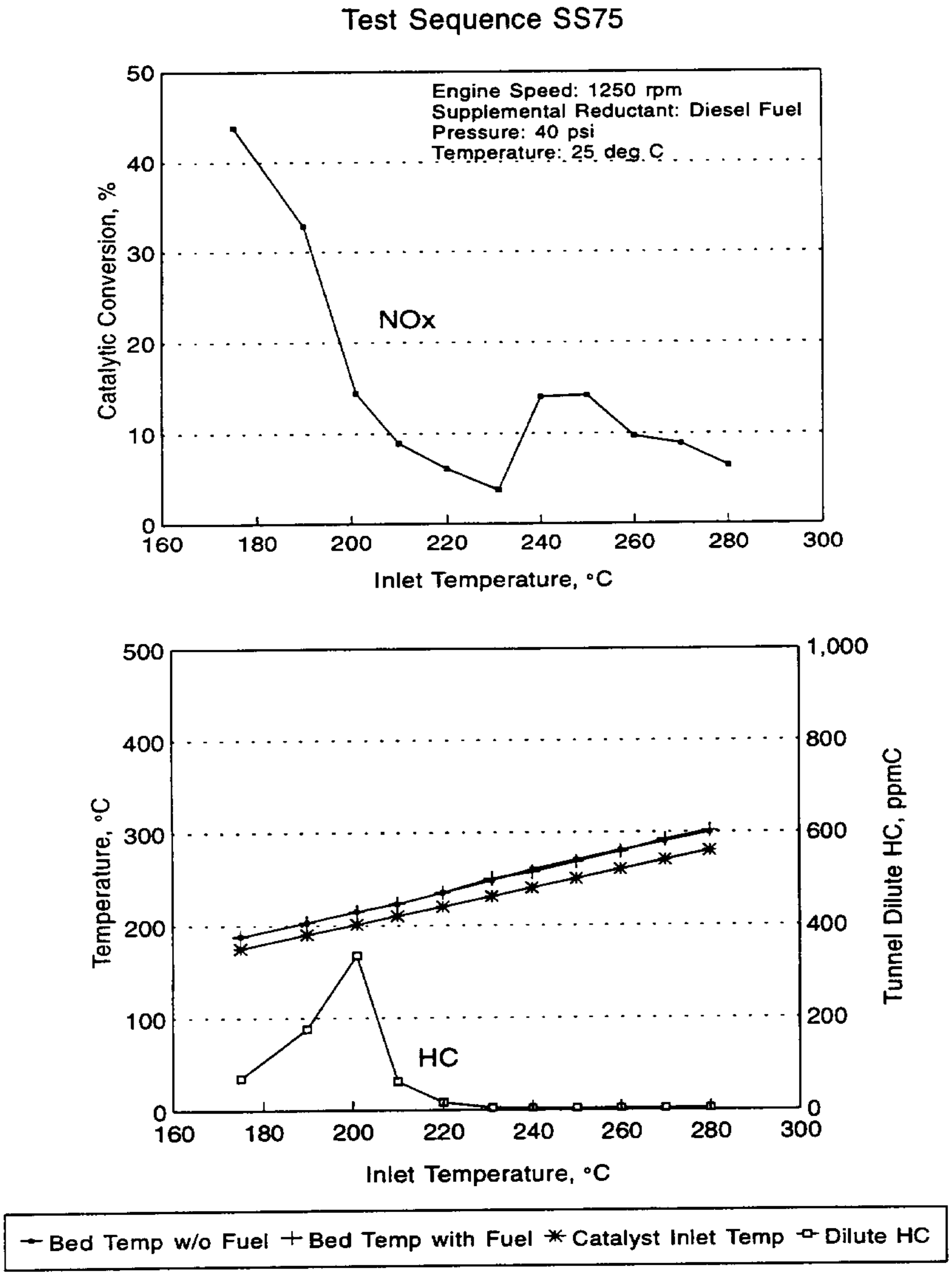


FIGURE 32. DIESEL NO_x CATALYTIC CONVERTER PERFORMANCE – CATALYSTS JM1 + JM2, TEST SEQUENCE SS75

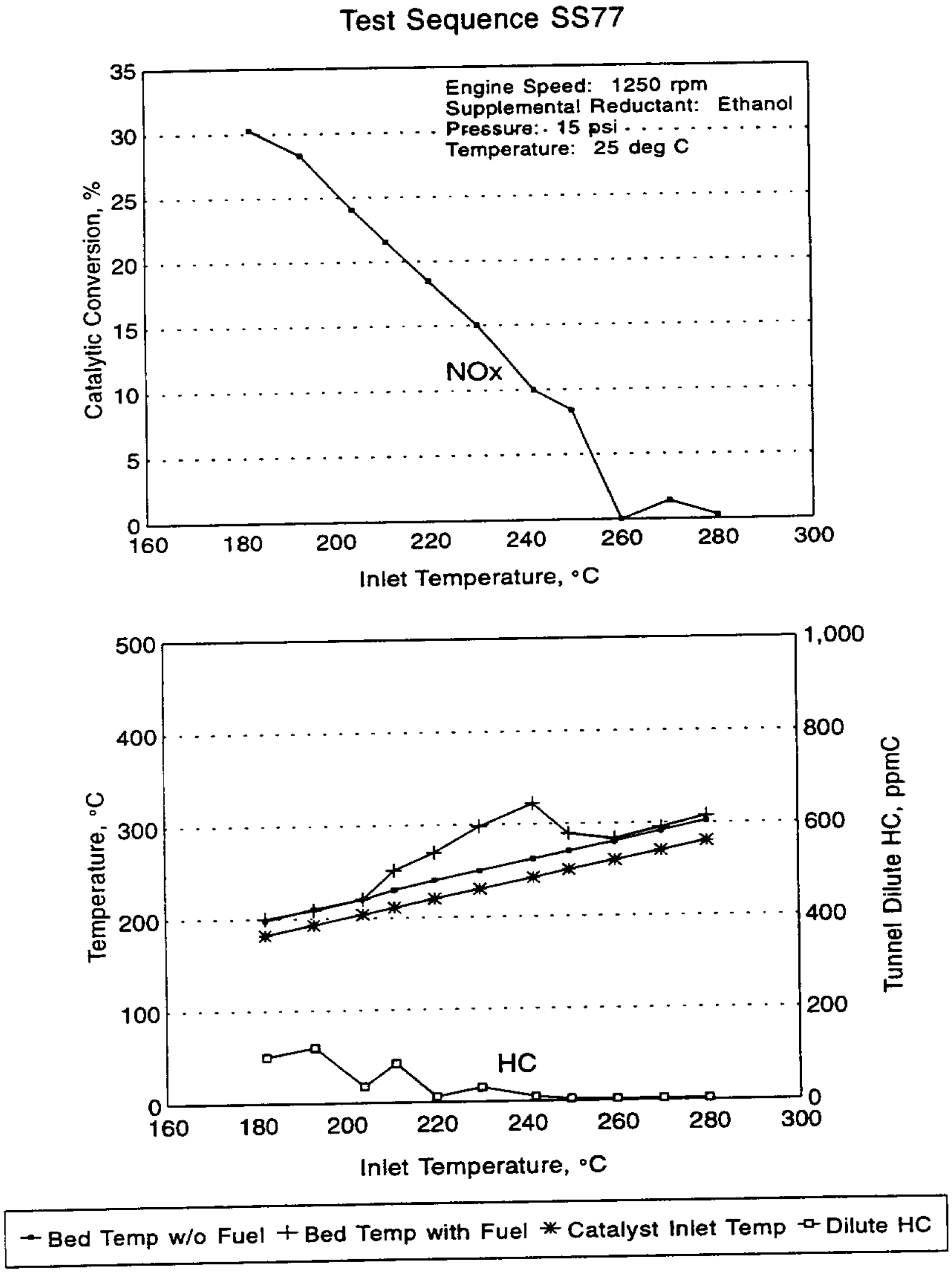


FIGURE 33. DIESEL NO_x CATALYTIC CONVERTER PERFORMANCE – CATALYSTS JM1 + JM2, TEST SEQUENCE SS77

TABLE 37. SUMMARY OF STEADY-STATE NO_x CATALYST TEST RESULTS – CATALYSTS JM1 AND JM2

Test Sequence No.	Catalyst	Catalyst Inlet Temp, °C [a]	Supplementary Reductant			Feedgas HC/NO_x Ratio (typical) [b]	Maximum NO_x Reduction Efficiency, % [c]
			Material	Spray Pressure, psi	Spray Temp., °C		
SS48	JM2	210	Diesel Fuel	40	25	7	30
SS49	JM2	220	Diesel Fuel	40	25	10	26
SS53	JM1 + JM2(P)[f]	180	Diesel Fuel	40	25	9	30
SS53	JM1 + JM2(P)[f]	210	Diesel Fuel	40	25	7	20
SS74	JM1 + JM2(P)[f]	180	Diesel Fuel	15	25	1.5[e]	39
SS75	JM1 + JM2(P)[f]	180	Diesel Fuel	40	25	8	44
SS76	JM1 + JM2(P)[f]	180	Diesel Fuel/ Ethanol	15	25	1.4(1.6)[d,e]	29
SS76	JM1 + JM2(P)[f]	200	Diesel Fuel/ Ethanol	15	25	1.2(1.4)[d,e]	28
SS77	JM1 + JM2(P)[f]	180	Ethanol	15	25	2.4(3.0)[d,e]	30

[a] Catalyst inlet temperature at maximum measured NO_x reduction efficiency.

[b] Feedgas HC/NO_x ratio measured as C_1/NO_x by volume at catalyst inlet temperature specified.

[c] NO_x reduction efficiency calculated with respect to the no-added-reductant test performed with the catalyst in the exhaust system.

[d] HC/NO_x ratio assuming the FID response factor with ethanol is 0.8.

[e] Diesel fuel and ethanol/diesel fuel blends apparently oxidized in this catalytic converter at low temperatures (<180°C) making inlet HC/NO_x ratio difficult to verify. Data show HC/NO_x ratio to be at least 1.4 to 3.0, however, higher ratios may have occurred.

[f] (P) - Catalysts in parallel; Space velocity divided in half; Total catalyst volume = 28 liters.

TABLE 38. DIESEL NO_x CATALYST FTP NITROUS OXIDE EMISSIONS – CATALYSTS JM1 AND JM2 IN PARALLEL

Test Number	Date	Catalyst	Reductant Spray	Caterpillar 3116 Engine Hot-Start Heavy-Duty Transient Emissions, g/bhp-hr	
				NO_x	N_2O
300-A-71	4/11/95	Uncoated	None	4.46	0.035
300-A-72	4/11/95	Uncoated	None	4.22	0.035
JM12-A-73	4/12/95	JM1+JM2 (P)	None	4.17	0.009
JM12-B-74Fi	4/12/95	JM1+JM2 (P)	Diesel Fuel	3.60	0.332
JM12-C-75Fi	4/12/95	JM1+JM2 (P)	Diesel Fuel	3.38	0.344
JM12-A-76Ei	4/18/95	JM1+JM2 (P)	Ethanol	4.13	0.066
JM12-B-77	4/18/95	JM1+JM2 (P)	None	4.25	0.041

Test Number:
Fi - Supplemental reductant (diesel fuel) spray. Intermittent spray controlled manually.
Ei- Supplemental reductant (ethanol) spray. Intermittent spray controlled manually.
Catalyst Configuration:
(P) - Catalysts in parallel

TABLE 39. DIESEL NO_x CATALYST STEADY-STATE NITROUS OXIDE EMISSIONS – CATALYSTS JM1 AND JM2 IN PARALLEL

Test Number	Date	Catalyst	Reductant Spray	Catalyst Inlet Temperature, °C	Caterpillar 3116 Engine Steady-State Emissions, g/bhp-hr		NO_x Reduced, g/bhp-hr	N_2O Formed, g/bhp-hr
					NO_x	N_2O		
UNC-72-200	4/11/95	Uncoated	None	200	9.09	0.052	Basis	Basis
UNC-72-220				220	8.80	0.043	Basis	Basis
UNC-72-240				240	8.55	0.043	Basis	Basis
JM12-74-200F	4/13/95	JM1+JM2 (P)	Diesel Fuel	200	5.67	1.048	3.42	0.996
JM12-74-220F				220	5.83	1.024	2.97	0.981
JM12-74-240F				240	6.49	0.812	2.06	0.770
JM12-75-200F	4/14/95	JM1+JM2 (P)	Diesel Fuel	200	5.99	0.855	3.10	0.803
JM12-75-220F				220	6.26	0.774	2.54	0.731
JM12-75-240F				240	6.56	0.680	1.99	0.638
JM12-76-200FE	4/17/95	JM1+JM2 (P)	Diesel Fuel/ Ethanol	200	6.44	0.785	2.65	0.734
JM12-76-220FE				220	7.60	0.343	1.20	0.300
JM12-76-240FE				240	7.99	0.206	0.56	0.164
JM12-77-200E	4/19/95	JM1+JM2 (P)	Ethanol	200	6.41	0.583	2.68	0.531
JM12-77-220E				220	6.50	0.601	2.30	0.558
JM12-77-240E				240	7.10	0.344	1.45	0.301

Catalyst Configuration:
(P) - Catalysts in Parallel

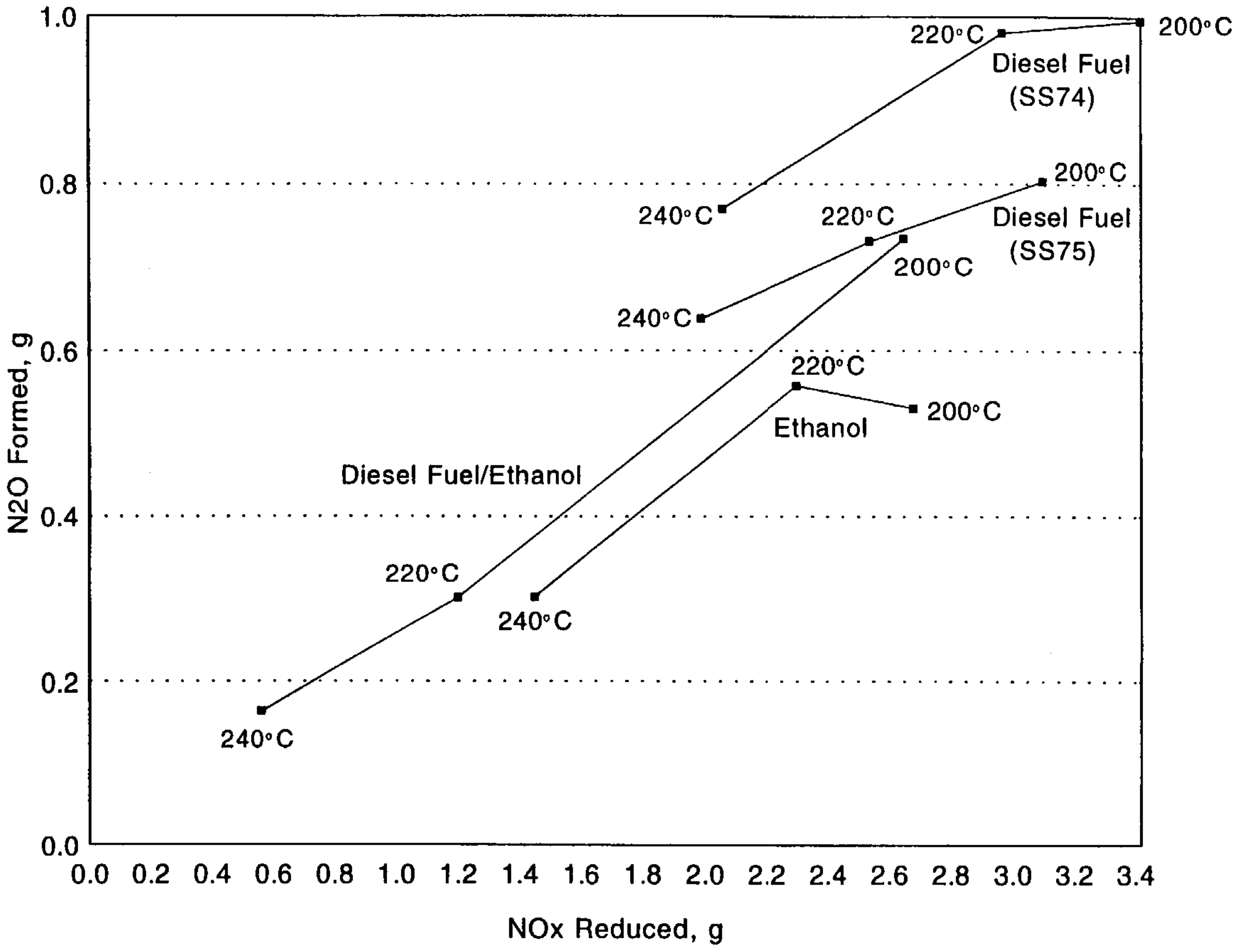


FIGURE 34. NITROUS OXIDE FORMATION AS A FUNCTION OF NO_x REDUCED -- CATALYSTS JM1 AND JM2

G. Diesel NO_x Catalyst Test Results -- Catalysts 220 and 221

1. Transient Tests

Diesel NO_x Catalysts 220-K-1 and 221-K-1 (Catalysts 220 and 221) were evaluated on a Caterpillar 3116 diesel engine using the heavy-duty engine FTP and the temperature-based steady-state test conditions described in Section III. Diesel fuel was added to the exhaust as a supplementary reductant during these tests. Heavy-duty engine FTP emission test results are given in Table 40. These catalysts reduced NO_x up to 5 percent on the Caterpillar 3116 engine over the heavy-duty FTP cycle with diesel fuel as a supplementary reductant.

2. Steady-State Tests

Catalysts 220 and 221 were also evaluated together in series, as shown in Figure 35. Steady-state engine tests were conducted with inlet temperatures ranging from 180°C to 440°C, as shown in Figures 36 and 37. Measured NO_x reduction efficiencies peaked at approximately 17 percent at 260°C with diesel fuel as the supplementary reductant. The HC-to-NO_x ratio at the inlet of the catalyst was approximately 10-to-1 by volume during the steady-state tests. The steady-state tests were conducted using an exhaust gas space velocity of approximately 20,000 h^{-1} to 22,000 h^{-1}. A summary of the maximum steady-state NO_x conversion efficiencies is given in Table 41.

The series combination of Catalysts 220 and 221 had a peak NO_x reduction efficiency at an inlet temperature of 260°C. This peak-conversion temperature differed from many of the other catalysts evaluated in this project. Other catalysts had peak NO_x conversions near 220°C. No other tests were performed on Catalysts 220 or 221.

H. Diesel NO_x Catalyst Test Results -- Catalysts NP-3 and NP-6

1. Transient Tests

Diesel NO_x Catalysts NP-3 and NP-6 were evaluated on a Caterpillar 3116 diesel engine using the heavy-duty engine FTP. Diesel fuel was added to the exhaust as a supplementary reductant during these tests. Heavy-duty engine FTP emission test results are given in Table 42. Catalyst NP-3 reduced NO_x by 5 percent on the Caterpillar 3116 engine over the heavy-duty FTP cycle with diesel fuel as a supplementary reductant.

2. Steady-State Tests

Catalyst NP-6 was evaluated under steady-state engine conditions at catalyst inlet temperatures ranging from 180°C to 240°C, as shown in Figure 38. The measured NO_x reduction efficiencies were nominally zero percent at these temperatures. The HC-to-NO_x ratio at the inlet of the catalyst was approximately 10-to-1 by volume. Tests were conducted using an exhaust gas space velocity of approximately 40,000 h^{-1} to 44,000 h^{-1}. The steady-state NO_x conversion efficiencies, along with other important data, are given in Table 43. It is possible that this catalyst would have performed better at higher inlet exhaust gas temperatures. Unfortunately, it was tested only up to 240°C during the steady-state conversion evaluations. No additional tests were performed on catalysts NP-3 or NP-6.

TABLE 40. DIESEL NO_x CATALYST FTP TEST RESULTS – CATALYSTS 220 AND 221

				Caterpillar 3116 Engine Hot-Start Heavy-Duty Transient Emissions, g/bhp-hr			
Test No.	Date	Catalyst	Reductant Spray	HC	CO	NO_x	PM
300-A-30	1/6/95	Uncoated	None	0.26	1.36	4.39	0.17
300-A-31	1/6/95	Uncoated	None	0.27	1.39	4.41	0.17
300-A-36	1/12/95	Uncoated	None	0.34	1.40	4.48	0.19
AS1-A-37	1/13/95	220	None	0.12	0.50	4.53	0.17
AS1-B-38Fi	1/13/95	220	Diesel Fuel	4.53	0.77	4.28	0.53
AS3-A-39	1/16/95	221	None	0.12	0.62	4.58	0.17
AS3-B-40Fi	1/16/95	221	Diesel Fuel	6.88	1.10	4.41	1.06
300-A-43	1/17/95	Uncoated	None	0.34	1.18	4.50	--
300-B-44	1/17/95	Uncoated	None	0.30	1.35	4.53	--

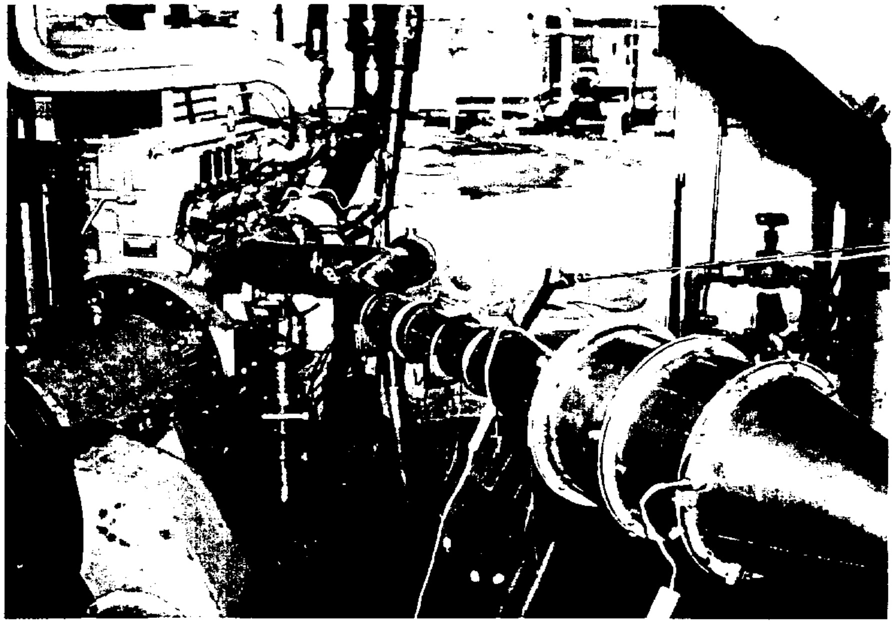


FIGURE 35. CATALYSTS 220 AND 221 CONFIGURED IN SERIES

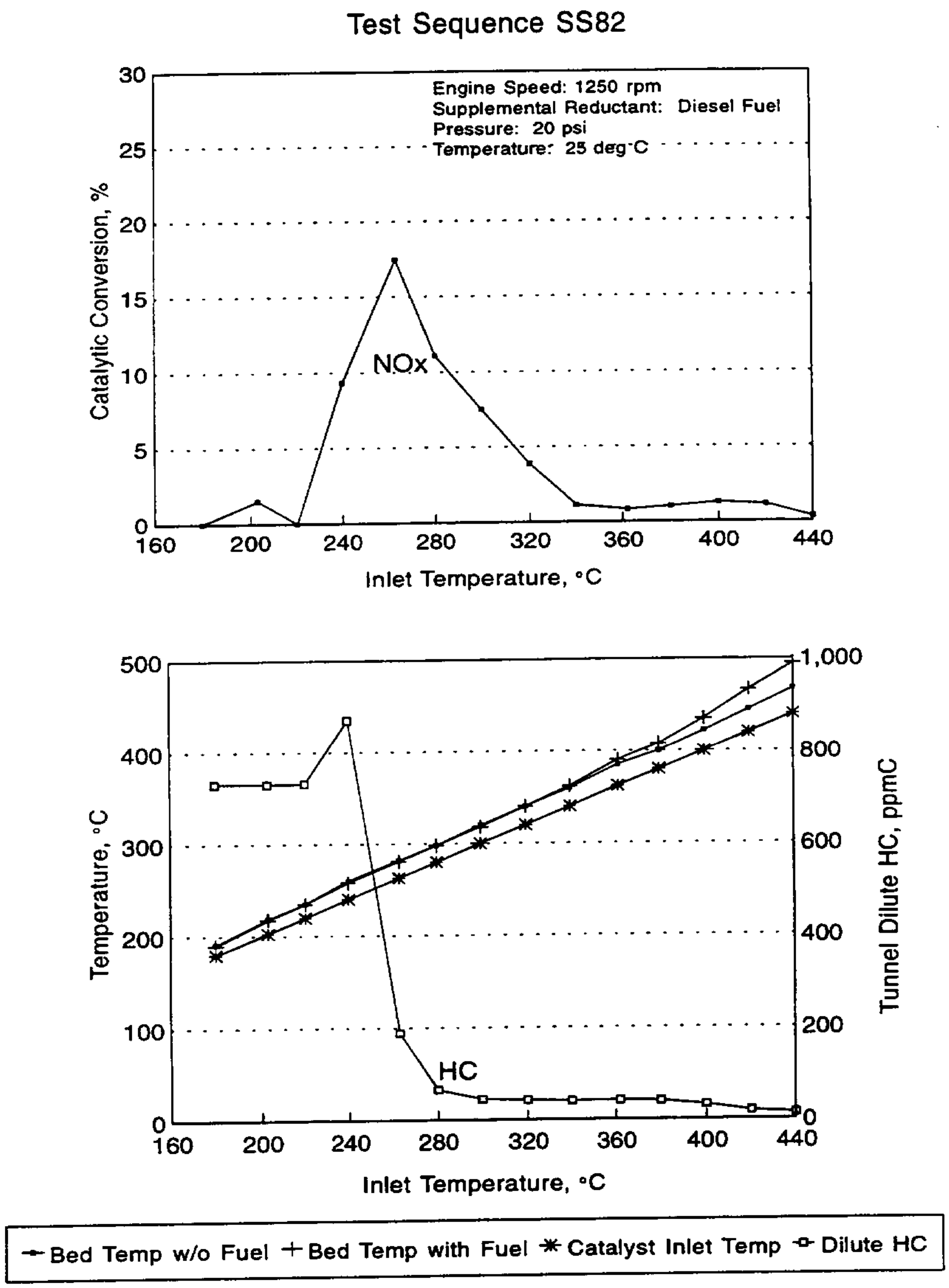


FIGURE 36. DIESEL NO_x CATALYTIC CONVERTER PERFORMANCE – CATALYSTS 220 + 221, TEST SEQUENCE SS82

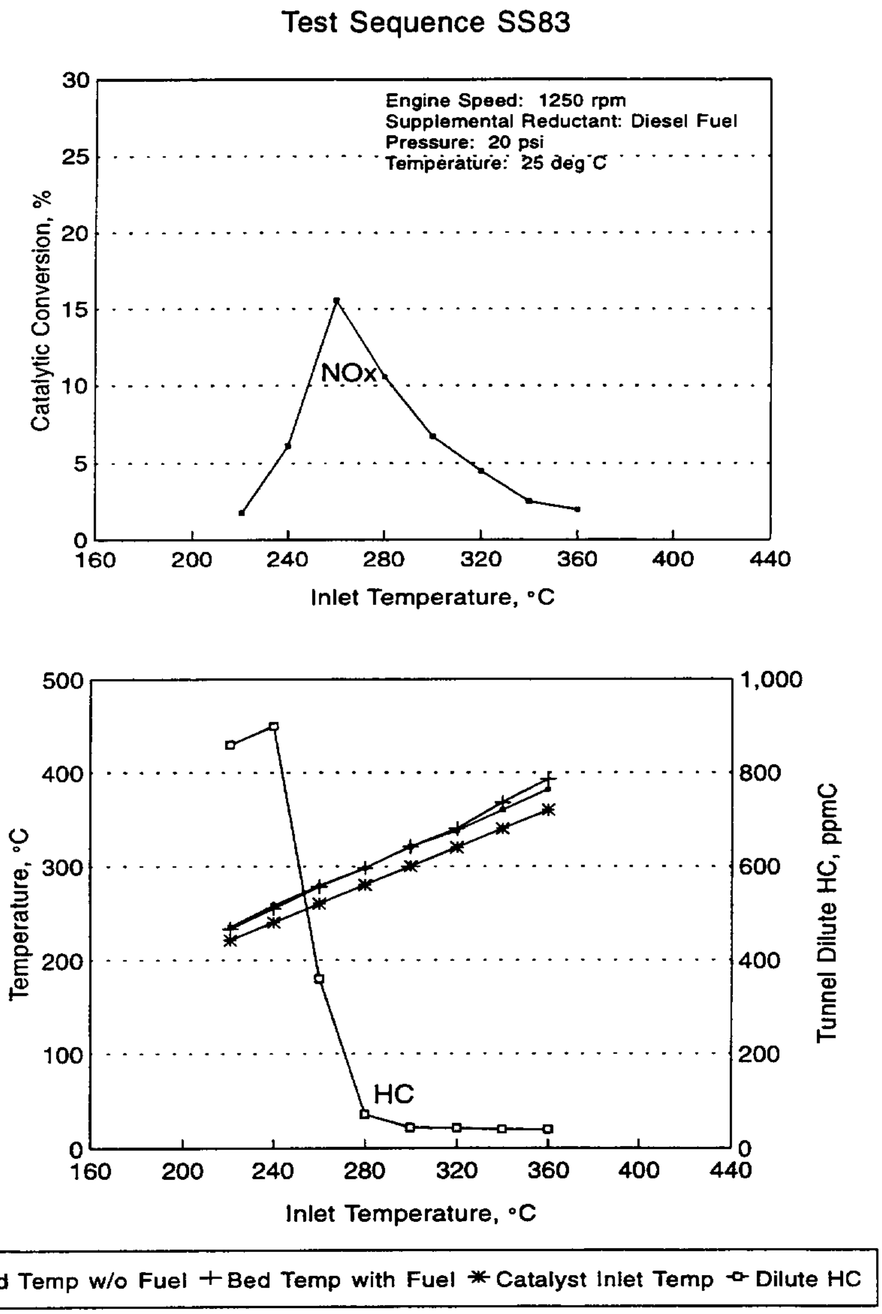


FIGURE 37. DIESEL NO$_x$ CATALYTIC CONVERTER PERFORMANCE – CATALYSTS 220 + 221, TEST SEQUENCE SS83

TABLE 41. SUMMARY OF STEADY-STATE NO_x CATALYST TEST RESULTS – CATALYSTS 220 AND 221 IN SERIES

Test Sequence No.	Catalyst Inlet Temp, °C [a]	Supplementary Reductant			Feedgas HC/NO_x Ratio (typical) [b]	Maximum NO_x Reduction Efficiency, % [c]
		Material	Spray Pressure, psi	Spray Temp., °C		
SS82	260	Diesel Fuel	20	25	8	17[d]
SS83	260	Diesel Fuel	20	25	10	16[d]

[a] Catalyst inlet temperature at maximum measured NO_x reduction efficiency.

[b] Feedgas HC/NO_x ratio measured as C_1/NO_x by volume at catalyst inlet temperature of 260°C.

[c] NO_x reduction efficiency calculated with respect to the no-added-reductant test performed with the catalyst in the exhaust system.

[d] Catalysts 220 and 221 configured in series - Total catalyst volume 14 liters

TABLE 42. DIESEL NO_x CATALYST FTP TEST RESULTS – CATALYSTS NP-3 AND NP-6

Test No.	Date	Catalyst	Reductant Spray	Caterpillar 3116 Engine Hot-Start Heavy-Duty Transient Emissions, g/bhp-hr			
				HC	CO	NO_x	PM
300-A-43	1/17/95	Uncoated	None	0.34	1.18	4.50	--
300-B-44	1/17/95	Uncoated	None	0.30	1.35	4.53	--
NP3-A-47Fi	1/19/95	NP-3	Diesel Fuel	1.11	0.22	4.31	0.41
300-A-50	1/25/95	Uncoated	None	0.26	1.51	4.71	0.19
NP6-A-51F	1/25/95	NP-6	Diesel Fuel	4.60	0.63	4.44	0.59
300-A-55	2/15/95	Uncoated	None	0.32	1.30	4.26	0.19
300-A-56Fi	2/15/95	Uncoated	Diesel Fuel	19.36	1.33	4.27	5.68

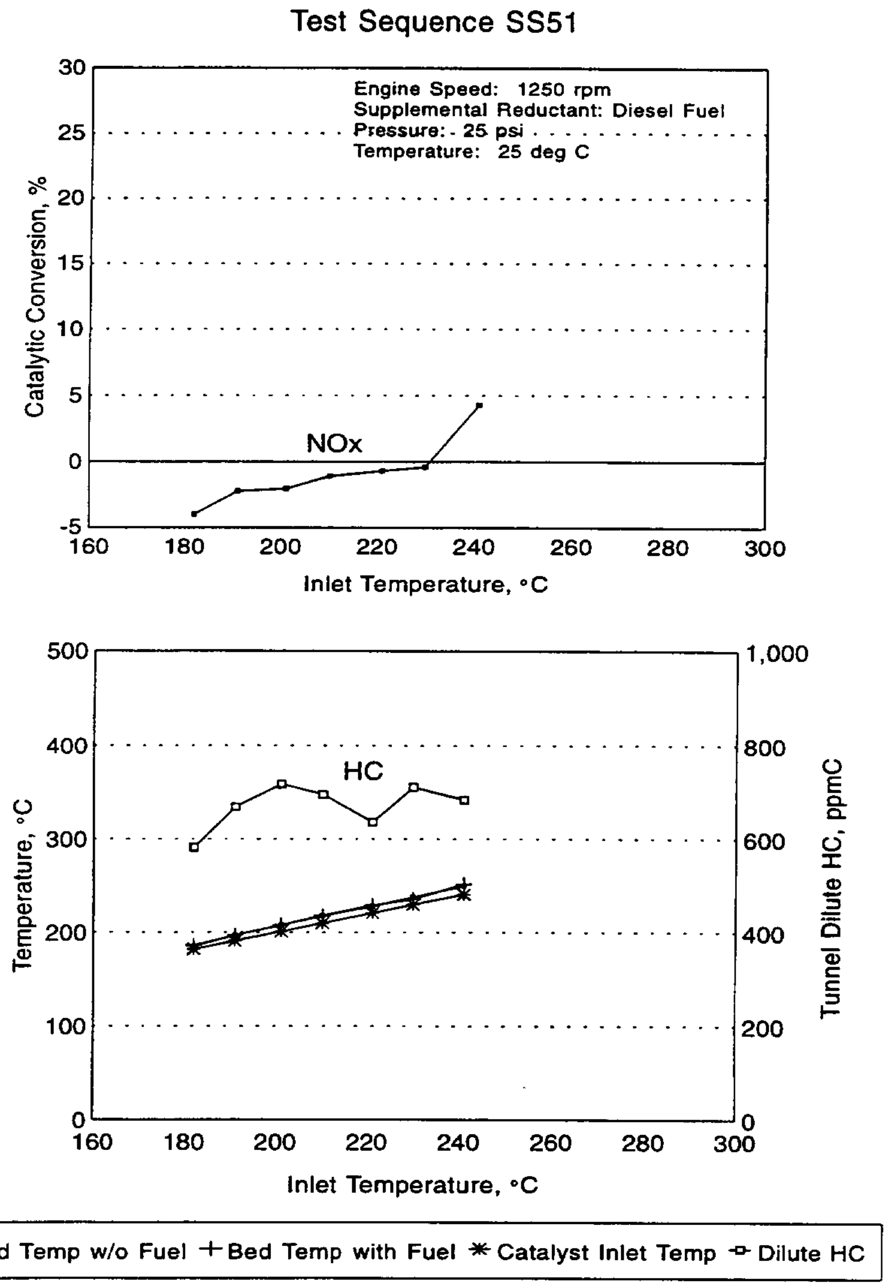


FIGURE 38. DIESEL NO_x CATALYTIC CONVERTER PERFORMANCE – CATALYST NP-6, TEST SEQUENCE SS51

TABLE 43. SUMMARY OF STEADY-STATE NO_x CATALYST TEST RESULTS – CATALYST NP-6

Test Sequence No.	Catalyst Inlet Temp, °C [a]	Supplementary Reductant			Feedgas HC/NO_x Ratio (typical) [b]	Maximum NO_x Reduction Efficiency, % [c]
		Material	Spray Pressure, psi	Spray Temp., °C		
SS51	240[b]	Diesel Fuel	25	25	8	4

[a] Catalyst inlet temperature at maximum measured NO_x reduction efficiency.
[b] Feedgas HC/NO_x ratio measured as C_1/NO_x by volume at catalyst inlet temperature of 260°C.
[c] NO_x reduction efficiency calculated with respect to the no-added-reductant test performed with the catalyst in the exhaust system.

I. Summary of Diesel NO_x Catalyst Performance

1. Steady-State and Transient Performance - Catalyst Group "B"

The greatest NO_x reduction efficiencies measured for each catalyst in Group "B" are given in Table 44. Results from both FTP transient and steady-state tests are provided. Catalysts JM1 and JM2 configured in parallel provided the overall greatest NO_x conversion efficiencies for the FTP and the steady-state tests (at selected temperatures). The NO_x conversion results for the parallel combination of catalysts JM1 and JM2 was greater than the conversion from the other catalysts primarily because of the large total catalyst volume (resulting in a low average catalyst space velocity). Another possible reason for the improved performance is that the exhaust gas entering the parallel configuration of catalysts was at a slightly lower temperature due to the slightly increased length of exhaust pipe that the exhaust gas traveled through during these tests. Catalyst DG-2 performed well, both for the FTP and the steady-state test, at a space velocity of 40,000 hr^{-1} for the steady-state test (refer to Table 44).

2. Nitrous Oxide Emissions

A plot of all the steady-state N_2O measurements taken during this part of the project and the corresponding reductions in NO_x emissions is given in Figure 39. Nitrous oxide emissions tended to increase as NO_x emissions were reduced. From these data, there appears to be an average increase of 0.3 grams N_2O for every 1.0 gram of NO_x reduced.

3. Maximum NO_x Conversion, Supplemental Reductants, and Temperature

Catalytic hydrocarbon conversion began at a temperature of 200°C and increased with higher inlet temperature, for the catalysts tested. This phenomenon is referred to as hydrocarbon "light-off" of the catalyst. Many of the diesel NO_x catalytic converters tested with diesel fuel as the supplementary reductant had maximum NO_x reduction efficiency when the catalyst inlet temperature was near 220°C, or near the temperature where hydrocarbon light-off began to occur. Possibly, the low level of hydrocarbon oxidation at the onset of hydrocarbon light-off produced the most highly active

TABLE 44. SUMMARY OF DIESEL NO_x CATALYST PERFORMANCE – CATALYST GROUP "B"

Catalyst	Total Volume of Catalyst, L	Caterpillar 3116 Diesel Engine				
		FTP	Steady-State			
		Maximum NO_x Reduction Efficiency, %	Catalyst Inlet Temp., °C	Feedgas HC/NO_x Ratio	Exhaust Space Velocity, hr^{-1}	Maximum NO_x Reduction Efficiency, %
JM1+JM2(P)	28	24	180	8-9	10,000	44
DG-2	7	14	210-220	11	40,000	30
JM2	14	13	210-220	7-10	20,000	30
JM1	14	13	---	---	20,000	---
PS-1	7	13	220	8-11	40,000	24
ORP	7	14	220	11	40,000	19
NP-3	7	5	240	8	40,000	4[a]
220	7	5	---	---	---	---
220+221(S)	14	---	260	8	20,000	17[a]

(P) Catalysts tested in parallel.
(S) Catalysts tested in series.
[a] Steady-state test results for Catalyst NP-6. Catalyst may not have been tested at its optimal NO_x reduction temperature.

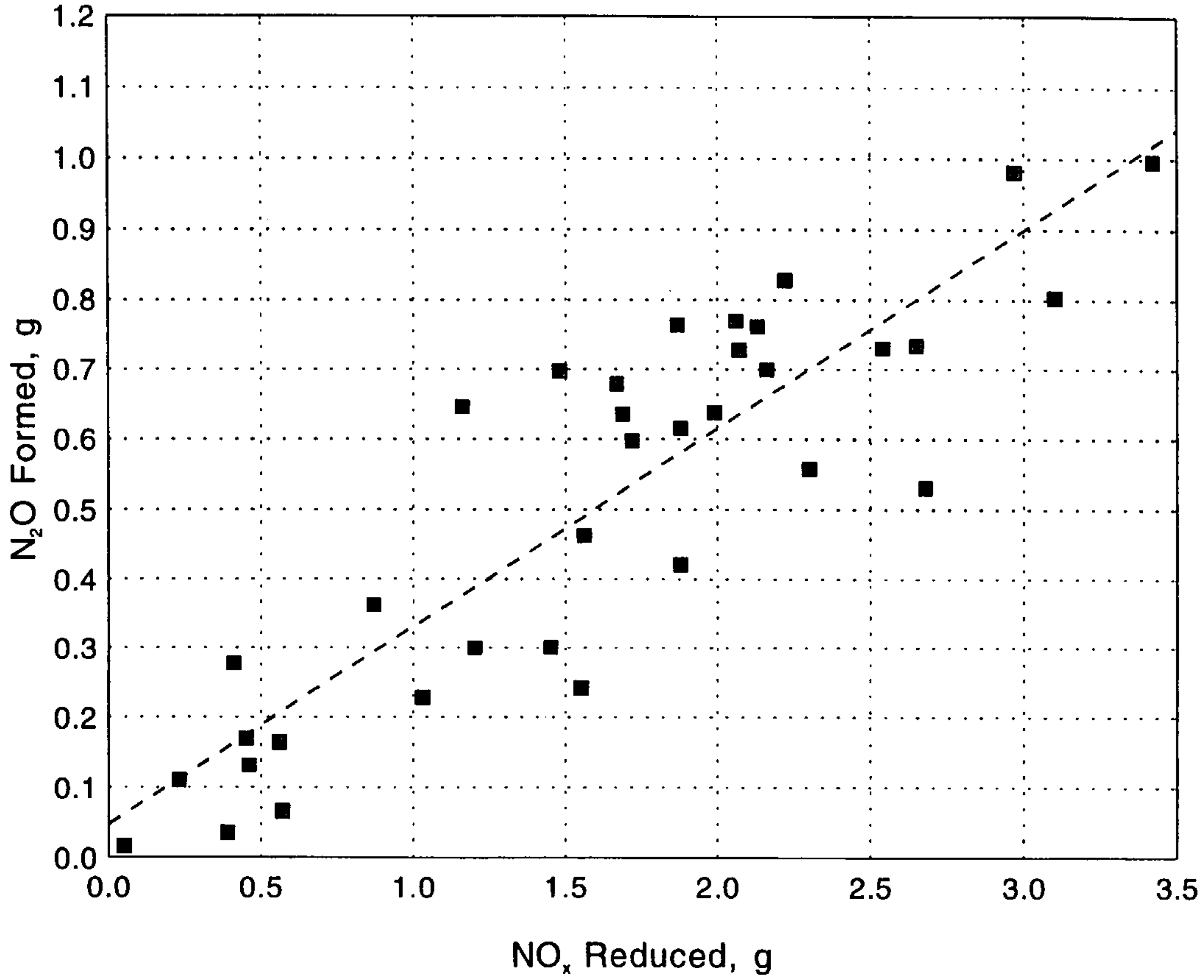


FIGURE 39. NITROUS OXIDE FORMATION AS A FUNCTION OF NO_x REDUCED SUMMARY OF ALL GROUP "B" CATALYST STEADY-STATE TESTS

NO_x reducing compounds. This observation suggests possibly that the ideal diesel NO_x catalyst (a catalyst with a wide temperature window of NO_x reduction) might have a wide temperature window of <u>low</u> hydrocarbon oxidation efficiency, ideally from 200°C to 400°C. This ideal diesel NO_x catalyst could theoretically require less supplemental hydrocarbon addition because less hydrocarbon would be completely oxidized, particularly at higher exhaust system temperatures.

Ethanol addition to the exhaust as a supplemental reductant was attempted on a few of the catalysts. Ethanol resulted in maximum NO_x reduction efficiencies at lower temperatures than diesel fuel. Catalytic NO_x reduction efficiency with ethanol as the supplementary reductant tended to be less than the NO_x reduction efficiency with diesel fuel as the supplementary reductant. Ethanol was observed to produce less of a temperature exotherm in the catalyst bed than diesel fuel. This result is most likely due to the lower energy content of ethanol compared to diesel fuel. Differences in the quantities of diesel fuel and ethanol added also may have accounted for the exotherm and emission performance differences between these supplementary reductants. In the few experiments performed with toluene as a supplemental reductant, toluene performed in a manner similar to diesel fuel. Further research on the effect of different reductants is recommended to better understand NO_x reduction in lean exhaust.

4. Space Velocity and Catalyst Formulation

Figures 32 and 33 previously showed the NO_x reduction capability of catalysts JM1 and JM2 configured in parallel. With these two 14 liter catalysts in parallel, and an engine speed of 1250 rpm, the catalyst exhaust gas space velocity was the lowest tested, approximately 10,000 hr^{-1}. Note that NO_x removal efficiency was over 40 percent at a temperature of 180°C. These NO_x reduction curves (Figures 32 and 33) are characteristically different that the majority of other curves generated in this study. The efficiency of NO_x reduction started at 30 to 40 percent and decreased slowly with increasing temperature. Other catalysts tested had low NO_x reduction efficiencies that initially increased, then decreased with temperature. The parallel combination of Catalysts JM1 and JM2 (total volume 28 liters) had a peak NO_x reduction efficiency at a temperature at or below 180°C. The Caterpillar 3116 engine, unfortunately, did not produce exhaust temperatures much less than 180°C.

The relatively high NO_x conversion efficiency of Catalysts JM1 and JM2 in parallel at 180°C could have been the result of the lower space velocity (discussed previously), the relatively low concentration of NO_x at idle (where the 180°C catalyst inlet temperature occurred), or the catalyst formulation itself. Catalyst formulation specifications were not disclosed by the suppliers. Catalysts JM1 and JM2, however, were believed to contain platinum on a non-zeolite surface.

Catalysts 220 and 221 in series, with a total catalyst volume of 14 liters, also had a relatively wide temperature window, albeit at low NO_x reduction efficiencies. These catalysts may have contained copper, which would account for the low efficiencies at the temperatures tested. At higher catalyst inlet temperatures, copper may have a wider temperature window of NO_x reduction than platinum, based on the tests performed and the catalyst companies consulted.

5. Hydrocarbon Breakthrough and Particulate Emissions

Hydrocarbon breakthrough or hydrocarbon "slip" of the catalysts was suprisingly low, even when spraying diesel fuel as a supplementary reductant. The majority of diesel NO_x catalysts tested were also excellent hydrocarbon oxidation catalysts. Particulate emissions, however, increased significantly. This increase was presumed to be due to an increased level of organics associated with the total particulate. With further development, supplementary hydrocarbon addition levels could be lowered if catalyst selectivity toward the NO_x reduction reaction is increased. In other words, hydrocarbon addition levels could be lowered if the catalyst promoted the NO_x reduction reaction preferentially over the hydrocarbon oxidation reaction.

6. Comment on HC-to-NO_x Ratio Calculations

Measured HC-to-NO_x ratios were summarized for many steady-state test points in this study, particularily in Tables 25, 29, 33, 37, 41, and 44. The HC-to-NO_x ratio given for a particular test point is the ratio of the HC concentration (in ppmC) to the NO_x concentration (in ppm) at the <u>inlet</u> side of the catalyst. Catalyst inlet HC concentration is assumed to be approximately the HC emission level measured at low temperatures (where catalyst HC conversion level is essentially zero). Inlet NO_x is assumed to be the NO_x emission concentration measured without the addition of a supplemental reductant at the specified temperature. Concentrations of HC and NO_x were each measured from dilute exhaust, which is a routine practice for exhaust emissions measurement. Background levels of NO_x and HC in dilution air are negligible compared to raw exhaust concentrations of NO_x and HC (with supplementary reductant added). Therefore, the HC-to-NO_x ratio of dilute exhaust is essentially equivalent to the HC-to-NO_x ratio in raw exhaust.

VII. RECOMMENDATIONS FOR FUTURE WORK

Areas of future research for the development of the diesel NO_x catalyst and emission control system include:

- Widening the temperature range where maximum catalytic NO_x reduction occurs. A lean NO_x catalyst with a wider catalytically active temperature range is necessary for controlling NO_x emissions during transient exhaust temperature operation.

- Improving catalyst hydrocarbon selectivity for the NO_x reduction reaction. Current-technology demonstration catalysts are observed to make inefficient use of added hydrocarbon reductants.(20)

- Improving diesel NO_x catalyst performance with complete NO_x reduction from N_2O to N_2.

- Improving catalytic NO_x removal efficiency over transient engine operation. Total particulate emissions can be further reduced with a diesel NO_x catalyst (diesel particulate organics(21) can be oxidized over lean NO_x catalysts containing platinum).

- Obtaining higher NO_x reduction efficiency at higher exhaust gas space velocities. Moderate NO_x reduction efficiencies have been achieved at space velocities in the range of 20,000 h^{-1} to 40,000 h^{-1}. For heavy-duty diesel truck engines, space velocities near 100,000 h^{-1} are desired so that catalytic converters will not be excessively large.

- Minimizing the catalytic production of undesirable organic and sulfate emissions. Proper selection of a catalyst washcoat, for example, has been shown to lower the production of sulfates.(21)

- Further development of methods to provide NO_x reductants. The quantity of NO_x reductants in the exhaust stream could be increased using engine-out hydrocarbon emissions or injecting fuel directly into the exhaust system.(20)

- The development of an efficient fuel spray schedule to minimize the potential fuel economy penalty. The net fuel economy penalty could be further lessened by calibrating the diesel engine for more efficient operation with further advanced fuel injection timing, and controlling the resulting increase in NO_x emissions catalytically. This calibration also would result in reduced engine-out particulate emissions.(13)

The ultimate goal for lean NO_x catalyst research is the development of a decomposition catalyst that does not require additional hydrocarbon for NO_x removal. The decomposition catalyst, however, has not yet shown practical feasibility in actual engine exhaust.

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