

Final Report
An Assessment of the Effects of Lead Additives in
Gasoline on Emission Control Systems which
Might Be Used to Meet the 1975-76
Motor Vehicle Emission Standards

71 NOV 15

Prepared for DIVISION OF EMISSION CONTROL TECHNOLOGY
MOBILE SOURCE POLLUTION CONTROL PROGRAM
OFFICE OF AIR PROGRAMS
ENVIRONMENTAL PROTECTION AGENCY



Office of Corporate Planning
THE AEROSPACE CORPORATION

Report No.
TOR-0172(2787)-2

FINAL REPORT

AN ASSESSMENT OF THE EFFECTS OF LEAD ADDITIVES IN
GASOLINE ON EMISSION CONTROL SYSTEMS WHICH
MIGHT BE USED TO MEET THE 1975-76
MOTOR VEHICLE EMISSION STANDARDS

71 NOV 15

Office of Corporate Planning
THE AEROSPACE CORPORATION
El Segundo, California

Prepared for
DIVISION OF EMISSION CONTROL TECHNOLOGY
MOBILE SOURCE POLLUTION CONTROL PROGRAM
OFFICE OF AIR PROGRAMS
ENVIRONMENTAL PROTECTION AGENCY

Contract No. F04701-71-C-0172

FOREWORD

The Aerospace Corporation has performed (for the Environmental Protection Agency, Division of Emission Control Technology) an overall assessment of the effects of lead additives in gasoline on the performance, durability, and costs of emission control devices/systems which may be used to meet the 1975-76 emission standards for light-duty vehicles. This assessment was performed in fulfillment of Section 211c(2)B of the Clean Air Amendments of 1970 which states in pertinent part:

No fuel or fuel additive may be controlled or prohibited by the Administrator pursuant to clause (B) of paragraph (1) except after consideration of available scientific and economic data including a cost benefit analysis comparing emission control devices or systems which are or will be in general use and require the proposed control or prohibition with emission control devices or systems which are or will be in general use and do not require the proposed control prohibition.

This report is the final summary of the overall assessment performed in the period of June-October 1971. Material related to emission control system performance, durability, and fuel economy characteristics is contained in Section 4. A general assessment of the effects of lead additives in gasoline on emission control system components is presented in Section 5, and a similar assessment of lead effects on other engine parts is given in Section 7. Section 6 briefly summarizes the feasibility and implications of lead traps or exhaust gas scrubber devices. Cost data, in terms of specific system hardware costs and overall consumer costs, are summarized in Section 8.

ACKNOWLEDGEMENTS

Appreciation is acknowledged for the assistance and guidance provided by Mr. G.D. Kittredge and Dr. J.H. Somers of the Environmental Protection Agency, Office of Air Programs, Division of Emission Control Technology, for whom this study was conducted. Dr. Somers served as EPA Project Officer for the study and was instrumental in providing timely access to the data necessary for the conduct of the study.

The following technical personnel of The Aerospace Corporation participated in the study and made valuable contributions to the assessment performed under this contract:

Mr. F.E. Cook
Dr. L.M. Dormant
Mr. J.A. Drake
Mr. L. Forrest
Mr. P.P. Leo
Mr. W.U. Roessler

Mr. M.J. Russi
Mr. W.M. Smalley
Dr. G.W. Stupian
Mr. K.B. Swan
Mr. J.D. Wilson

M.G. Hinton Jr.

M.G. Hinton, Jr.
Manager, Lead Cost-Benefit Study

Approved by

T. Iura

T. Iura
Associate Director of Pollution
and Resources Programs
Office of Corporate Planning

J. Meltzer

J. Meltzer
Director of Pollution and
Resources Programs
Office of Corporate Planning

ACRONYMS, TERMS, AND ABBREVIATIONS

| | |
|--------------------------|--|
| A/F | air-fuel ratio |
| AMOCO | American Oil Company |
| APCO* | Air Pollution Control Office |
| Arco | Arco Chemical Company, Division of Atlantic Richfield Company |
| ASTM | American Society for Testing and Materials |
| CARB | California Air Resources Board |
| CID | cubic inches displacement |
| CO | carbon monoxide |
| C. R. | compression ratio |
| CVS | constant volume sampling (test procedure) |
| CVS-1 | single-bag CVS test procedure (pre-July 1971) using DHEW Urban Dynamometer Driving Cycle |
| CVS-3 | three-bag weighted average CVS test procedure (post-July 1971) using DHEW Urban Dynamometer Driving Cycle |
| DHEW | Department of Health, Education and Welfare |
| Dual Catalytic Converter | converter with two beds; one for oxidizing HC and CO and one for reducing NO and NO ₂ |
| EGR | exhaust gas recirculation |

*Former and current names for EPA air pollution control agencies

ACROYNMS, TERMS, AND ABBREVIATIONS (cont.)

| | |
|---------------------------|--|
| EPA | Environmental Protection Agency |
| Esso | Esso Research & Engineering Company |
| Gasoline Lead Content | Lead-sterile gasoline is that gasoline having less than 0.003 gram of lead per gallon Lead-free, clear, or unleaded gasoline as used in this report, is that gasoline having less than 0.07 gram of lead per gallon Low-lead gasoline is that gasoline having approximately 0.5 gram of lead per gallon Fully leaded gasoline is that gasoline having a normal range of 2 to 3 grams of lead per gallon |
| HC | hydrocarbons |
| HC/CO Catalytic Converter | Converter with single catalyst bed for oxidizing HC and CO |
| IIEC | Inter-Industry Emission Control Program |
| LTR | Lean Thermal Reactor (air-fuel ratio >15:1) |
| MBT | Spark advance at maximum torque |
| NAPCA* | National Air Pollution Control Administration |
| N-O-R | nitric-oxide-reduction system (by Arco) |
| NO _x | oxides of nitrogen (NO plus NO ₂) |

* Former and current names for EPA air pollution control agencies

ACRONYMS, TERMS, AND ABBREVIATIONS (cont.)

| | |
|-------------------------------------|---|
| NO _x Catalytic Converter | Converter with single catalyst bed for reducing NO and NO ₂ |
| OAP* | Office of Air Programs |
| RAM | Rapid Action Manifold (thermal reactor) (by Esso) |
| RON | research octane number |
| RTR | Rich Thermal Reactor (air-fuel ratio <15:1) |
| SFC | specific fuel consumption |
| TEL | tetraethyl lead compound (one of several lead compounds used in gasoline) |
| Tricomponent Catalytic Converter | Converter with single catalyst bed for simultaneously oxidizing HC and CO and reducing NO and NO ₂ |
| UOP | Universal Oil Products Company |
| WOT | wide-open-throttle (engine operating condition) |

*Former and current names for EPA air pollution control agencies

CONTENTS

| | |
|---|------|
| FOREWORD | iii |
| ACKNOWLEDGEMENTS | v |
| ACRONYMS, TERMS, AND ABBREVIATIONS | vii |
| 1. SUMMARY | 1-1 |
| 1.1 General Conclusions | 1-1 |
| 1.2 Specific Findings | 1-3 |
| 1.2.1 Effect of Lead on Performance and Durability of Emission Control Devices | 1-3 |
| 1.2.1.1 Catalytic Converter Systems | 1-3 |
| 1.2.1.2 Thermal Reactors | 1-4 |
| 1.2.1.3 Exhaust Gas Recirculation (EGR) Systems | 1-4 |
| 1.2.2 Feasibility of Use of Lead Traps or Exhaust Scrubber Devices | 1-4 |
| 1.2.3 Effect of Lead on Other Engine Parts | 1-5 |
| 1.2.4 General Evaluation of Emission Control Devices/Systems | 1-6 |
| 1.2.4.1 Categories of Devices/Systems | 1-6 |
| 1.2.4.2 Performance of Devices/Systems | 1-6 |
| 1.2.4.3 Durability of Devices/Systems | 1-8 |
| 1.2.4.4 Advanced Concepts | 1-8 |
| 1.2.5 General Cost Summary | 1-9 |
| 1.2.5.1 Unleaded Gasoline Cost Effects | 1-9 |
| 1.2.5.2 Emission Control System Cost Effects | 1-10 |
| 2. INTRODUCTION | 2-1 |
| 2.1 Purpose | 2-1 |
| 2.2 Scope of Study | 2-1 |
| REFERENCES | 2-3 |
| 3. METHOD OF APPROACH | 3-1 |

CONTENTS (cont.)

| | | |
|---------|---|------|
| 4. | GENERAL EVALUATION OF EMISSION CONTROL DEVICES/SYSTEMS | 4-1 |
| 4.1 | Engine Modifications and Operating Considerations | 4-1 |
| 4.2 | Emission Control Devices | 4-2 |
| 4.2.1 | Thermal Reactors | 4-2 |
| 4.2.1.1 | Thermal Reactor Descriptions--General | 4-2 |
| 4.2.1.2 | Engine Modifications | 4-8 |
| 4.2.1.3 | Emission Performance Characteristics | 4-9 |
| 4.2.1.4 | Fuel Economy Characteristics | 4-10 |
| 4.2.2 | Exhaust Gas Recirculation (EGR) Systems | 4-12 |
| 4.2.2.1 | EGR System Descriptions--General | 4-13 |
| 4.2.2.2 | NO _x Emission Performance Characteristics | 4-17 |
| 4.2.2.3 | Fuel Economy Characteristics | 4-17 |
| 4.2.2.4 | Driveability Characteristics | 4-22 |
| 4.2.2.5 | Octane Number Requirements | 4-23 |
| 4.2.3 | Catalytic Converters | 4-23 |
| 4.2.3.1 | Typical Catalysts | 4-24 |
| 4.2.3.2 | Types of Catalytic Converters | 4-25 |
| 4.2.3.3 | Other System Components/Factors | 4-30 |
| 4.2.3.4 | Fuel Economy Characteristics | 4-31 |
| 4.3 | Specific Emission Control Systems | 4-36 |
| 4.3.1 | Catalytic Converter Systems | 4-37 |
| 4.3.1.1 | HC/CO Catalytic Converter Alone (no EGR) | 4-37 |
| 4.3.1.2 | HC/CO Catalytic Converter plus EGR | 4-40 |
| 4.3.1.3 | Dual Catalytic Converter plus EGR | 4-41 |
| 4.3.1.4 | Tricomponent Catalytic Converter (no EGR) | 4-43 |
| 4.3.2 | Thermal Reactor Systems | 4-45 |
| 4.3.2.1 | LTR plus EGR Concept | 4-46 |
| 4.3.2.2 | RTR-Alone Concept | 4-53 |
| 4.3.2.3 | RTR plus EGR Concept | 4-57 |

CONTENTS (cont.)

| | | |
|------------|---|------|
| 4.3.3 | Combination Systems | 4-62 |
| 4.3.3.1 | LTR plus HC/CO Catalytic Converter plus EGR | 4-63 |
| 4.3.3.2 | RTR plus HC/CO Catalytic Converter plus EGR | 4-65 |
| 4.3.3.3 | RTR plus Dual Catalytic Converter plus EGR | 4-69 |
| 4.3.3.4 | RTR plus NO _x Catalytic Converter plus EGR | 4-71 |
| 4.3.3.5 | Stratified Charge Engine | 4-72 |
| 4.3.4 | Summary of Specific Emission Control Systems | 4-72 |
| 4.3.4.1 | Comparison of Emission Levels with 1975-76 Standards | 4-72 |
| 4.3.4.2 | Lifetime/Durability Effects | 4-76 |
| 4.3.4.3 | Fuel Economy Effects | 4-76 |
| REFERENCES | | 4-79 |
| 5. | GENERAL ASSESSMENT OF EFFECTS OF LEAD ADDITIVES ON EMISSION CONTROL DEVICES/SYSTEMS | 5-1 |
| 5.1 | Catalytic Converters | 5-1 |
| 5.1.1 | Summary of Experimental Data | 5-2 |
| 5.1.1.1 | Laboratory Tests | 5-2 |
| 5.1.1.2 | Vehicle Tests | 5-9 |
| 5.1.2 | Maximum Allowable Lead Levels | 5-15 |
| 5.1.3 | Summary | 5-17 |
| 5.2 | Thermal Reactors | 5-18 |
| 5.2.1 | Erosion/Corrosion Effects | 5-18 |
| 5.2.2 | Emission Level Effects | 5-22 |
| 5.2.3 | Summary | 5-22 |
| 5.3 | Exhaust Gas Recirculation (EGR) Systems | 5-24 |
| 5.3.1 | Relevant Technology Discussions | 5-24 |
| 5.3.2 | 1973-74 EGR Systems | 5-26 |

CONTENTS (cont.)

| | | |
|------------|---|------|
| 5.3.3 | 1975-76 EGR Systems | 5-27 |
| 5.3.4 | Summary | 5-27 |
| REFERENCES | | 5-28 |
| 6. | FEASIBILITY AND IMPLICATIONS OF LEAD TRAPS AND EXHAUST GAS SCRUBBERS | 6-1 |
| 7. | EFFECT OF LEAD ADDITIVES ON OTHER ENGINE PARTS . . . | 7-1 |
| 7.1 | Engine Durability--General | 7-1 |
| 7.2 | Fuel-Sensitive Components | 7-2 |
| 7.2.1 | Exhaust Systems | 7-2 |
| 7.2.2 | Spark Plugs | 7-4 |
| 7.2.2.1 | Misfiring Mechanism | 7-4 |
| 7.2.2.2 | Life | 7-5 |
| 7.2.2.3 | Cost | 7-6 |
| 7.2.3 | Exhaust Valve Recession | 7-7 |
| 7.3 | Maintenance | 7-7 |
| REFERENCES | | 7-11 |
| 8. | COST ANALYSIS | 8-1 |
| 8.1 | Control Device/System Cost Analysis | 8-2 |
| 8.1.1 | Control Device Costs | 8-2 |
| 8.1.1.1 | Engine Modifications | 8-2 |
| 8.1.1.2 | Emission Control System Components | 8-3 |
| 8.1.1.3 | Discussion of Device Costs | 8-6 |
| 8.2 | Overall Costs to the Consumer | 8-9 |
| 8.2.1 | Maintenance Costs | 8-9 |
| 8.2.2 | Operating Costs | 8-12 |
| 8.2.2.1 | Fuel Economy Cost Penalty | 8-12 |
| 8.2.3 | Excluded Costs | 8-23 |
| 8.2.4 | Cost Analyses Results | 8-23 |
| REFERENCES | | 8-27 |

CONTENTS (cont.)

APPENDICES

| | | |
|---------|--|------|
| A. | VISITS AND CONTACTS | A-1 |
| A.1 | Organizations Visited | A-1 |
| A.2 | Organizations Contacted | A-1 |
| B. | POSSIBLE CATALYST POISONING MECHANISMS | B-1 |
| B.1 | Summary of Catalyst Poisoning Mechanisms | B-1 |
| B.2 | Chemical and Mechanical Poisoning Mechanisms | B-1 |
| B.2.1 | Chemical Poisoning Mechanisms | B-1 |
| B.2.2 | Mechanical Poisoning Mechanisms | B-3 |
| | REFERENCES | B-5 |
| C. | LEAD TRAP DEVICES FOR AUTOMOTIVE VEHICLES OPERATING ON LEADED GAS | C-1 |
| C.1 | Introduction | C-1 |
| C.2 | Technique for Removing Combinations of Lead Compound Vapors and Particles from Exhaust Emissions | C-2 |
| C.2.1 | Atomics International Molten Carbonate Process | C-2 |
| C.3 | Techniques for Removing Lead Compound Particles Only from Exhaust Emissions | C-8 |
| C.3.1 | Du Pont Cyclone Trap System | C-8 |
| C.3.2 | Ethyl Corporation Particulate Traps | C-9 |
| C.3.3 | Dow Chemical Molten Salt Particulate Trap | C-10 |
| C.3.4 | Cooper Union Molten Salt | C-11 |
| C.3.5 | IIT Research Institute Devices | C-11 |
| C.3.5.1 | Thermal Packed Bed Device | C-11 |
| C.3.5.2 | Sonic Fluidized Bed Device | C-12 |
| C.3.6 | Houston Chemical Company Particulate Trap | C-14 |
| | REFERENCES | C-15 |

TABLES

| | | |
|--------|---|------|
| 4-1. | Thermal Reactor Summary | 4-5 |
| 4-2. | EGR Systems Description Summary | 4-15 |
| 4-3. | Catalytic Removal of HC, CO, and NO _x -- Laboratory-Scale Experiments | 4-26 |
| 4-4. | Catalytic Removal of HC, CO, and NO _x -- Stationary Engine Tests | 4-27 |
| 4-5. | Catalytic Removal of HC, CO, and NO _x -- Road Tests | 4-28 |
| 4-6. | Effect of Catalytic Converter System on Fuel Economy and Performance. | 4-33 |
| 4-7. | 1971 Domestic Engine (350 CID)--Normal Choke, PZ-195 Catalyst | 4-39 |
| 4-8. | 1971 Domestic Engine (350 CID)--Fast Choke | 4-39 |
| 4-9. | Federal Test Results for Some Foreign Vehicles | 4-39 |
| 4-10. | Emission Test Results--1970 Volkswagen with UOP Catalytic Converter (1972 Federal Test Procedure) | 4-44 |
| 4-11. | Ethyl Lean Reactor--Emission Data for 1970 Pontiac (Vehicle 766) | 4-47 |
| 4-12. | Ethyl Lean Reactor--Emission Data for 1971 Plymouth (Vehicle 18M-448). | 4-47 |
| 4-13. | Ethyl Lean Reactor--Fuel Economy, Modified and Standard Cars | 4-50 |
| 4-14. | Ethyl Lean Reactor--Emission Data for Modified Pontiac (No. 761) Supplied to CARB. | 4-51 |
| 4-15A. | Summary of Emission Control System Emission Data--Catalytic Converter Systems (Laboratory, Low-Mileage Tests) | 4-74 |
| 4-15B. | Summary of Emission Control System Emission Data--Thermal Reactor Systems (Laboratory, Low-Mileage Tests) | 4-74 |
| 4-15C. | Summary of Emission Control System Emission Data--Combination Systems (Laboratory, Low- Mileage Tests). | 4-75 |
| 5-1. | Effect of TEL on Catalytic Activity | 5-4 |

TABLES (cont.)

| | | |
|------|--|------|
| 7-1. | Spark Plug and Exhaust System Costs | 7-9 |
| 8-1. | EGR System Cost Data | 8-4 |
| 8-2. | Installed Hardware Cost Summary (Cost to Consumer in New Car) | 8-8 |
| 8-3. | Cost Effects of Use of Unleaded Gasoline | 8-19 |

FIGURES

| | | |
|-------|--|------|
| 1-1. | Overall Cost Increase to Consumer Over Lifetime of Car. | 1-11 |
| 4-1. | Effect of Air-Fuel Ratio on Emission Levels (Gasoline Spark Ignition Engine) | 4-2 |
| 4-2. | Du Pont Type V Thermal Reactor | 4-5 |
| 4-3. | Air Pump Power Requirements (300-400 CID Engines) | 4-7 |
| 4-4. | Air-Fuel Ratio and Spark Timing Effects on NO _x Emissions | 4-11 |
| 4-5. | Air-Fuel Ratio and Spark Timing Effects on Specific Fuel Consumption | 4-11 |
| 4-6. | Arco N-O-R EGR System | 4-14 |
| 4-7. | Toyo Kogyo "Mazda" EGR System (Entry Above Throttle Valve) | 4-14 |
| 4-8. | General Motors 1972 Design EGR System (Entry Below Throttle Valve) | 4-16 |
| 4-9. | Effect of Recycle Rate on NO Reduction | 4-18 |
| 4-10. | Effect of Recycle Rate on SFC | 4-18 |
| 4-11. | Effect of Spark Advance and Recycle--Hot California Cycle Data | 4-19 |
| 4-12. | Effect of Rich Mixtures on NO Reduction | 4-21 |
| 4-13. | Effect of EGR and Rich Mixture on NO Reduction and Increase in Specific Fuel Consumption | 4-21 |
| 4-14. | Reduction in Octane Requirement as a Function of Recycle. | 4-23 |
| 4-15. | Ford Programmed Protection System--Logic Schematic | 4-32 |
| 4-16. | Ford Programmed Protection System (Vehicle No. 4)--Catalyst Container and PPS Hardware | 4-32 |
| 4-17. | Converter Flow Development | 4-33 |
| 4-18. | Dual-Bed Axial-Flow Converter | 4-34 |
| 4-19. | Bifurcated Dual-Bed Catalytic Converter | 4-34 |
| 4-20. | Cutaway Sketch of Oxy-Catalyst Converter | 4-35 |

FIGURES (cont.)

| | | |
|-------|---|------|
| 4-21. | Exhaust System Backpressures (Road Load Conditions) | 4-35 |
| 4-22. | Universal Oil Products Mini-Converter Installation | 4-38 |
| 4-23. | Ford Concept Emission Package "B" | 4-42 |
| 4-24. | Ford Concept Emission Package "C" | 4-42 |
| 4-25. | Tricomponent Conversion vs Air-Fuel Ratio | 4-44 |
| 4-26. | Ethyl Lean Reactor Emissions of Modified Pontiac (No. 761) Supplied to CARB | 4-52 |
| 4-27. | ESSO Rapid Action Manifold (RAM) Reactor | 4-54 |
| 4-28. | IIEC Type H Exhaust Manifold Reactor (V-8 Engine)--Small Volume with Concentric Core Design | 4-54 |
| 4-29. | Ford Type J Reactor Durability and Cold Start Emissions Data | 4-55 |
| 4-30. | General Motors 1975 Experimental Emission Control System | 4-63 |
| 4-31. | Ford Combined Maximum Effort/Low-Emission Concept Vehicle | 4-66 |
| 4-32. | Ford Maximum Effort Vehicle--NO _x Emissions vs Fuel Economy | 4-68 |
| 4-33. | General Motors Quick-Heat Manifold and Fast Choke Configuration | 4-70 |
| 4-34. | NO _x vs SFC Increase | 4-78 |
| 5-1. | Catalyst Life--Leaded vs Unleaded Gasolines | 5-2 |
| 5-2. | Effect of TEL on Catalyst Efficiency for HC Oxidation | 5-4 |
| 5-3. | NO _x Catalyst (CuO/Cr ₂ O ₃) Deactivation by Lead | 5-5 |
| 5-4. | NO _x Catalyst (CuO/Cr ₂ O ₃) Pellet Composition Profile (Upon Deactivation with Motor Mix in the Fuel). | 5-5 |
| 5-5. | Effect of Lead Content in Fuel on Catalyst Type "BH" Oxidation Activity | 5-7 |

FIGURES (cont.)

| | | |
|-------|--|------|
| 5-6. | Effect of Lead Content in Fuel on Catalyst Type "G" Oxidation Activity | 5-7 |
| 5-7. | Effect of Lead Content in Fuel on Catalyst Type "AJ" Oxidation Activity | 5-8 |
| 5-8. | Effect of Lead Content in Fuel on Catalyst Type "BI" Oxidation Activity | 5-8 |
| 5-9. | Effect of Lead on Catalyst Life | 5-9 |
| 5-10. | Typical Vehicle Emissions with a Catalytic Converter | 5-11 |
| 5-11. | Catalyst Efficiency--Cold Start, NDIR HC Data (Average of Two Vehicles) | 5-12 |
| 5-12. | Catalyst Efficiency--Cruise 30 FID HC Data (Average of Two Vehicles) | 5-12 |
| 5-13. | Catalyst Efficiency--Cold Start CO Data (Average of Two Vehicles) | 5-12 |
| 5-14. | Ford 24-Car Fleet Tailpipe HC/CO Emissions (302 CID Engine) | 5-13 |
| 5-15. | Ford 24-Car Fleet Tailpipe NO _x Emissions (302 CID Engine) | 5-13 |
| 5-16. | Ford 24-Car Fleet Tailpipe HC/CO Emissions (390 and 428 CID Engines) | 5-14 |
| 5-17. | Ford 24-Car Fleet Tailpipe NO _x Emissions (390 and 428 CID Engines) | 5-14 |
| 5-18. | Effect of Fuel Additives on Corrosion Weight Loss of Inconel 601 | 5-19 |
| 5-19. | Effect of Fuel Variables on Average Thickness Losses of OR-1 Alloy During Continuous Thermal Cycling | 5-20 |
| 5-20. | Weight Change of Test Reactor Cores in Engine Dynamometer Endurance Test | 5-20 |
| 5-21. | Du Pont Type V Thermal Reactor--HC, CO, and NO _x Emissions with Leaded and Unleaded Fuel | 5-23 |
| 5-22. | Effect of Leaded Fuel on the Control Efficiency of Air Cleaner EGR Systems (302 CID Engine) | 5-25 |
| 7-1. | Muffler Lifetime Probability (Operation on Unleaded Fuel). | 7-3 |

FIGURES (cont.)

| | | |
|------|--|------|
| 7-2. | Spark Plug Lifetime Probability (Operation on Unleaded Fuel) | 7-6 |
| 8-1. | Fuel Economy Penalty due to NO _x Emission Reduction | 8-14 |
| 8-2. | Cost of Unleaded Gasoline (Exclusive of Distribution Costs) | 8-16 |
| 8-3. | Fuel Cost Penalty | 8-22 |
| 8-4. | Increased Consumer Costs Over Lifetime of Car | 8-22 |
| 8-5. | Breakdown of Increased Consumer Costs over Lifetime of Car | 8-24 |
| C-1. | Schematic of an Engine-Compartment-Mounted Molten-Salt Scrubber | C-3 |
| C-2. | Fabricated Engine-Compartment-Mounted Molten-Salt Scrubber | C-5 |
| C-3. | Installation of Engine-Compartment-Mounted Molten-Salt Scrubber | C-6 |
| C-4. | Under-the-Car Lead Trap--Conceptual Design | C-7 |
| C-5. | Experimental Dual-Anchored Vortex Trap | C-10 |
| C-6. | Packed Beds for Collection of Submicron Particles by Thermal Precipitation | C-13 |

1. SUMMARY

SECTION 1

SUMMARY

Based on a review and assessment of data in the open literature and on discussions with industrial/agency sources, the following conclusions have been made relative to the effects of lead additives in gasoline on emission control devices/systems which may be used to meet the 1975-76 emission standards for light-duty vehicles. For convenience of presentation, some general conclusions are given first, followed by more specific findings grouped according to distinctive areas of investigation in the study.

1.1 GENERAL CONCLUSIONS

1. All emission control systems currently planned for use by major automobile manufacturers and being evaluated by them to meet the 1975-76 Federal emission standards incorporate or include a catalytic converter.
2. Lead additives in gasoline are toxic to catalytic materials. Use of leaded or low-lead gasoline with catalytic converters has demonstrated that it greatly reduces catalyst activity, thereby preventing the achievement of a 50,000-mile lifetime at low enough emission levels to meet the required standards. In addition to its effect on catalyst activity, lead has been observed to degrade the structural integrity of NO_x bulk metal catalysts.
The scavengers added to gasoline to prevent the accumulation of harmful lead deposits in the engine also have detrimental effects upon catalysts. Sulfur and phosphorus have also been noted to have toxic effects.
3. Lead effects on other major emission control system components, e.g., thermal reactors and exhaust gas recirculation systems, although observed to be present to some degree, are such that materials selection and design techniques can be applied to allow lead-tolerant systems.
4. Lead traps or exhaust scrubber devices for removal of lead from the exhaust gases of an engine using leaded gasoline, prior to passage through a catalytic converter, are not felt to have adequate lead removal capability nor the technological development status consistent with other emission system components being considered for meeting 1975-76 standards.

5. Unleaded gasoline should be made available in sufficiently large quantities to satisfy the demands of vehicles with an installed catalytic converter unit. The lead content of the gasoline should be at that level compatible with obtaining a 50,000-mile useful lifetime. However, substantive data to precisely establish this level are not available. Most of the major automakers and catalyst suppliers have been performing their catalytic converter development work with lead levels below 0.06 gm/gal, with most of the development at levels of 0.02-0.03 gm/gal. At this lead level, no automobile manufacturer has stated to date that 50,000 miles of operation at satisfactory emission levels has been achieved. It is not known whether this durability/lifetime deficiency is related to the lead level (0.02-0.03 gm/gal), to other trace elements in the gasoline, or to other catalyst properties. One automobile manufacturer and one catalyst supplier have stated that a maximum lead content of 0.03 gm/gal should be an adequately low level. It should be noted that this value is below the proposed ASTM specification for unleaded gasoline of 0.07 gm/gal.
6. With regard to 1975 emission standards, both lead-tolerant systems (e.g., Esso's rich thermal reactor system) and lead-intolerant systems (e.g., systems incorporating catalytic converters) have demonstrated approaching the standards on an experimental basis at low mileage. However, in order to meet the lower NO_x levels required in 1976, the lead-tolerant system would require the addition of a NO_x catalyst (and possibly additional components) which would render it sensitive to lead.
7. A general evaluation of emission control devices/systems envisioned by the automobile industry and ancillary development organizations has indicated that none of the systems planned for 1976 have demonstrated the capability of meeting the 1976 NO_x emission standard. Several combination systems incorporating a NO_x catalyst have met the 1976 emission levels on an experimental basis with a new catalyst. At this time, a 50,000-mile lifetime has not been demonstrated. In fact, durability tests over approximately 10-15,000 miles have not been reported.
8. At this time, estimated overall costs to the consumer (initial, operating and maintenance) for emission control systems being considered for the 1976 Federal emission standards are approximately \$860 above 1970 vehicle costs over an 85,000-mile vehicle lifetime. This estimate is based on a system incorporating a dual-bed catalytic converter (with assumed replacement of the converter unit at 50,000 miles), a "low-grade" rich thermal reactor, and exhaust gas recirculation.

1.2 SPECIFIC FINDINGS

1.2.1 Effect of Lead on Performance and Durability of Emission Control Devices

1.2.1.1 Catalytic Converter Systems

Lead is toxic to catalysts. It can act as a poison through both chemical and mechanical mechanisms, which are not mutually exclusive. Scavengers added to gasoline to prevent the accumulation of harmful lead deposits in the engine also have detrimental effects upon catalysts. Sulfur and phosphorus have also been noted to have toxic effects on catalysts.

Data on catalyst activity versus lifetime are available on some catalysts for gasoline lead levels of: (1) 2-3 gm/gal, (2) 0.5 gm/gal, and (3) in the range of 0.02-0.06 gm/gal. For the lowest levels (0.02-0.06 gm/gal), the exact amount of lead used is not clearly identified. In general, the catalyst lifetime decreases as lead content is increased. However, at the very low levels, the data are not sufficient to establish a meaningful correlation. The data do show that activity and lifetime are drastically affected with lead levels over 0.5 gm/gal; at levels of 0.02-0.06 gm/gal, the catalyst showed significantly better performance than at the higher values tested.

Some catalysts have been designed and tested for operation with leaded gasoline; however, test data are not available in sufficient quantity and under the appropriate vehicle operating conditions to permit an evaluation at this time.

Since catalysts are so adversely affected by lead quantities in leaded gasoline, a system must be devised to prevent accidental contamination. It has been stated that a single tankful of regular leaded gasoline can destroy a catalyst (see Section 4.3.3.2.4). Although this cannot be substantiated, it is apparent from available data that such quantities could seriously reduce the catalyst's useful lifetime.

1.2.1.2 Thermal Reactors

Lead concentrations in gasoline of approximately 0.5 gm/gal should have no significant detrimental effects on the better oxidation-resistant materials available. There seems to be no obvious reason (although direct data are lacking) why such materials could not function with up to 3 gm/gal of lead. However, the combined presence of lead and phosphorus additives has an accelerating influence on the corrosive deterioration of a number of different metallic alloys.

1.2.1.3 Exhaust Gas Recirculation (EGR) Systems

Lead-free or low-lead gasoline is not required for the implementation of EGR systems, per se. Although the presence of lead additives can result in deposits in EGR orifices, throttle plate areas, etc., the actual severity of such deposits would appear to be strongly related to the particular type of EGR system as well as to control orifice sizes used, and/or to the utilization of self-cleaning designs (plungers, specially coated surfaces, flexible snap-rings, etc.) in areas susceptible to deposit buildup.

1.2.2 Feasibility of Use of Lead Traps or Exhaust Scrubber Devices

Several lead-removal devices are currently under development. One basic type, requiring cool exhaust gases to enable a particulate form of lead for collection (e.g., cyclone separators, fiberglass filter devices), is inherently not suitable for use upstream of a catalytic converter. A second type, capable of removing lead in the gaseous as well as particle form, is compatible in principle. The only known and demonstrated device of this type is the molten carbonate lead trap.

A molten carbonate lead trap device has undergone considerable development and testing and the results suggest that it might be installed upstream of a catalytic converter and have the potential for removing an average of 90 percent of the lead, essentially all the sulfur oxides, and in excess of 80 percent

of all the particulates. Aside from system design complexities, the need for adding another component to the already complicated emission control systems, and the need for periodic chemical replacement, it is felt that the 90-percent lead removal capability from leaded gasoline will not be adequate for the lead-sensitive catalysts presently predicted for use by the automobile industry. Moreover, durability test data on prototype systems are not available to permit the assessment of the decrease in effectiveness versus mileage. Therefore, it is not felt that this system could be incorporated in 1975-76 model automobiles.

1.2.3 Effect of Lead on Other Engine Parts

The principal deleterious effect of lead additives in gasoline on engine parts other than the emission control system, per se, is to reduce the usable life-time of exhaust systems and spark plugs. Other reported differential effects (varnish, sludge, rust, wear, etc.), due to unleaded versus leaded gasoline, do not result in a quantifiable impact on the consumer in terms of operational considerations or cost. The use of unleaded gasoline can essentially double the exhaust system life and increase spark plug life approximately 50 percent in conventional (pre-1971) cars.

Similar spark plug life increases with unleaded gasoline are expected in 1975-76 systems; if long-life exhaust systems (e.g., stainless steel) compatible with either leaded or unleaded gasoline are incorporated in 1975-76 systems, no lifetime variabilities would exist for this component.

There is considerable evidence that excessive valve seat wear can occur with the use of unleaded fuel, particularly at sustained high-speed and high-load conditions. However, this problem can be solved at very low cost by changing to induction-hardened exhaust valve seats. One domestic manufacturer has introduced such valve seats in some 1972 models, with plans for full implementation by the end of the 1972 model year. Other manufacturers are also phasing in compatible exhaust valves and seats. All U.S. automakers plan to market a system compatible with unleaded gasoline by the 1975 model year.

1.2.4 General Evaluation of Emission Control Devices/Systems

1.2.4.1 Categories of Devices/Systems

A broad spectrum of emission control devices has been evaluated by the automotive industry and ancillary development companies. In general, they fall into the following categories:

- a. Catalytic Converter Systems (no form of thermal reactor warmup device)
 - 1. HC/CO Catalytic Converter Alone
 - 2. HC/CO Catalytic Converter plus Exhaust Gas Recirculation (EGR)
 - 3. Dual Catalytic Converter plus EGR
 - 4. Tricomponent Catalytic Converter Alone
- b. Thermal Reactor Systems
 - 1. Lean Thermal Reactor (LTR) plus EGR
 - 2. Rich Thermal Reactor (RTR) Alone
 - 3. Rich Thermal Reactor (RTR) plus EGR
- c. Combination Systems
 - 1. LTR plus HC/CO Catalytic Converter plus EGR
 - 2. RTR plus HC/CO Catalytic Converter plus EGR
 - 3. RTR plus Dual Catalytic Converter plus EGR
 - 4. RTR plus NO_x Catalytic Converter plus RTR

A summary of the available emission data for these emission control system concepts is presented in Table 4-15 in Section 4.3.4.

1.2.4.2 Performance of Devices/Systems

Several emission control systems have met, or show promise of meeting, the Federal 1975 emission standards. These systems are experimental versions, and emission data do not reflect consideration of any factor to account for variabilities in production tolerances, testing procedures, or degradation with mileage.

The following general observations are pertinent for the performance of emission control systems:

1. In general, the catalytic-converter-only systems suffer because of high emissions during the cold start portion of the CVS test procedure due to slow warmup. In addition, the tricomponent catalytic converter requires a precision in air-fuel ratio control not adequately demonstrated to date.
2. LTR plus EGR systems have yet to demonstrate meeting 1975-76 HC and CO standards, although improvements in thermal reactor design (flameholders, improved mixing, etc.) and fast warmup choke devices could improve this situation. NO_x levels below approximately 1.3 gm/mi have not been reported for this concept.
3. The most advanced RTR plus EGR systems meet the 1975-76 HC standard and approach the CO standard. NO_x levels below approximately 0.5-0.7 gm/mi have not been demonstrated. At this NO_x level, however, the fuel economy penalty is severe (approximately 25-30 percent).
4. "Combination systems," i.e., various combinations of thermal reactors, EGR, and catalytic converters, are judged by the automotive industry to offer the best hope for achieving minimum emission levels and are under intensive development at this time for incorporation in 1975-76 model cars. In these combination systems, the primary function of the thermal reactor is to warm up a catalyst bed. Therefore, it need not be a "full-size" thermal reactor, but rather a "low-grade," less complex type.
5. Thermal reactor (LTR or RTR) plus HC/CO catalytic converter plus EGR systems are meaningful in terms of 1975 standards; however, it is generally agreed that a NO_x catalytic converter would have to be added for the lower NO_x levels required by the 1976 standards. At this time, NO_x catalysts with the required durability (50,000 miles) have not been demonstrated. In this case (NO_x catalyst), the thermal reactor is restricted to rich operation, inasmuch as all known NO_x catalysts require a reducing atmosphere.

It is emphasized that the foregoing observations are based on experimental laboratory data only. If, as the various automakers have suggested, levels of approximately 50 percent of the 1975-76 standards have to be achieved to account for the variation of production tolerances, test reproducibility, degradation with accumulated mileage effects, etc., then it would appear

that none of the emission control systems proposed and evaluated to date will meet the 1975-76 emission standards on a consistent basis.

1.2.4.3 Durability of Devices/Systems

There are no meaningful lifetime or durability data available for any combined emission control system seriously being considered for implementation by the U.S. automakers. The approximately 90,000-mile durability test of a thermal reactor by Ford is certainly significant, but did not include an EGR system or a catalytic converter. Engelhard has reported a 50,000-mile durability test for their PTX catalyst; however, it did not include an EGR system for NO_x control. At this point in time, then, emission control system durability or lifetime remains simply as a goal, with little or no demonstrated capability.

1.2.4.4 Advanced Concepts

A prototype stratified charge engine installed in a one-quarter-ton light truck was recently tested by EPA, Willow Run, Michigan, and met the 1976 emission standards at a 3000-pound inertia weight on the dynamometer. However, the power-to-weight ratio of this vehicle was not sufficiently high to meet all of the acceleration requirements of the dynamometer driving cycle. This system incorporated a thermal reactor, EGR, and a HC/CO catalytic converter. The Ford Motor Company, developer of this engine, states that it is not sufficiently well developed to permit quantity production in the near future. On this basis, then, the stratified charge engine concept has not been compared with the previously identified emission control system concepts which are compatible with present generation spark ignition engines.

A variety of other advanced engine concepts are in various stages of research and development. In this category are such concepts as the "lean-burn" and "prechamber" approaches. There are insufficient data at this time to fully evaluate the emission control, mass producibility, and costs of these systems. Therefore, they were not included in this assessment.

1.2.5 General Cost Summary

It should be noted that in the consumer cost analysis reported herein, the exhaust system life variability with gasoline lead content is not a factor, since a long-life exhaust system (e.g. stainless steel) compatible with either leaded or unleaded gasoline was incorporated into all considered systems in view of the generally higher temperature levels expected.

The following observations can be made on the estimated costs of unleaded gasoline and of emission control systems:

1.2.5.1 Unleaded Gasoline Cost Effects

1. If unleaded gasoline is made available, the eventual (circa 1980) estimated unit cost differential for a single-grade (93 RON) unleaded gasoline is 0.46 cent per gallon more than the current conventional two-grade leaded gasoline weighted average price per gallon. This cost differential is the increase in manufacturing costs for the unleaded gasoline plus a distribution cost increase necessary for introduction and implementation of a new (93 RON) unleaded gasoline grade.
2. Utilization of a single-grade (93 RON) unleaded gasoline requires a reduction in compression ratio (to approximately 8.35:1) from pre-1971 values (approximately 9.37:1 weighted average). This reduction in compression ratio increases the specific fuel consumption, thereby increasing the fuel cost over the lifetime of the average car (85,000 miles) by approximately \$130, while the additional cost per gallon of unleaded gasoline increases the fuel cost by approximately an additional \$30. Both of these fuel costs are independent of any fuel economy degradation attributable to the emission control system concept, per se.
3. Implementation of a three-grade unleaded gasoline system, at the same clear-pool octane number (93 RON), enables an increase in compression ratio (approximately 8.95:1 weighted average) over the single-grade (93 RON) system (approximately 8.35:1). This increase in compression ratio reduces the fuel cost penalty due to compression ratio change from \$130 to \$50 for this three-grade unleaded gasoline case over the lifetime of the average car. (A two-grade system would have similar, but not identical, fuel cost savings.)

1.2.5.2 Emission Control System Cost Effects

1. Implementation of emission control systems designed to meet 1975-76 emission standards implies very high costs to the consumer. This cost is a strong function of the required NO_x emission level as shown in Fig. 1-1. Only systems incorporating a NO_x catalyst appear to have the potential to meet the Federal 1976 NO_x standard of 0.4 gm/mi. As shown in the figure, if a 50,000-mile NO_x catalyst durability is achieved, the estimated overall consumer cost (initial, maintenance, and operating costs) over the life of the car is approximately \$860 for a single-grade unleaded gasoline system and approximately \$780 for a three-grade unleaded gasoline case. If the NO_x catalyst durability is only 25,000 miles, for example, additional converter replacements increase these overall costs to \$1170 and \$1090, respectively.
2. As most emission control systems which might be employed to meet 1975 emission standards are the same as, or building-block portions of, 1976 systems, it is not clearly meaningful to attempt to compare system costs at the 1975 emission standards (e.g., NO_x = 3.1 gm/mi). It would not appear either prudent or cost effective to attempt to implement one distinctive type of system in 1975 model cars and a completely different type of system in 1976 model cars.
3. For the system currently considered most promising to meet 1976 emission standards (low-grade RTR plus dual catalytic converter plus EGR), the estimated overall consumer cost with the single-grade unleaded gasoline supply system previously noted (\$860 above average 1970 vehicle costs over the life of the car) includes \$362 for the fuel cost penalty, \$388 for initial installed hardware costs, and \$110 net maintenance cost. A cost summary of all systems evaluated can be found in Fig. 8-5, Section 8.2.4.

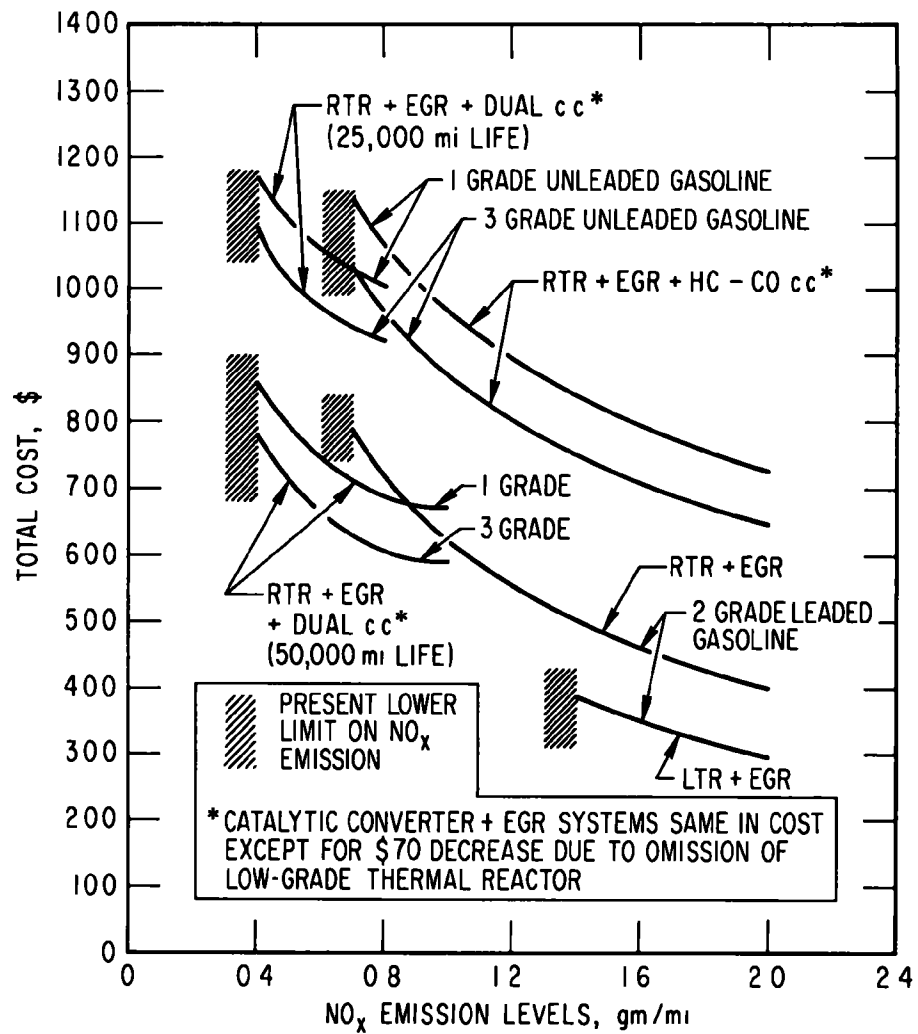


Fig. 1-1. Overall Cost Increase to Consumer Over Lifetime of Car

2. INTRODUCTION

SECTION 2

INTRODUCTION

2.1 PURPOSE

The purpose of this report is to present an assessment of the effects of lead additives in gasoline on emission control devices/systems which may be used to meet the 1975-76 Federal emission standards for light-duty vehicles in fulfillment of Section 211c (2)B of the 1970 Clean Air Act (Ref. 2-1). These standards are:

| <u>Emission</u> | <u>Standards (gm/mi)</u> | |
|--------------------------------------|--------------------------|-------------|
| | <u>1975</u> | <u>1976</u> |
| HC (hydrocarbons) | 0.41 | 0.41 |
| CO (carbon monoxide) | 3.40 | 3.40 |
| NO _x (oxides of nitrogen) | 3.10 | 0.40 |

when determined by the DHEW urban dynamometer driving cycle using the Federal CVS (constant volume sampling) test procedure and the three-bag weighted-average technique (CVS-3) for 1975-76 (Ref. 2-2).

2.2 SCOPE OF STUDY

This assessment of emission control system effects encompassed performance, durability, and cost aspects. In the performance area, emission performance characteristics, fuel economy characteristics, power, driveability, and fuel octane number requirements were examined. In the cost area, initial, maintenance, and operational cost factors were included.

A primary limitation on the type of and level of assessment in the above areas is that it was to be based on current knowledge and the state of the art as could be determined from existing data in the open literature or data

obtainable from industrial/agency sources. In this regard, it is noted that the most meaningful and comprehensive data have been made and accumulated by the automobile manufacturers.

The recent change in Federal test procedures from the single-bag CVS method to the three-bag weighted-average CVS method (Ref. 2-2) could have substantial effects on the resultant emission levels of certain systems. At the time of writing, a large portion of the available CVS emission test data is single-bag CVS test data. For comparison purposes, therefore, the present effort is limited in some instances to single-bag CVS emission test data. The 1975-76 emission standards for the single-bag CVS tests were:

| <u>Emission</u> | <u>Standards (gm/mi)</u> | |
|-----------------|--------------------------|-------------|
| | <u>1975</u> | <u>1976</u> |
| HC | 0.46 | 0.46 |
| CO | 4.70 | 4.70 |
| NO _x | 3.00 | 0.40 |

These standards are pertinent only when single-bag CVS test data are presented in the report.

In the cost area, there is a minimal amount of information pertaining to specific emission control system costs. The cost data reported herein, then, are limited to engineering estimates based on raw material costs and to comparisons with more conventional hardware components.

REFERENCES

- 2-1. Public Law 90-148, The Clean Air Act, As Amended.
- 2-2. "Control of Air Pollution from New Motor Vehicles and New Motor Vehicle Engines," Federal Register, Vol. 36, No. 128 (2 July 1971).

3. METHOD OF APPROACH

SECTION 3

METHOD OF APPROACH

In accomplishing the stated purpose in Section 1, within the scope and limitations noted, the following specific steps were performed in accomplishing the study:

1. A literature survey was made and relevant material obtained. This material included letters from the automobile manufacturers to the Administrator of EPA (April 1971) in response to his request for information regarding progress towards meeting the requirements of the Clean Air Act.
2. Visits were made to the four domestic U.S. automobile manufacturers, various major oil companies active in the emission control area, catalyst manufacturers, the two major lead additive manufacturers, and three foreign automobile manufacturers for direct discussions of emission control system technology. These visits not only provided direct comments and information, but also resulted in published data to supplement the original literature survey. (See Appendix A for a list of organizations contacted.)
3. Pertinent emission control system information was compiled and assessed to provide a comprehensive picture for emission control systems in general.
4. Specific emission control systems likely to be used for 1975-76 emission standards were then examined relative to the effects of lead additives on performance, durability, and costs.

The following discussions, then, summarize the significant results of the assessment in the sectional order of presentation in the report:

1. The basic effect of engine air-fuel ratio variation and engine component modifications on uncontrolled spark ignition engine HC, CO, and NO_x emission levels is briefly outlined (Section 4.1).
2. Specific emission control devices which are useful to control one or more of the HC, CO, and NO_x emission species are defined and their basic method of operation delineated (Section 4.2).

3. A wide variety of emission control "systems" (i.e., combinations of emission control devices to simultaneously control HC, CO, and NO_x emissions) is defined by generic classification. Specific emission control systems evaluated by various companies to date are used to illustrate the generic class in terms of emission control characteristics, fuel economy characteristics, and durability. Where appropriate, stated effects of lead additives in gasoline on a particular emission control system are delineated (Sections 4.3.1 through 4.3.3).
4. The overall spectrum of potential emission control systems is then compared in emission level capability with the 1975-76 standards, and summarized with respect to their (1) durability, and (2) fuel economy effects (Section 4.3.4).
5. An overall assessment of the effects of lead additives in gasoline on the various emission control system concepts is presented in Section 5.
6. The feasibility and implications resulting from the use of lead traps or exhaust gas scrubber devices to remove lead additives from engine exhaust gas are presented in Section 6.
7. The effects of lead additives on engine parts other than the emission control system, per se, are summarized in Section 7.
8. Finally, the estimated costs of various emission control system concepts are summarized in terms of (1) initial consumer costs (as installed in a new car), and (2) overall consumer costs, which reflect maintenance cost and operating cost in addition to initial acquisition costs (Section 8).

**4. GENERAL EVALUATION
OF EMISSION CONTROL
DEVICES/SYSTEMS**

SECTION 4

GENERAL EVALUATION OF EMISSION CONTROL DEVICES/SYSTEMS

Gaseous emissions from automobile exhausts may be controlled either by inhibiting formation of the gases in the engine cylinders or by lowering their concentration externally. In general, methods of controlling exhaust emissions from automotive spark ignition internal combustion engines to meet the stringent 1975-76 Federal standards involve certain engine modifications and the use of a combination of several devices. Multiple methods are necessary because of the requirement for simultaneous control of the hydrocarbon (HC), carbon monoxide (CO), and oxides of nitrogen (NO_x) constituents in the exhaust gas.

4.1 ENGINE MODIFICATIONS AND OPERATING CONSIDERATIONS

As illustrated in Fig. 4-1, HC, CO, and NO_x concentrations in the exhaust of uncontrolled engines are strongly a function of the operating air-fuel ratio. As can be noted from the figure, at the stoichiometric air-fuel ratio NO_x production is very high while HC and CO production is relatively low. For air-fuel ratios between approximately 17 and 19, levels for all three constituents are reduced considerably from peak values. Currently, engine operation is restricted to air-fuel ratios below approximately 19 to avoid excessive power loss and rough engine operation. Operation in the 17-19 range minimizes HC and CO levels, and lowers that of NO_x , but the concurrent reduction of exhaust levels of all three species is far from sufficient to meet 1975-76 emission requirements. NO_x formation can be suppressed by operating in the "rich" regime (air-fuel ratios of approximately 11-13); however, in this region HC and CO concentrations are very high.

Other factors affecting emissions include spark timing, and induction system and combustion chamber design. Retarding the spark results in lower peak

temperatures and less NO_x formation. Also, the exhaust gas temperature is higher with a retarded spark, which promotes further combustion of the HC and CO species in the exhaust system. Induction system modifications can result in lower emissions by providing a more uniform mixture to the cylinders and better atomization and vaporization of the fuel. Combustion chamber design affects the combustion process and, as a result, peak and exhaust gas temperatures.

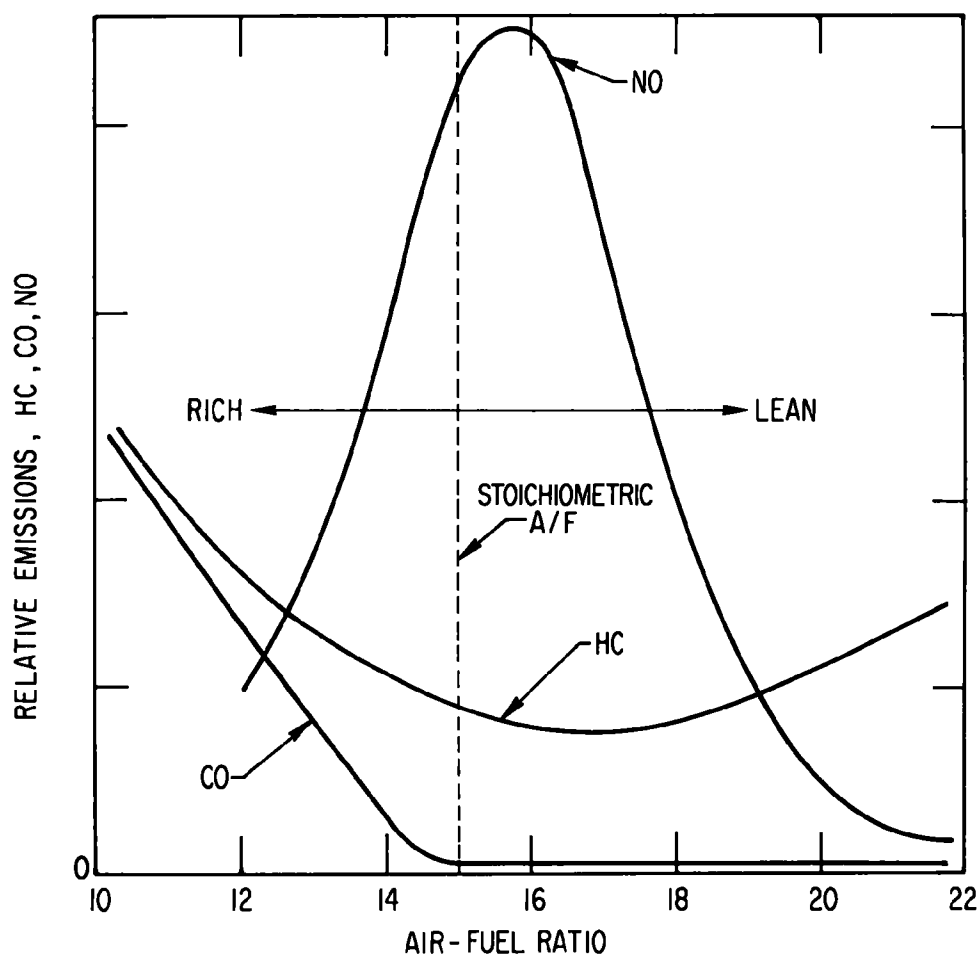


Fig. 4-1. Effect of Air-Fuel Ratio on Emission Levels (Gasoline Spark Ignition Engine)

4.2 EMISSION CONTROL DEVICES

4.2.1 Thermal Reactors

A thermal reactor is a chamber (replacing the conventional engine exhaust manifold) into which the hot exhaust gases from the engine are passed. The chamber is sized and configured to increase the residence time of the gases and permit further chemical reactions, thus reducing HC and CO concentrations. In general, the thermal reactor embodies a double-walled and insulated (between walls) configuration, with port liners to direct the exhaust gases to its inner core section. In some instances, baffles and/or swirl plates are used to further promote mixing.

There are two different types of thermal reactors under consideration at this time: the Rich Thermal Reactor (RTR) and the Lean Thermal Reactor (LTR).

4.2.1.1 Thermal Reactor Descriptions-- General

4.2.1.1.1 Rich Thermal Reactor (RTR)

The RTR is designed for fuel-rich engine operation. As a result of the associated chemically reducing atmosphere and lower combustion temperatures, the amount of NO_x formed in the engine cylinders is reduced (Fig. 4-1). If the engine is run rich enough (A/F approximately 11-12), it is possible to limit the formation of NO_x to less than 2 gm/mi (Ref. 4-2); however, fuel economy penalties at these rich mixtures are as high as 20 percent. As the exhaust from the cylinders contains large quantities of HC and CO, secondary air supplied by a pump is injected into the reactor to permit further oxidation of these species.

The thermal reactor should be designed for minimum thermal capacity to heat promptly to lower emissions for cold start conditions. Since relatively high temperatures (1700-2000°F) are achieved in the RTR, high-temperature materials (e.g., Inconel 601 containing 60 percent Ni, 23 percent Cr, 14 percent Fe, 1-1/2 percent Al) are required for the inner core, baffles, and port

liners. At these high temperatures, engine misfiring, which produces high HC levels, could lead to excessive local temperatures and material burnout conditions in the RTR; therefore, temperature control devices are necessary to protect it. (Ceramic materials, which could be more tolerant to over-temperature conditions than metals, have not to date demonstrated the necessary thermal and mechanical shock properties.)

A typical RTR design is shown in Fig. 4-2. The system illustrated is the Du Pont Type V reactor, one of many experimental versions created by this company in the course of an evolutionary development program begun in 1962 (Ref. 4-1). The reactor consists of a cast iron outer shell which houses a tubular core and a shield to reduce the heat loss from the hot core to the cooler outer shell. Exhaust gases mixed with air supplied by a belt-driven air pump first enter the tubular core, which is designed to promote mixing and initiate oxidation. The reacting gases then pass through the core-shield annulus and the shield-shell annulus where oxidation is completed before the gases exit into the conventional exhaust system. Sheet metal inserts at the engine exhaust ports are provided in a number of different reactor designs to reduce heat loss to the water-jacketed exhaust port surfaces.

Other RTR configurations differ from the Du Pont Type V system principally in the arrangement of the internal core geometry and in the volume provided for the shell and core chambers. A summary description of proposed experimental designs for RTR types is presented in Table 4-1. One of these, the Esso Modified Rapid Action Manifold (RAM) rich reactor system (Ref. 4-2) is unique in that the reactor geometry is toroidal rather than cylindrical. Exhaust gases flow from a manifold collector, around the torus, and exit through a slot in a central plenum which discharges to an exhaust pipe. This flow arrangement is said to provide superior mixing of the secondary air with the exhaust combustibles. Also unique in the RAM system is the use of flameholders. These devices are designed to produce a stabilized flame at the outlet of the engine exhaust ports during startup, when the engine is

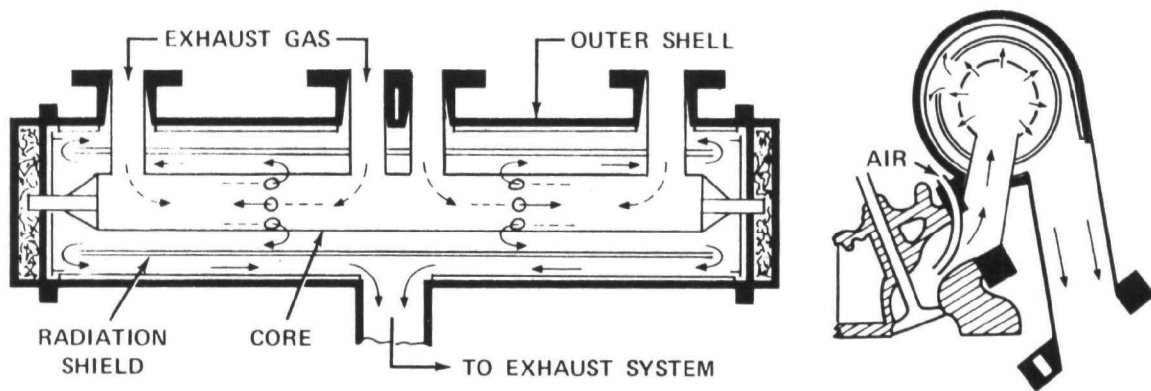


Fig. 4-2. Du Pont Type V Thermal Reactor (from Ref. 4-1)

Table 4-1. Thermal Reactor Summary

| Reactor Type | Induction Air-Fuel Ratio | Reactor Operating Temperature | Reactor Volume (in. ³) | | Reactor Air Injection | Port Liners | Reference |
|---|--------------------------|-------------------------------|------------------------------------|-------|-----------------------|-------------|-----------|
| | | | Core | Total | | | |
| Rich Reactors | | | | | | | |
| Du Pont Type V | 14 | (a) | 60 | (a) | Yes | Yes | 4-53 |
| Du Pont Type VII (b) | 11.5-12.5 | (a) | (a) | (a) | Yes | Yes | 4-54 |
| Esso Synchrothermal | 12.2 | 1600-1900(c) | 103 | (a) | Yes | No | 4-12 |
| Esso Modified RAM | 11-13 | 1600-1750 | 71(d) | (a) | Yes | No(e) | 4-2 |
| IIEC/Ford Type H | (a) | 1600-1850(c)(f) | 40 | 97 | Yes | Yes | 4-3 |
| IIEC/Toyo Kogyo | (a) | 1600-1800(c)(f) | 61 | (a) | Yes | Yes | 4-10 |
| IIEC/Nissan | (a) | (a) | (a) | 220 | Yes | Yes | 4-10 |
| British Small Engine | 10-14 | 1600-1650 | 70 | (a) | Yes | No | 4-55 |
| Lean Reactor | | | | | | | |
| Ethyl Lean Reactor | 17-19 | 1400-1600(c) | - | 160 | No(g) | Yes | 4-5/4-52 |
| (a) Not specified | | | | | | | |
| (b) Recent Du Pont system | | | | | | | |
| (c) With EGR | | | | | | | |
| (d) Torus volume | | | | | | | |
| (e) Flameholders | | | | | | | |
| (f) Thermal protection cutoff temperature | | | | | | | |
| (g) Air injection possibly required during choke period | | | | | | | |

choked. The flame serves the purpose of oxidizing CO and HC and accelerates reactor warmup from cold conditions. Model II RAM reactors were made from Type 310 stainless steel.

Aside from air-fuel ratio effects, small fuel economy losses are directly attributable to the thermal reactor. These include the additional backpressure created by reactor flow resistance, and the power required to drive the air pump for secondary air injection in rich reactor systems. Esso studies on the RAM reactor indicated that the device added the equivalent of about one muffler to the total engine exhaust backpressure (Ref. 4-2). An early Ford/IIEC RTR design (Type D, Ref. 4-3) produced backpressures 8 in. Hg higher than the 2 in. Hg values obtained for standard production exhaust systems. However, a later design with revised internal geometry in combination with the use of a dual exhaust system reduced the backpressure to the production exhaust system level.

Power requirements for the air pump may be gauged from Fig. 4-3. The data shown are based on current pump designs for V-8 engines ranging from 300 to 400 cubic inches of displacement (CID) (Ref. 4-4). For example, at 2500 rpm (equivalent to a cruise speed of about 65 mph), and estimating a backpressure of 5 in. Hg, the power requirement indicated is 0.5 hp, which corresponds to a fuel economy loss of less than one percent.

As mentioned previously, by comparison with these small fuel economy losses a carburetor calibration change of three A/F units (15 to 12) to minimize NO_x to less than 2 gm/mi may incur a fuel economy penalty of 15 to 20 percent. And if an exhaust gas recirculation system (EGR), described in Section 4.2.2, is added to the RTR to further control NO_x to levels below approximately 1 gm/mi, fuel economy penalties are as high as 20-30 percent.

Although it is instructive to consider these component contributions to the fuel penalty, the total system loss is more directly useful to an evaluation of alternate control schemes. These data are discussed in Section 4.3 in

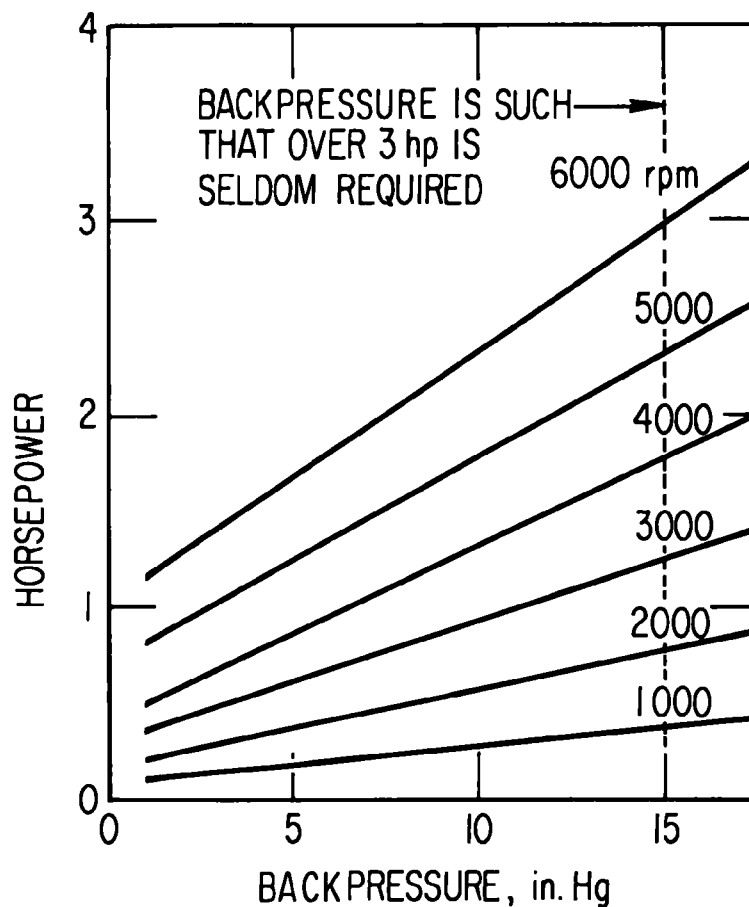


Fig. 4-3. Air Pump Power Requirements
(300-400 CID Engines)
(from Ref. 4-4)

conjunction with the specific combined emission control systems described in that section.

4.2.1.1.2 Lean Thermal Reactor (LTR)

The LTR is used in conjunction with an engine operated on the lean side of stoichiometric mixtures, i.e., with excess air. Currently, LTR systems are limited to air-fuel ratios of approximately 19. As shown in Fig. 4-1, HC and CO concentrations in the engine exhaust are much lower than in the case of the RTR (but NO_x levels are somewhat higher). Therefore, little chemical heat is generated in the reactor and its temperature is governed to

a large extent by the sensible heat in the exhaust gas. This means that the oxidation of HC and CO is accomplished within the LTR at lower temperatures than for the RTR, and without the requirement for additional air (i.e., no air pump or mixing limitation). Because of the lower operating temperatures, the durability requirement can be met by less expensive materials for the construction of the reactor core and baffles; however, careful attention must be given to minimizing heat losses or conversion is limited by low reaction rates. On the other hand, more stringent requirements exist for engine air-fuel mixture control and cylinder-to-cylinder distribution. This may require utilization of an advanced carburetor or electronic fuel injection. EGR is generally added for additional NO_x control. Although little or no fuel economy penalty is chargeable to the LTR itself, with EGR an approximate 10-percent decrease in fuel economy is realized for NO_x levels of approximately 1.5 gm/mi. Peak power loss due to lean operation causes a small loss in vehicle performance.

The Ethyl Corporation Lean Reactor is the only known design of a lean operating system for which specific details of configuration and performance are available. It is designed for operation at air-fuel ratios of between 17 and 19. As shown in Table 4-1, its operating temperature is 1400-1600°F, or 200-300 degrees lower than those for rich reactor systems. The reactor is cylindrical and consists of an open-tube liner made of 310 stainless steel surrounded by a layer of insulation which in turn is enclosed by an outer casing of 310 or 430 sheet stainless steel (Ref. 4-5).

4.2.1.2 Engine Modifications

Engine modifications required for thermal reactor operation generally differ for rich and lean systems. For the rich reactor, the modifications are minor. In addition to the adjustment of carburetor calibration to rich mixtures, the timing may be retarded from current production settings to increase the temperature of the gases leaving the exhaust port. Some form of overtemperature sensing and control system may be necessary in order to

prevent excessive reactor temperatures due to possible malfunctions (e.g., spark plug misfire) or to sustained high-load operation. Peak temperatures may be limited by terminating secondary air injection to the exhaust gases entering the reactor.

Lean reactor operation requires a departure from conventional carburetor design in order to achieve satisfactory vehicle driveability. Ethyl has actively pursued this problem and has developed an experimental high-velocity carburetor which provides the necessary mixture preparation for satisfactory operation at all operating conditions. Modifications in ignition timing and carburetor operation during deceleration and idle have also been made. In addition, lean carburetion involving the use of smaller, dual, or staged venturis to provide stronger fuel metering signals and better fuel mixture preparation is being explored by Chrysler with support from Ethyl and Bendix (Ref. 4-6). The results of Ethyl tests indicate that overtemperature protection for the lean operating system is not required. In one case, Ethyl disconnected three spark plug wires and found the reactor temperature did not increase (however, HC and CO emissions would increase).

4.2.1.3 Emission Performance Characteristics

In general, the performance of thermal reactors relative to the control of HC and CO is dependent on such configurational factors as the reactor volume, mass, internal geometry, and heat exchange characteristics. In addition, the performance may be influenced strongly by engine operating conditions such as air-fuel ratio and spark timing, particularly when these operating parameters are adjusted to extreme values for the purpose of achieving concurrent control of NO_x .

Large reactor volume is desirable for good reactor performance because it provides for longer residence times needed to complete mixing and the HC/CO oxidation reactions. Appropriate design of the exhaust gas flow path using internal baffling may mitigate the volume requirement through better

mixing and control of reactant concentrations. This is the preferred design route because it minimizes the problem of engine-compartment packaging, reduces the surface area for heat loss, and tends to provide a low-mass system. Thin-gauge materials are preferred because they provide for lower mass designs with low thermal inertia. Rapid response to warmup is an important reactor design objective because of the heavy discharge of HC and CO which occurs under cold start engine conditions. Thermal considerations also dictate close coupling of the reactor to the engine to minimize heat losses. Frequently, sheet metal liners are provided in such areas as the water-jacketed exhaust port surfaces and the reactor inlets to conserve heat in the exhaust gas.

Because of the requirement to control NO_x emissions to lower levels in future systems, the development of thermal reactor devices has evolved in coupling with other emission control devices such as EGR and catalysts. For this reason, it is not useful to present the emission performance characteristics of thermal reactors in isolation from other emission equipment, except where a specific system has been actually operated in this mode. The bulk of the available emissions data concerns the operation of emission control systems comprised of RTRs or LTRs combined with EGR. Thermal reactor system emission data are presented in Section 4.3 in conjunction with the specific combined emission control systems described in that section.

4.2.1.4 Fuel Economy Characteristics

Generally, the principal factors governing fuel economy losses in thermal reactor control devices are the selected engine air-fuel ratios and spark timing adjustments needed to suppress NO_x emissions. The relationship between NO_x emissions, air-fuel ratio, and spark timing is shown in Fig. 4-4 for an engine operating at constant rpm (Ref. 4-7). The effects of these engine adjustments on specific fuel consumption (SFC) are shown in Fig. 4-5 for the same engine operating conditions. The sensitivity of the

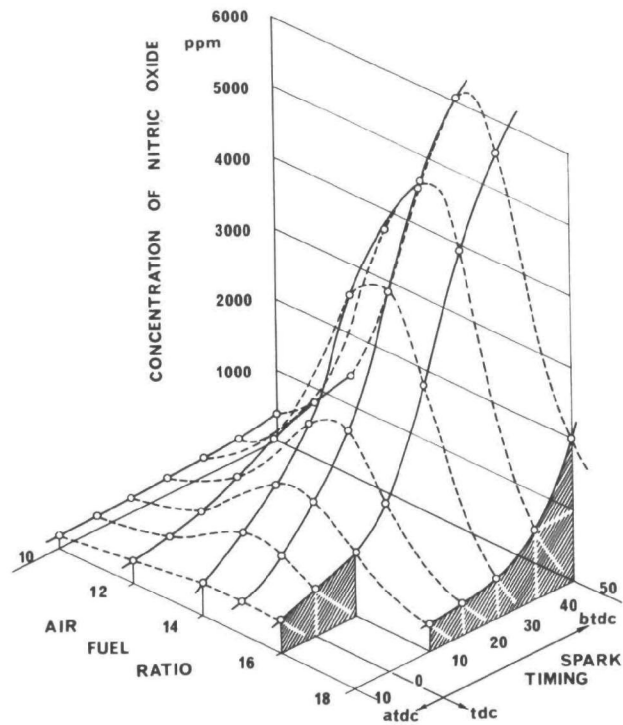


Fig. 4-4. Air-Fuel Ratio and Spark Timing Effects on NO_x Emissions (from Ref. 4-7)

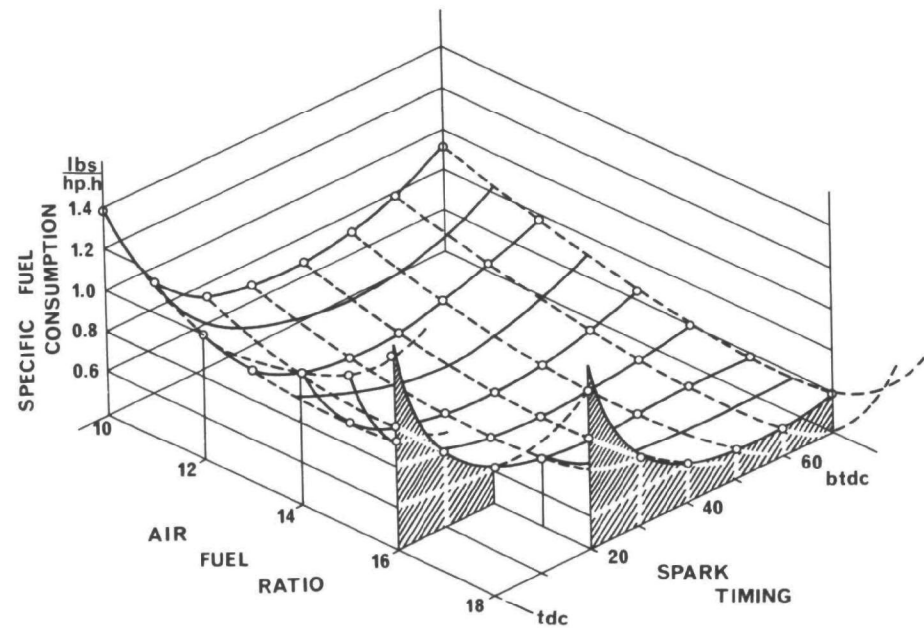


Fig. 4-5. Air-Fuel Ratio and Spark Timing Effects on Specific Fuel Consumption (from Ref. 4-7)

fuel consumption parameter to air-fuel ratio at spark-retarded conditions may be noted.

For the sole control of HC and CO, both rich and lean thermal reactor devices may be operated with lower fuel economy losses than is the case when very low NO_x values are also of concern. In this mode, the rich reactor air-fuel setting may be calibrated nearer stoichiometric. Du Pont has operated its Type V rich reactor under these conditions and has reported HC and CO emissions of 0.20 gm/mi and 4.50 gm/mi, respectively, (using the 7-mode test procedure) with a loss in fuel economy of only 1.3 percent (Ref. 4-8). Ethyl quotes little or no loss for its lean reactor when operated without EGR (Ref. 4-5).

4.2.2 Exhaust Gas Recirculation (EGR) Systems

An EGR system is a means for introducing a portion of the exhaust gas back into the incoming air-fuel mixture. The amount of NO_x formed during the combustion process in the engine cylinder is related to the temperature of combustion: higher temperatures yield more NO_x . The temperature of combustion can be lowered by the introduction into the combustion chamber of chemically inert substances that absorb part of the heat of combustion. Exhaust gases from an engine provide a convenient source of such substances.

The specific EGR systems which form the basis of most of the following discussion were evaluated in the following programs:

1. Arco N-O-R EGR System (Ref. 4-9)
An evaluation by Arco Chemical Company, Division of the Atlantic Richfield Company, of their nitric-oxide-reduction (N-O-R) EGR system on 1966 and later model vehicles.
2. Toyo Kogyo "Mazda" EGR System (Ref. 4-10)
An evaluation 1.5 liter "Mazda" vehicle equipped with a thermal reactor and EGR (accomplished as part of the IIEC Program).

3. Toyota EGR Test System (Ref. 4-7)
An experimental dynamometer evaluation of the effects of EGR on three small passenger car gasoline engines.
4. Esso EGR System (Ref 4-11)
An evaluation of EGR system potential for two 1966 vehicles (Plymouth and Chevrolet). This program was sponsored by NAPCA.
5. Esso Synchrothermal EGR System (Ref. 4-12)
An evaluation of a synchrothermal reactor system combined with EGR.
6. Esso RAM EGR System (Ref. 4-2)
An evaluation of a rapid action manifold thermal reactor system combined with EGR.
7. Esso Extended-Use Program (Ref. 4-13)
A durability evaluation of three 1969 Plymouths and three 1969 Chevrolets with EGR systems developed in Ref. 4-11. This program was sponsored by NAPCA.
8. Arco Fleet Test Program (Refs. 4-14, 4-15, 4-16)
An evaluation by the California Air Resources Board (CARB) (under Federal Grant No. 68A0605D) of the Arco N-O-R EGR system on a 120-vehicle fleet test basis.
9. Du Pont Reactor Test Vehicles (Ref. 4-17)
An evaluation by CARB (Project CI) of six 1970 Chevrolets equipped with the Du Pont thermal reactor and EGR.

4.2.2.1 EGR System Descriptions --General

Many different EGR system designs have been employed by the various investigators. The location of the exhaust gas pickup, the point of introduction of the recycled gas into the engine induction system, the metering devices, and their signal sources have all been varied greatly. For example, Fig. 4-6 illustrates the Arco N-O-R system (Ref. 4-9) in which the recycle gas is picked up from the heat riser area of the exhaust manifold and metered directly (below the carburetor throttle plate) to the intake manifold. Fig. 4-7 illustrates the Toyo Kogyo system (Ref. 4-10) in which the recycle gas is picked up downstream of the exhaust manifold (and cooled)

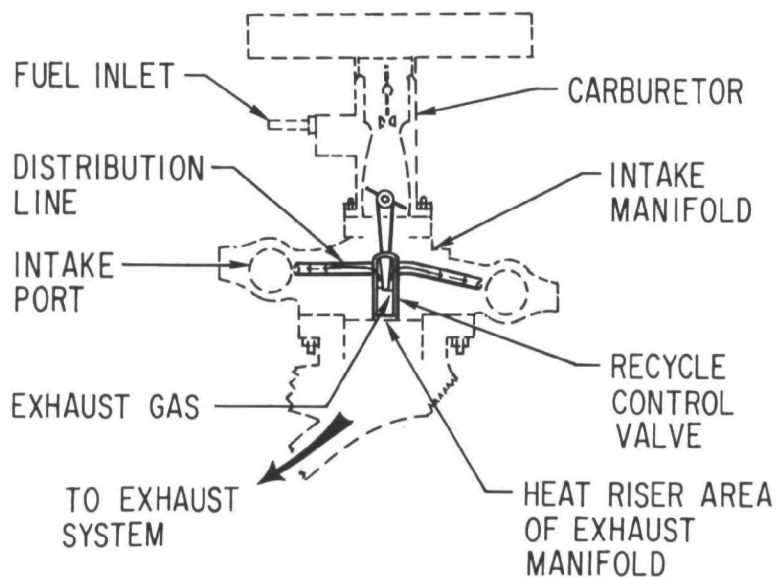


Fig. 4-6. Arco N-O-R EGR System (from Ref. 4-9)

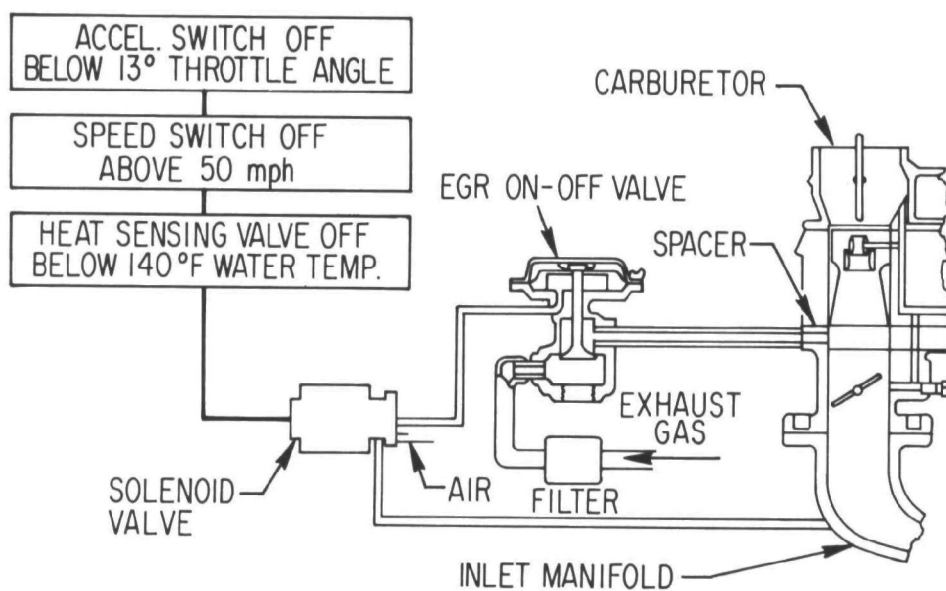


Fig. 4-7. Toyo Kogyo "Mazda" EGR System (Entry Above Throttle Valve)(from Ref. 4-10)

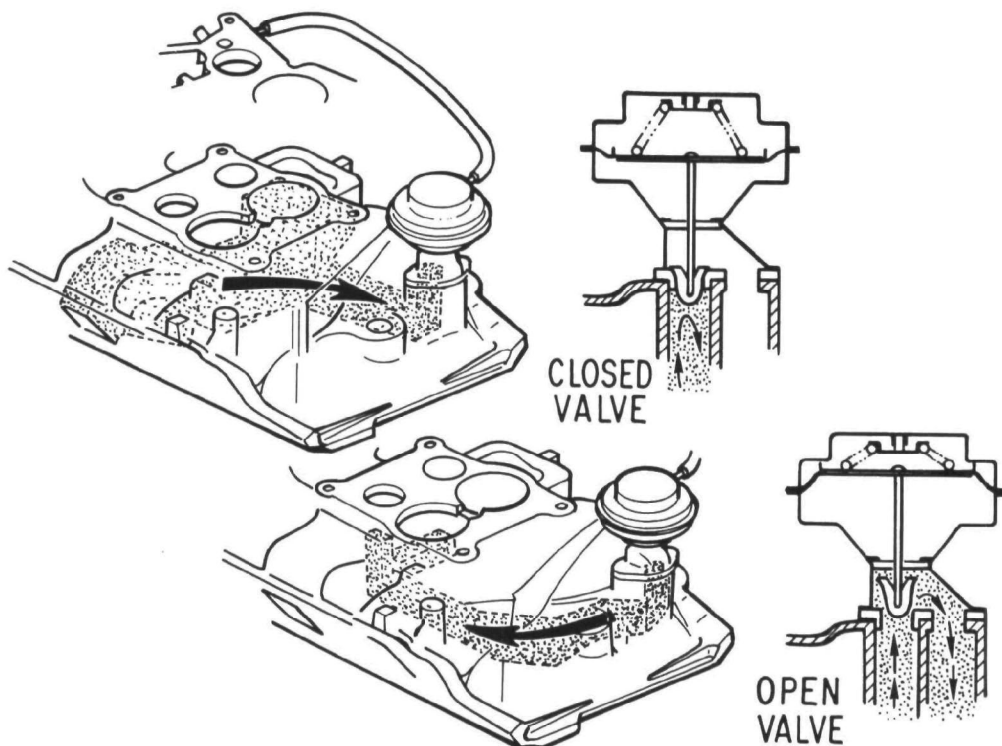
and introduced into a spacer plate above the carburetor throttle plate.

Fig. 4-8 illustrates a below-the-throttle system evaluated by General Motors (Ref. 4-18). This system is currently installed on some 1972 Buick models sold in California.

Other significant variabilities in EGR system design include exhaust gas recycle rate, and restrictions as to when the EGR flow is on or off. For example, without such restrictions EGR can cause rough idling as well as loss of power during wide-open-throttle (WOT) operation. Therefore, in most systems EGR is eliminated at idle or WOT conditions, or restricted to a lower vehicle speed range. Table 4-2 summarizes the more salient features of a number of selected systems incorporating EGR with regard to the foregoing.

Table 4-2. EGR Systems Description Summary

| System | Tap-off Location | Injection Location | Recycle Rate (%) | EGR Shutoff At | Reference |
|--|---------------------------------|--------------------|--------------------------|------------------------------|----------------|
| Arco N-O-R | Heat riser below carburetor | Below throttle | 15-22 | Idle, WOT | 4-9 |
| Toyo Kogyo | After exhaust manifold (cooled) | Above throttle | ~10 | | 4-10 |
| Esso EGR | Upstream of muffler (cooled) | Above throttle | varied | varied | 4-11 |
| Esso Synchrothermal Reactor plus EGR | Upstream of muffler (cooled) | Above throttle | ~11 | Idle, WOT | 4-12 |
| Esso RAM Reactor plus EGR | Upstream of muffler (cooled) | Above throttle | ~12 | Idle, below 20-25 mph cruise | 4-2 |
| Arco Fleet Test Program | Heat riser below carburetor | Below throttle | 0-15 (~10) | Idle, WOT | 4-14/4-15/4-16 |
| Esso EGR Extended-Use Program | Upstream of muffler (cooled) | Above throttle | 9-17 | Below ~20 mph cruise | 4-13 |
| Du Pont Reactor Vehicles | Upstream of muffler (cooled) | Above throttle | ~15 | Idle, WOT | 4-17 |
| Ethyl Lean Reactor plus EGR | Near muffler (cooled) | Above throttle | variable (as high as 30) | Idle, WOT | 4-5/4-52 |
| General Motors EGR System (see Fig. 4-8) | Exhaust manifold | Below throttle | 6-20 | Idle, WOT | 4-18 |



DESIGN PRINCIPLE:

EGR IS CONTROLLED BY A VALVE WHICH METERS EXHAUST GAS FROM THE INTAKE MANIFOLD CROSSOVER AND DISTRIBUTES IT INTO THE INTAKE SYSTEM. A VACUUM SIGNAL, MODULATED BY THROTTLE BLADE POSITION, ACTUATES THE DIAPHRAGM EGR VALVE, WHICH IN TURN POSITIONS A CONTOURED SPOOL THAT REGULATES EXHAUST GAS FLOW.

RECIRCULATION RATE: 6 TO 20%

TESTS HAVE BEEN CONDUCTED ON 95 EGR-EQUIPPED 1972 PRODUCTION ENGINES.

TYPICAL NO_x EMISSION RESULTS (1972 FEDERAL TEST PROCEDURE)

| <u>WITH EGR</u> | <u>WITHOUT EGR</u> |
|-----------------|--------------------|
| 3-1/2 — 5 gm/mi | 6 — 8 gm/mi |

Fig. 4-8. General Motors 1972 Design EGR System (Entry Below Throttle Valve) (from Ref. 4-18)

4.2.2.2 NO_x Emission Performance Characteristics

Experimental and theoretical data relating NO_x reduction to exhaust gas recycle rate are presented in Fig. 4-9 for engines operating at conventional air-fuel ratios. The agreement between prediction and test data is good. For low recycle rates, the reduction of NO_x is nearly proportional to the amount of exhaust gas recycled. For higher quantities of recycle, the effect diminishes. Substantial (approximately 40-80 percent) NO_x reductions are achievable at 10-20 percent recycle rates in the conventional air-fuel ratio range.

4.2.2.3 Fuel Economy Characteristics

Because of the dilution of the charge and reduced peak combustion temperature, a reduction in power output occurs (at the same spark advance setting) which effectively translates into a fuel economy loss. SFC test results for the vehicle systems previously shown in Fig. 4-9 are shown in Fig. 4-10 and compared with the theoretical prediction of Newhall (Ref. 4-19). Again, the correlation is good. The specific data points shown for the Arco N-O-R system are plotted at the average of the 15-22 percent recycle rates quoted.

Because of the interrelationship of spark timing, cycle temperature, and power output, it is possible to advance spark timing to avoid or minimize the effects of EGR on power and SFC. In tests performed by Esso (Fig. 4-11, from Ref. 4-11), EGR was shown to have a much lower fuel economy penalty than spark retard for the same NO_x reduction. It was found possible to operate with both recycle and some spark advance and obtain some NO_x reduction with a slight improvement (approximately 2 percent) in SFC in one case.

For any given vehicle, then, the fuel consumption penalty would be strongly influenced by the baseline engine air-fuel ratio and NO_x emission characteristics, the amount of NO_x reduction required to meet a given standard, and

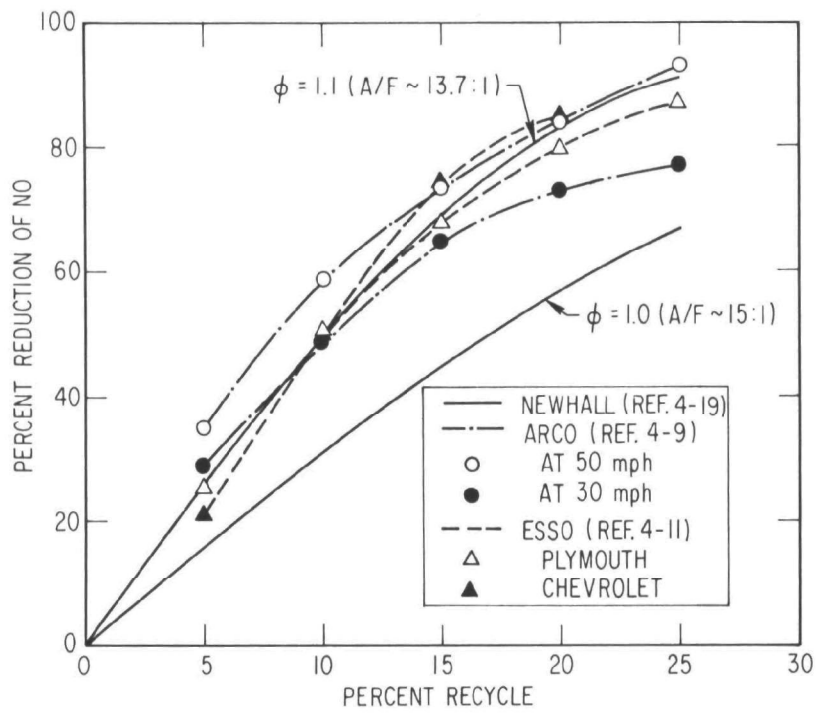


Fig. 4-9. Effect of Recycle Rate on NO Reduction

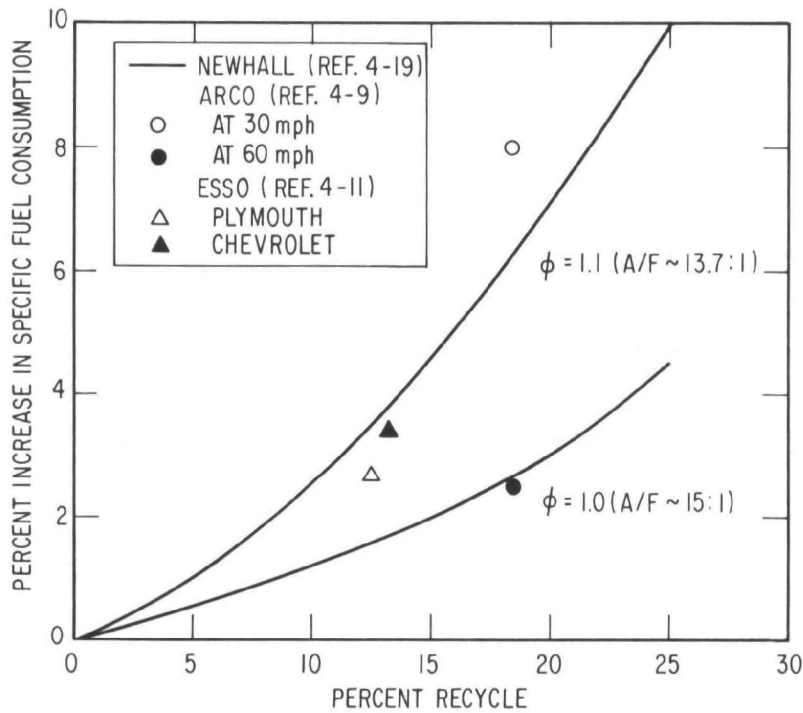


Fig. 4-10. Effect of Recycle Rate on SFC

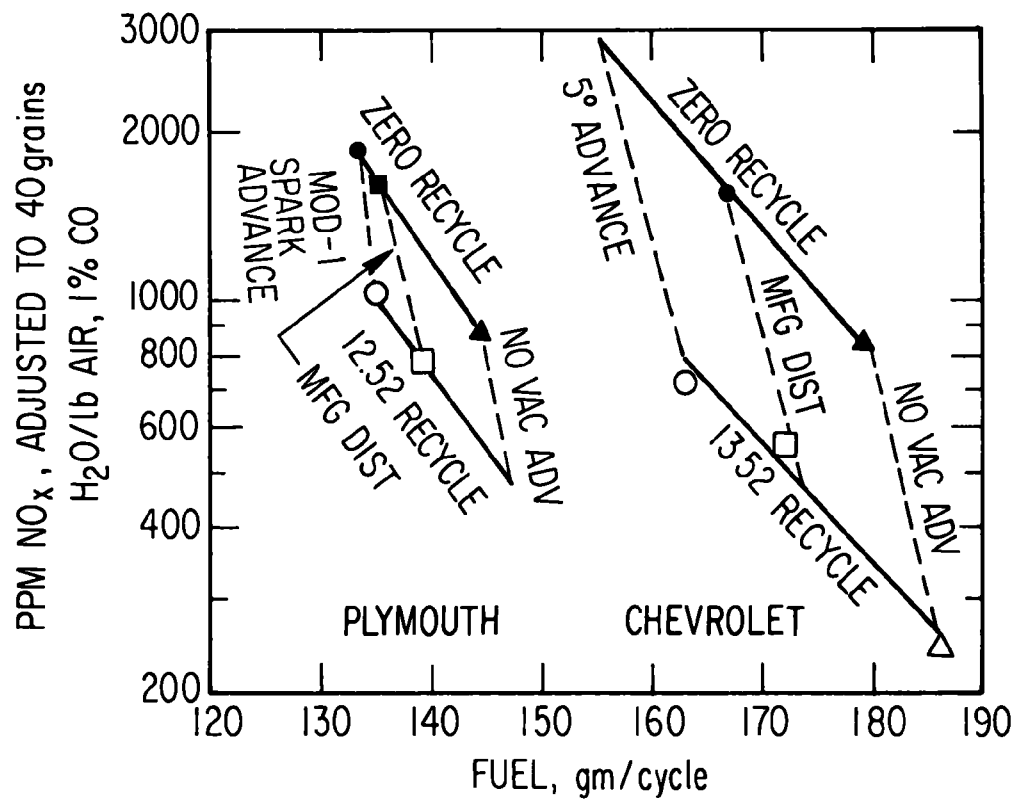


Fig. 4-11. Effect of Spark Advance and Recycle--Hot California Cycle Data (from Ref. 4-11)

the potential for optimizing spark timing and recycle rate within these constraints. Therefore, the data of Figs. 4-9 and 4-10 should be considered as broadly representative only.

Figures 4-12 and 4-13 (from Ref. 4-20) illustrate the separate and combined effects of air-fuel ratio and EGR recycle rate on SFC and NO_x reduction. Figure 4-12 shows the dramatic reduction in NO occasioned by extremely rich air-fuel ratios and the concurrent very high increase in SFC resulting from such rich operation. Figure 4-13 combines these air-fuel ratio effects with similar EGR effects to provide a map of EGR flow rate and air-fuel ratio effects on NO reduction and concurrent SFC increase.

In general, at a given air-fuel ratio, the maximum amount of EGR flow rate consistent with vehicle "driveability" constraints is required for a minimum NO_x level. Therefore, the various air-fuel ratio plus EGR rate lines of Fig. 4-13 combine to indicate an upper limit of NO reduction limit. It would be expected, then, that emission control systems employing only air-fuel ratio control and EGR for NO_x reduction (i.e., non- NO_x catalyst systems) would be characterized by the type of data shown in Fig. 4-13.

Fleet test fuel economy results (with leaded gasoline) for EGR systems are available in one instance (Ref. 4-16). The prototype N-O-R system-equipped 1967 Comet fleet (approximately 10 percent EGR, EGR off at WOT) had essentially the same average SFC when tested 4 months (approximately 5000 miles) after installation of the EGR system. After 12 months (about 14,000 miles), this same fleet had an approximate 6 percent SFC increase compared to a comparable nonequipped Comet fleet. In the case of a similarly equipped 1968 Plymouth fleet, EGR-equipped cars had an approximate 4-5 percent average SFC increase over the nonequipped fleet at 4 months (about 8000 miles) after installation. At 12 months (about 11,000 miles), this increase was approximately 9 percent.

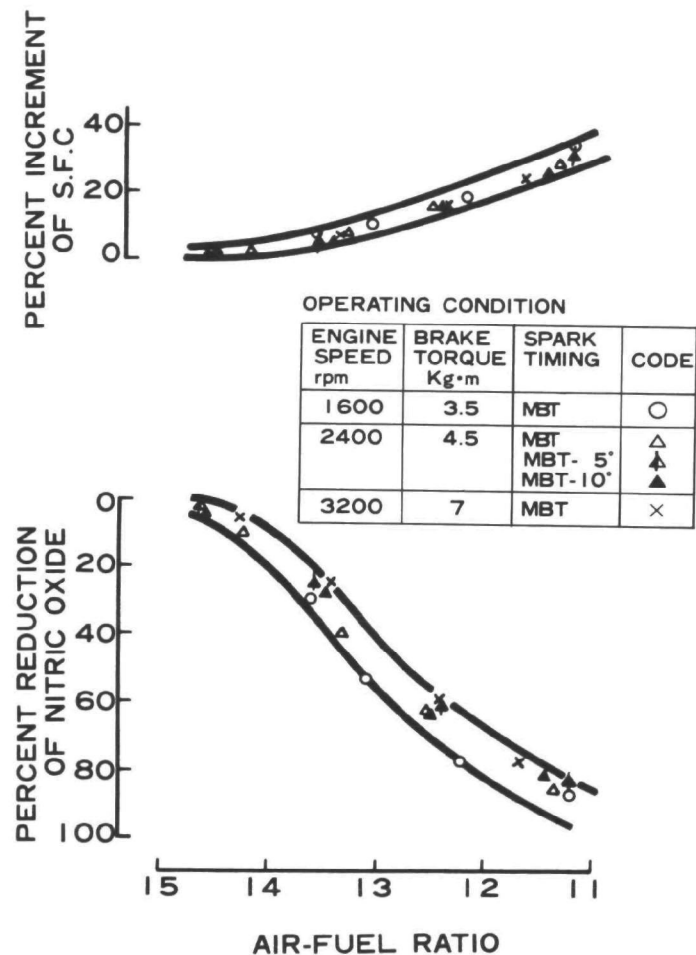


Fig. 4-12. Effect of Rich Mixtures on NO Reduction (from Ref. 4-20)

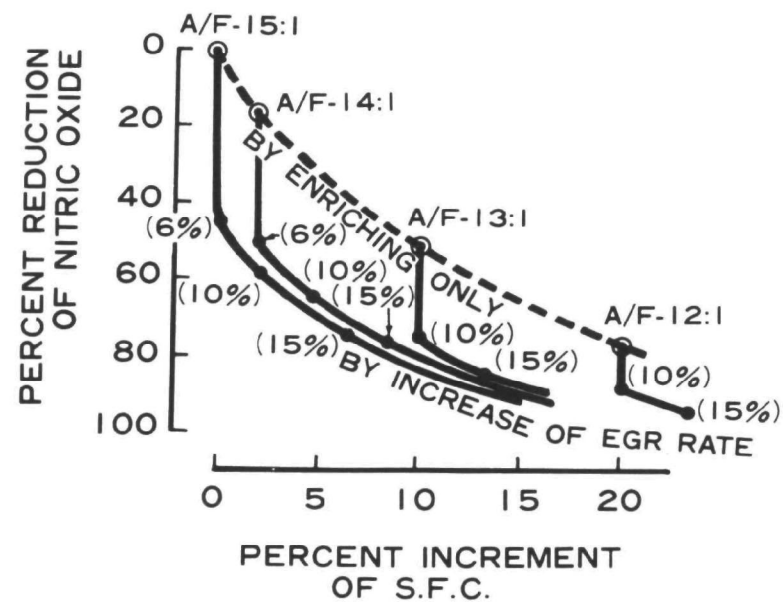


Fig. 4-13. Effect of EGR and Rich Mixture on NO Reduction and Increase in Specific Fuel Consumption (from Ref. 4-20)

4.2.2.4 Driveability Characteristics

As mentioned previously, EGR decreases maximum combustion temperature and pressure. Concurrent with this loss in maximum pressure is an increase in ignition delay time and a decrease in flame speed, resulting in a retarded pressure peak. The net effect is a more pronounced cycle-to-cycle pressure (and torque) variation which affects the smoothness of operation and/or response ("driveability") which is more pronounced as the EGR flow rate is increased.

Other noticeable performance effects can be rough idle, stumble during part-throttle operation, surge at certain cruise speeds, and an increase in full throttle acceleration time. In general, these effects increase in severity with increase in EGR flow rate.

Therefore, acceptable driveability effectively sets a limit on recycle flow rate, particularly for conventional engines operating in the nominal 13-15 air-fuel ratio range. Extensive driveability tests conducted by Esso (Ref. 4-11) showed the EGR rate limit to be dependent on the vehicle tested. One vehicle showed nominal driveability at 17 percent recycle, while another was borderline on acceptability at 15.7 percent recycle.

Driveability evaluations were made in the Arco fleet test program conducted by CARB (Ref. 4-15). They were based on the impressions of individuals assigned to drive the cars in the motor pool. The major complaints for EGR-equipped cars included: "the car sounds noisy," "the car idles too fast," "the car hesitates when the throttle is depressed to the floor," and "the engine does not idle smoothly when cold." However, the overall driveability rating, as evaluated by more than 200 drivers in this Arco test, favored the EGR-equipped vehicles over the nonequipped vehicles. It should be noted that the EGR rate was only approximately 10 percent.

4.2.2.5 Octane Number Requirements

Esso data (Fig. 4-14, from Ref. 4-11), indicate that the use of EGR can result in a reduction in the fuel octane requirement for knock prevention. This result occurred with EGR present at WOT conditions to prevent high NO_x emissions at such periods. But it was previously shown (Table 4-2) that most EGR system approaches to date shut off EGR at WOT to negate WOT power loss. Therefore, the true effect of EGR on fuel octane number requirement is dependent upon the EGR mode of operation at WOT conditions.

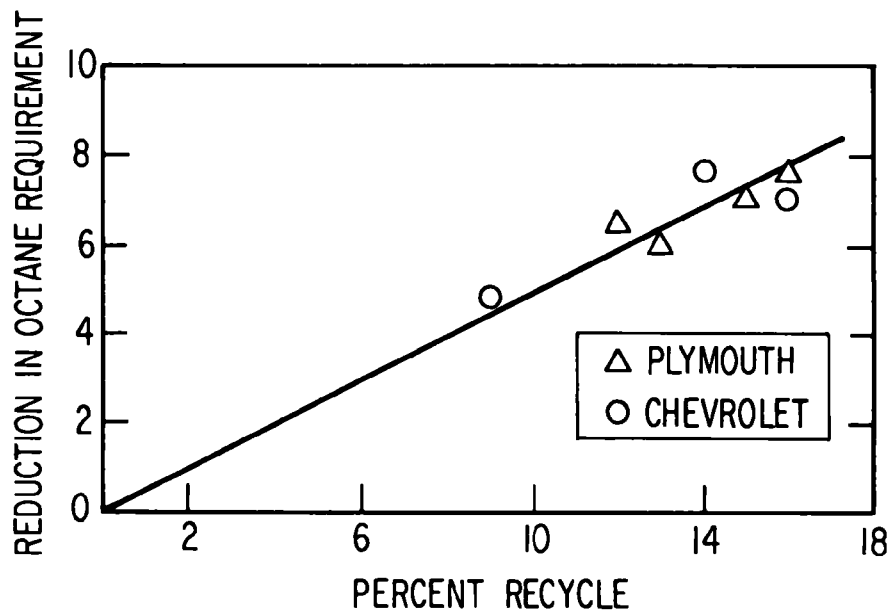


Fig. 4-14. Reduction in Octane Requirement as a Function of Recycle
(From Ref. 4-11)

To date, the automakers plan to shut off EGR at WOT; therefore, no further consideration is given herein to lowered octane number requirements occasioned by the use of EGR.

4.2.3 Catalytic Converters

An automotive catalytic converter is a device containing a catalyst material which chemically decreases exhaust gas emissions. Three basic catalytic systems are being considered:

1. Single-bed oxidation catalysts that remove HC and CO
2. Dual-bed devices having one oxidation catalyst bed to remove

- HC and CO and a separate reduction catalyst bed to remove NO_x
3. Tricomponent or single-bed catalytic devices that simultaneously remove HC, CO, and NO_x

Both base metal and noble metal catalysts are under intensive evaluation and development by the automobile industry. Specific configurations of catalytic converters vary widely. One approach is to use a monolithic coated substrate contained in a cylindrical shell. Another approach is to use a pelletized form of catalyst held in place by interior louvered members, within an outer container. In general, the specific structural and chemical formulations are considered "trade secrets" by the catalyst suppliers. Necessary attributes for catalytic converters for automotive use include sufficient activity, long life, resistance to mechanical shock, and high-temperature capability.

4.2.3.1 Typical Catalysts

Literally hundreds of catalyst types have been examined for possible use in controlling automotive emission of HC, CO, and NO_x . Usually, these catalysts were first tested in laboratory-scale experiments, with the more promising ones then tested in engine dynamometer tests and, finally, in vehicle road tests. References 4-21 through 4-25 give a good account of many of the catalysts tested. However, the exact composition of the more promising types is usually considered proprietary and referred to by a letter designation or more generally as base (or transition) metal, noble (or precious) metal, or metallic.

4.2.3.1.1 Base Metal Catalyst

Base metal catalysts employ metals or oxides of metals from the transitional group (Periodic Table of Elements) which includes vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), and zinc (Zn). Several metals and their oxides are usually combined to form a catalyst. Supports such as alumina (Al_2O_3) and/or

silica (SiO_2) are used to provide structural strength. Tables 4-3 through 4-5 include a small fraction of the formulations that have been tested. It should be noted that a few base metal catalysts also incorporate trace amounts of noble metals such as platinum (Pt) or palladium (Pd).

4.2.3.1.2 Noble or Precious Metal Catalysts

The noble or precious metal catalysts that have been tested are primarily Pt and Pd. They are deposited on Al_2O_3 or SiO_2 supports and are characterized by relatively low concentrations of active metal (approximately 0.1-0.6 percent by weight). Tables 4-3 through 4-5 list a few of the noble metal catalysts.

4.2.3.1.3 Metal or Bulk Metal Catalysts

Bulk metal catalysts, as the name implies, are homogeneous metals of varying shapes that require no support material. Pellets, wires, and honeycomb structures are some of the shapes that have been used. Monel, copper, stainless steel, and copper-coated stainless steel also have been used.

4.2.3.2 Types of Catalytic Converters

There are three basic types of catalytic converters that have been tested to varying degrees and with varying degrees of success.

4.2.3.2.1 HC/CO-Oxidation Catalysts

The catalysts which oxidize HC and CO into carbon dioxide (CO_2) and water (H_2O) are referred to as HC/CO catalysts. By far, the greatest effort has gone into developing this type of catalyst and literally hundreds of combinations have been tested, including base metals, precious metals, and combinations of both (Table 4-3). HC/CO oxidation catalysts, as the name implies, require excess oxygen (air) to convert the HC and CO to H_2O and CO_2 . This could be accomplished by operating at lean air-fuel mixtures or by adding secondary air to the engine exhaust. To date, the latter approach has been used almost exclusively.

Table 4-3. Catalytic Removal of HC, CO, and NO_x--Laboratory-Scale Experiments (from Ref. 4-21)

| Catalyst Composition (wt %) | Reactive Gas Composition (ppm) | | | Catalytic Conversion (vol %) | | | Test Conditions | | Notes |
|--|-----------------------------------|----------|-----------------|---------------------------------|--------|-----------------|---------------------|--|---|
| | HC | CO | NO _x | HC | CO | NO _x | Temperature (°C) | Space Velocity (hr ⁻¹) | |
| CuO/Cr ₂ O ₃ (Ba) ^a | 0 | 60000 | 4000 | - | - | >97 | 300-330 | 15-25 | Oxygen reduces catalytic efficiency |
| CuO/Cr ₂ O ₃ (Zn) ^b | 0 | 60000 | 4000 | - | - | 100 | 300-330 | 15-25 | Oxygen reduces catalytic efficiency |
| CuO/Cr ₂ O ₃ (Ba) ^a | 0 | 60000 | 4000 | - | 70-100 | 100 | 340 | 10 | Oxygen reduces catalytic efficiency, ^c attrition of catalyst with prolonged use |
| 6.8 CuO/6.8 Cr ₂ O ₃ /86.4 Al ₂ O ₃ | 0 | 60000 | 4000 | - | - | 91 | 200 | 10 | Al ₂ O ₃ -supported catalyst shows similar properties to unsupported CuO · Cr ₂ O ₃ |
| 82 CuO/17 Cr ₂ O ₃ ^d | 0 | 10000 | 1500 | - | - | >90 | 200-500 | - | At temperatures <200°C N ₂ O formed |
| 30 CuO/70 SiO ₂ | <3000 | 400-1400 | 40-1400 | - | - | 90 | 300 | 10 | Catalyst reduced in H ₂ , low conc. of Hc does not affect catalyst efficiency |
| 10 Fe ₂ O ₃ /85 Al ₂ O ₃ /5 SiO ₂ | 0 | 12000 | 20000 | - | >50 | >50 | 150-400 | 0.02 | N ₂ O formation at T <200°C |
| 10 CuCr ₂ O ₄ /85 Al ₂ O ₃ /5 SiO ₂ | 0 | 12000 | 20000 | - | >50 | >50 | 150-400 | 0.02 | Comparable efficiency to No. 7 |
| 5 Cu/95 Al ₂ O ₃ | 0 | 13000 | 125 | - | - | 100 | - | 7.9 | Conversion of sulfur compounds |
| 4 CuO/96 Al ₂ O ₃ | 250 | 10000 | - | >50 | >50 | - | 230-450 | - | CO ₂ and H ₂ O interfere with oxidation of CO and olefins at T ≤ 360°C |
| CuO · Cr ₂ O ₃ (Ba) ^a | 1000-2500 | 0-30000 | - | >90 | >90 | - | 180-400 | 5.5-11 | Poor attrition resistance |
| 3MnO ₂ /2CuO | 1000-2500 | 0-30000 | - | >90 | >90 | - | 180 | 5.7-11 | Loss of catalytic activity on prolonged use due to crystallization |
| 0.6 Pt/99.4 SiO ₂ | 2400 | 40000 | - | >90 | 90 | - | 280 | 5.7 | |
| 0.2 Pd/99.8 SiO ₂ | 2400 | 40000 | - | >90 | >90 | - | 260 | 5.7 | |
| 4 Cr ₂ O ₃ /96 Al ₂ O ₃ | 2000 | 20000 | - | >90 | >80 | - | 300-675 | 10 | Cr ₂ O ₃ better oxidation catalyst for Hc than for CO, CO ₃ O ₄ better for CO than Hc |
| 2CoO/12 MnO ₂ /0.03 Pd/76 Al ₂ O ₃ | 1000 | 38500 | - | 85 | >85 | - | 343 | 5 | |
| 4 Cr ₂ O ₃ /10 CuO/0.02 Pd/86 Al ₂ O ₃ | 1000 | 38500 | - | 75 | >100 | - | 343 | 5 | |
| 4 CoO/12 MnO ₂ /0.02 Pd/4 Fe ₂ O ₃ /80 Al ₂ O ₃ | 1000 | 38500 | - | 60 | 94 | - | 180-450 | 0.5 | |
| 18 Cr ₂ O ₃ /82 Al ₂ O ₃ ^e | 1700 | 24000 | - | 83 | 93 | - | 600 | 10 | |
| Molec sieve 13X/Cu, Cr ^f | 1700 | 24000 | - | 84 | 83 | - | 600 | 10 | |

a. Girdler catalyst G-22:32 Cu/25 Cr/11 Ba.
b. Girdler catalyst G-50:10 Cu/26 Zn/31 Cr.
c. For O₂ < 2 vol %.

d. Harshaw catalyst Cu-0203, pre-reduced in CO.
e. Catalyst promoted with CsO.
f. Molecular sieve, Linde 13X, exchanged with Cu²⁺ and Cr³⁺

Table 4-4. Catalytic Removal of HC, CO, and NO_x--Stationary Engine Tests (from Ref. 4-21)

| Catalyst Composition (wt %) | Exhaust Gas Composition, Before Converter (ppm) | | | Catalytic Conversion ^a (vol %) | | | Test Conditions | | | | | Notes |
|--|---|-------------|-----------------|---|-----|-----------------|------------------------------|-----------------------|-----------------------------|--|--|--|
| | HC | CO | NO _x | HC | CO | NO _x | TEL ^b (ml/gal) | Duration ^c | Engine ^d Type | Average Catalyst Temperature (°C) | Space Velocity (hr ⁻¹) | |
| MnO _x /CuO/NiO/CrO _x ^e | - | - | 310-630 | 80 | >80 | 87-99 | present | 341 hr | 8 cyl | 425-650 | 1000-20000 | Air added for Hc and CO conversion |
| NiO(Ba)/Al ₂ O ₃ | 1400 | 29000 | 155 | 85 | 77 | 96 | 0 | 3 hr | CFR | 485 | 10000 | |
| NiO(Ba)/Al ₂ O ₃ | - | - | - | 39 | 45 | 98 | 3 | 120 hr | CFR | - | 10000 | |
| 7CuO/ 09SiO ₂ /Al ₂ O ₃ | 325 | 10000 | - | 83 | 95 | - | 3 | 100 hr | CFR | - | 9000 | FTC ^d |
| 30CuO/70SiO ₂ | - | - | 1000 | - | - | 90 | present | - | 2 cyl | 380 | 6900 | |
| 6CuO/6Cr ₂ O ₃ /Al ₂ O ₃ | 418 | - | - | 54 | - | - | present | 350 hr | 8 cyl | - | - | Odorous exhaust subsequently removed by catalytic oxidation over 1 Pd/Al ₂ O ₃ |
| CuO/Cr ₂ O ₃ ^f | 20000 | 60000 | 4000 | 88 | 95 | - | present | - | 8 cyl | 285 | 3100 | O ₂ (7.3 vol %) added to exhaust |
| 10CuO/4Cr ₂ O ₃ / 02Pd/ Al ₂ O ₃ | - | - | - | 52 | 56 | - | present | 12000 mi | 8 cyl | - | - | FTC ^d |
| 62CuO/5Co ₂ O ₃ /33Al ₂ O ₃ | 2000 | 60000 | 1500 | - | - | 90 | ~1.6 | 238 hr | 8 cyl | 480 | 12000 | High thermal stability, high attrition resistance |
| 8CuO/4Co ₂ O ₃ /1V ₂ O ₅ / Al ₂ O ₃ | 325 | 40000 | - | 54 | 72 | - | 12 | 50 hr | CFR | - | 9000 | FTC ^d |
| 20CuO/0.1Ag ₂ O/Al ₂ O ₃ | 1400 | 3000 | - | >80 | >50 | - | - | - | - | - | - | |
| 6CuO/0.1Pd/6SiO ₂ /Al ₂ O ₃ | 140 | 1750 | - | 76 | 58 | - | 3 | - | CFR | 510 | - | Air added to exhaust |
| 25-15CuO/ 05- 3Pd/ SiO ₂ /Al ₂ O ₃ | - | - | - | 69 | 90 | - | 12 | 60 hr | CFR | - | - | 0.12% S in fuel, multilayer catalyst |
| 5-10V ₂ O ₅ /Al ₂ O ₃ | 2900 | - | - | 72 | - | - | 0 | - | 1 cyl | - | - | In presence of 3 TEL Hc conv. = 30 vol % |
| 5V ₂ O ₅ /7CuO/5SiO ₂ /Al ₂ O ₃ | 5000-8000 | 15000-25000 | - | 90 | 100 | - | 2.5 | 40 hr | 1 cyl | 440 | 13200 | Air added to exhaust |
| V ₂ O ₅ /CuO/Cr ₂ O ₃ /Al ₂ O ₃ | 418 | - | - | 75 | - | - | 2.2 | 11000 mi | 8 cyl | - | - | FTC ^d , odorous exhaust |
| 50Co ₃ O ₄ /GaAl ₂ O ₄ | 50-12000 | 10000-60000 | - | 77 | 63 | - | present | 600 hr | 1 cyl | - | - | |
| 4-15MnO _x (2-5Ti)/Al ₂ O ₃ | 375 | 40000 | - | 62 | 68 | - | 12 | 75 hr | CFR | - | 10000 | |
| 4U ₃ O ₈ /Al ₂ O ₃ | 4650 | - | - | 70 | - | - | 3 | - | 8 cyl | - | - | Air added to exhaust |
| MoO _x /Al ₂ O ₃ | 2800 | - | - | 71 | - | - | 2 | - | - | - | - | |
| 1Pd/1Pt/Al ₂ O ₃ | - | - | - | 83 | 76 | - | 2.7 | 188 hr | 1 cyl | - | - | FTC ^d , air added to exhaust |
| 0.19Pt(Ba)/Al ₂ O ₃ | - | - | - | 69 | 81 | - | 3 | 40 hr | 8 cyl | 435 | - | FTC ^d , air added to exhaust |
| 0.1Pt/Al ₂ O ₃ | - | - | - | 92 | 81 | - | 3 | - | - | - | - | FTC ^d , nonuniform distribution of Pt |
| 0.375Pt/0.5F/0.25Cl/ Al ₂ O ₃ | - | - | - | 61 | - | - | present | 12000 mi | 8 cyl | - | - | FTC ^d |
| 0.1Pt/0.5F/Al ₂ O ₃ | - | - | - | 93 | 80 | - | 4.8 | - | 8 cyl | - | - | |
| 0.4Pt/Al ₂ O ₃ | - | - | - | 55 | - | - | 3 | 40 hr | - | - | - | |
| 3.2Pd/Al ₂ O ₃ | - | - | - | 70 | 95 | - | 0.2 | 10000 mi | 8 cyl | - | - | Glass-fiber thread and fiber support, air added to exhaust |

a. At end of test period

d CFR Committee on Fuel Research engine, FTC Federal test cycle

b TEL tetraethyl lead

e Mn/Cu/Ni/Cr 4/1/1/6 (mole ratio)

c Hr hours, mi road miles

f Girdler catalyst G-13

Table 4-5. Catalytic Removal of HC, CO, and NO_x--Road Tests (from Ref. 4-21)

| Catalyst Composition (wt %) | Exhaust Gas Composition, Before Converter (ppm) | | | Catalytic Conversion ^a (vol %) | | | Test Conditions | | | | Notes |
|---|---|-------------|-----------------|---|-----|------------------|-----------------|---------------------|----------------|---------------------------------|--|
| | HC | CO | NO _x | HC | CO | NO _x | TEL (ml/gal) | Duration (miles) | Engine Type | Catalyst Temperature (°C) | |
| Cr ₂ O ₃ /MnO _y /NiO/CuO/Al ₂ O ₃ ^b | - | - | - | >80 | >80 | >80 ^c | present | 15800 | 8 cyl | >250 | Conversion at 50 mph, air injected into exhaust |
| | | | | 60 | 90 | - | present | - | 8 cyl | >250 | Conversion at idling speed, air injected into exhaust |
| 5CuO/0.5 CeO/Al ₂ O ₃ (e) | - | - | - | >80 | >90 | - | present | 5000 | 6 cyl | >250 | |
| 5CuO/1Pd/Al ₂ O ₃ | - | - | - | 53 | 76 | - | 3 | 10000 | 8 cyl | 200-900 | 0.07 wt % S in fuel |
| 10CuO/4Cr ₂ O ₃ /0.02 Pd/Al ₂ O ₃ (v) | 695 | 14400 | - | 66 | 57 | - | 2.9 | 15000 | 8 cyl | 180-460 | 0.04 wt % S in fuel |
| 15CuO/15Cr ₂ O ₃ /Al ₂ O ₃ | 303 | 11000 | - | 27 | 0 | - | 2.3 | 12000 | 8 cyl | 550 | FTC ^d , catalyst on steel-wool substrate |
| 9.5 K ₂ CrO ₄ /7.3 V ₂ O ₅ /Al ₂ O ₃ | 264 | 10700 | - | 17 | 32 | - | 2.3 | 12000 | 8 cyl | 550 | Odorous exhaust, FTC ^d , catalyst on steel-wool substrate |
| K ₂ CrO ₄ /Al ₂ O ₃ , V ₂ O ₅ /Al ₂ O ₃ | 264 | - | - | 17 | - | - | present | 12000 | 8 cyl | 510 | FTC ^d , two-stage catalyst, first stage for Pb-removal |
| 7.6 CuO/5.3 FeO _x /Al ₂ O ₃ | - | - | - | 55 | 76 | - | 3 | 11300 | 8 cyl | - | Air injected into exhaust gas, conversion at 60 mph, 0.07% S in fuel |
| 4.2ZnO ₃ /1.7 Cr ₂ O ₃ /1.7 CuO/Al ₂ O ₃ | 6900-7300 | 40000-50000 | - | 75 | 75 | - | 1.9 | 1250 | 6 cyl | ~710 | Engine at idling speed |
| 0.5 Pt/10 Al ₂ O ₃ /zirconmullite | 290 | 70000 | - | 75 | 100 | - | present | 1000 | 8 cyl | 510 | Air injected into exhaust, conversion measured at 30 mph using propane (after 1000 mi on leaded fuel) |
| Fe ₂ O ₃ /0.06 Pt/0.2 CuO/0.3 MgO/0.2 K ₂ O/0.2 Na ₂ O/27 SiO ₂ /71 Al ₂ O ₃ | 1650 | 6000 | 29 | 84 | 100 | 50 | - | 2400 | - | 250-900 | 2-stroke engine, catalyst stable to 1200°C |
| 4.7 V ₂ O ₅ /3.7 CuO/0.10-0.15 Pd/5 SiO ₂ /Al ₂ O ₃ | 289 | 1240 | - | 37 | 40 | - | 0.5 | 18000 | 8 cyl | - | FTC ^d , air injected into exhaust gas, catalyst activity sensitive to Pb-content of exhaust |

^a At end of test period
^b Cr/Mn/Cu/Ni = 6.2/4.1/1 (mole ratio), compare test for details.
^c Data from stationary tests after 341 hours of engine operation, catalyst temperature 515°C, conversion in absence of added air
^d FTC - federal test cycle.

4.2.3.2.2 NO_x and Dual-Bed Catalysts

Efforts to develop a catalyst which will decompose NO in the presence of excess oxygen have been singularly unsuccessful because the reaction rates are too slow (Ref. 4-26). It has been found that a number of catalysts will promote the reduction of NO by the CO and H₂ present in an oxygen-deficient (reducing) atmosphere. This is accomplished by operating the engine at a rich air-fuel mixture. Under these conditions and in the presence of a suitable catalyst, NO is converted resulting in nitrogen (N₂), CO₂ and H₂O. Some of the catalysts used for the oxidation of HC and CO can also reduce NO, if operated in the reducing conditions required for a NO_x catalyst. In addition, bulk metals such as Monel, copper, or stainless steel have been used (Ref. 4-24). Since the NO_x catalyst requires a reducing atmosphere whereas the HC/CO catalyst requires an oxidizing atmosphere, if used together they must be used in series in the exhaust system so that the exhaust conditions to each can be controlled. The two can be separated by some distance or be located within the same housing, commonly called a "dual-bed" catalyst. Warmup time of HC/CO catalysts favors the latter arrangement.

One of the major problems with NO_x catalysts has been the formation of ammonia (NH₃) which in itself is an objectionable exhaust product. Most of the NH₃ generated in the NO_x catalyst is re-oxidized in the HC/CO catalyst portion of the dual-bed reactor to NO_x and H₂O, thus defeating the purpose of the NO_x catalyst. A major effort in NO_x catalyst research has been to find one which not only has good NO_x conversion efficiency but one which also produces minimum NH₃ and has satisfactory durability.

4.2.3.2.3 HC/CO/NO_x-Tricomponent Catalyst

Theoretically, it should be possible to combine the functions of NO_x reduction and HC/CO oxidation in a single catalyst. At least one company (Ref. 4-23) has tested a tricomponent catalytic converter with some success. However,

the conversion efficiency is very sensitive to the air-fuel mixture and variations as little as ± 0.1 A/F units could substantially affect performance (Ref. 4-27). Since control of the air-fuel mixture to this level has not been demonstrated, not much attention is currently being directed to this approach.

4.2.3.3 Other System Components/Factors

The catalytic converter is only one component of the emission control systems being considered to meet the 1975-76 standards. The performance and life of the catalyst are dependent on engine operating conditions and other emission control components. In turn, the performance and characteristics of the catalytic converter affect the complete system.

The HC/CO catalysts are basically oxidation catalysts and require excess air to operate efficiently. If the engine operates at a rich mixture ratio an air pump is required to provide secondary air to the HC/CO catalyst.

Most HC/CO and NO_x catalysts have operating temperature limitations of approximately 1400°F-1500°F for long-life durability. In the event of an engine malfunction, such as spark plug misfire, where large quantities of unreacted fuel can reach the catalysts, higher temperatures (>1800°F) can be readily achieved. Since most catalytic materials undergo rapid deterioration at temperatures above 1800°F, a thermal control system may be required to prevent damage to the converter.

The area of catalytic converter overtemperature protection is very important because of: (1) the potential for converter burnup and vehicle fires if not protected, and (2) the need to preserve the emission control capability of the converter as an excessive temperature excursion may destroy the catalyst. The design of such control devices has not been finalized by industry at this time. In one approach a bypass flow loop is provided around the catalytic converter. This requires a sensing element and a hot-gas

valve, perhaps remotely located relative to one another. Another approach uses a similar overtemperature sensing device to shut off the engine and thus protect the catalyst. A programmed protection system utilized by Ford in the IIEC Program (Ref. 4-28) is illustrated in Figs. 4-15 and 4-16; as can be seen this results in a complex control system.

In view of the complexity and high cost of such overtemperature control systems, efforts are in progress to develop a catalyst with sufficiently high-operating-temperature capability to eliminate the need for such a system.

The location of the catalytic converter, relative to the exhaust manifold, is also important. Because of cold start requirements, it must be close enough to the manifold exhaust to warm up quickly, but be far enough removed to prevent overheating of the catalyst.

4.2.3.4 Fuel Economy Characteristics

Fuel economy is affected to some degree by a number of parameters related to the catalytic converter and its operation, including backpressure buildup, selected engine air-fuel ratio, and power requirement of the secondary air pump. The fuel economy penalties resulting from the higher backpressure and the air pump are generally small.

The backpressure is a function of the catalyst design. Dual-bed catalyst data shown in Fig. 4-17 (Ref. 4-24) indicate a wide range of pressure drops, with one design approaching that of a standard muffler. The corresponding designs are shown in Figs. 4-18 and 4-19, with Fig. 4-19 representing the later design. The effect on backpressure of a single-bed converter installation (Fig. 4-20), compared to a standard vehicle without a converter, is shown in Fig. 4-21 (Ref. 4-22).

In the same program (Ref. 4-22), a dual-bed (parallel) installation was operated with a special carburetor providing a rich air-fuel ratio of 11.5. A fuel consumption of 11.8 mpg was observed for the 2500-mile driving schedule.

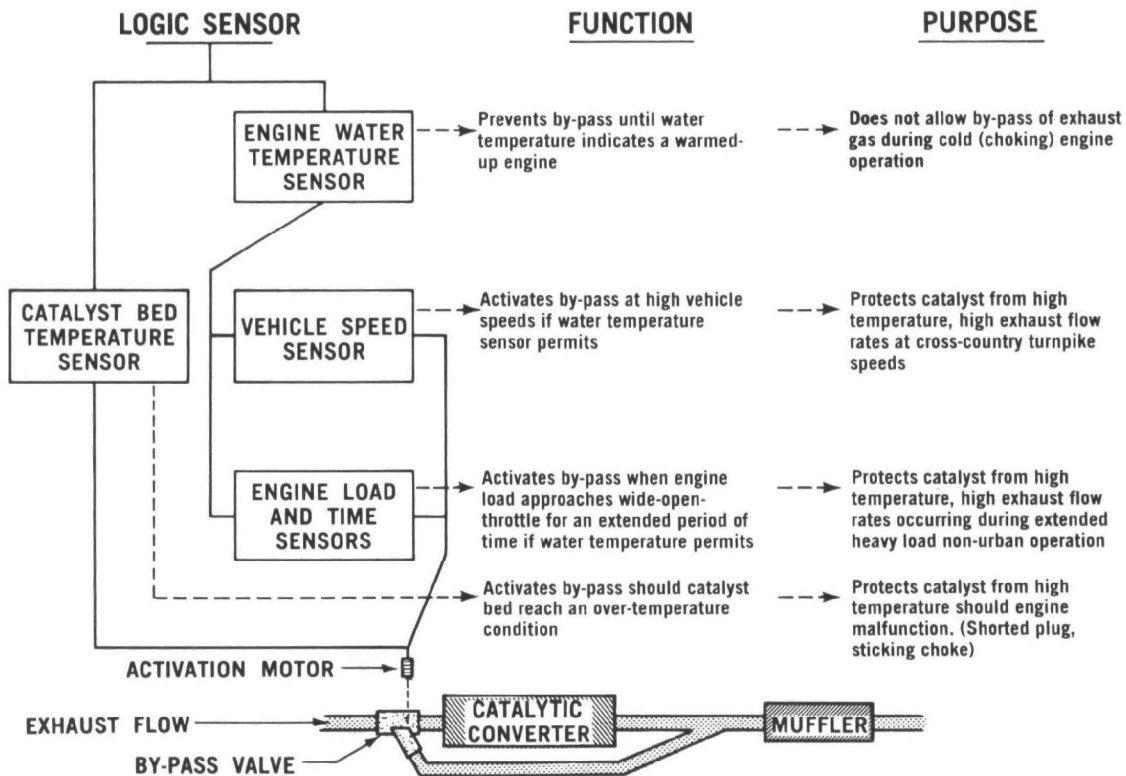


Fig. 4-15. Ford Programmed Protection System--Logic Schematic (from Ref. 4-28)

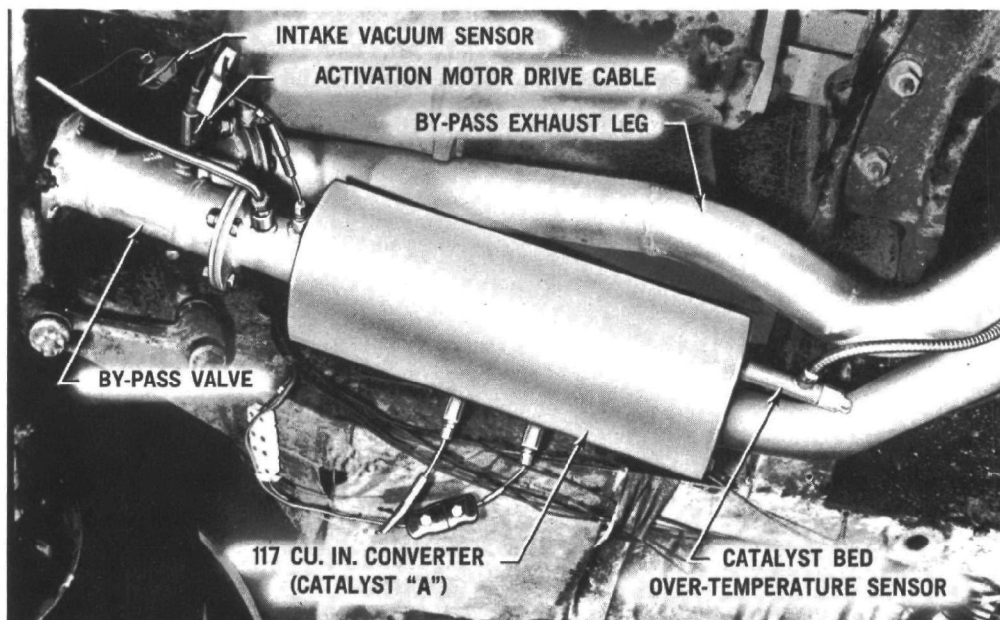


Fig. 4-16. Ford Programmed Protection System (Vehicle No. 4)--Catalyst Container and PPS Hardware (from Ref. 4-28)

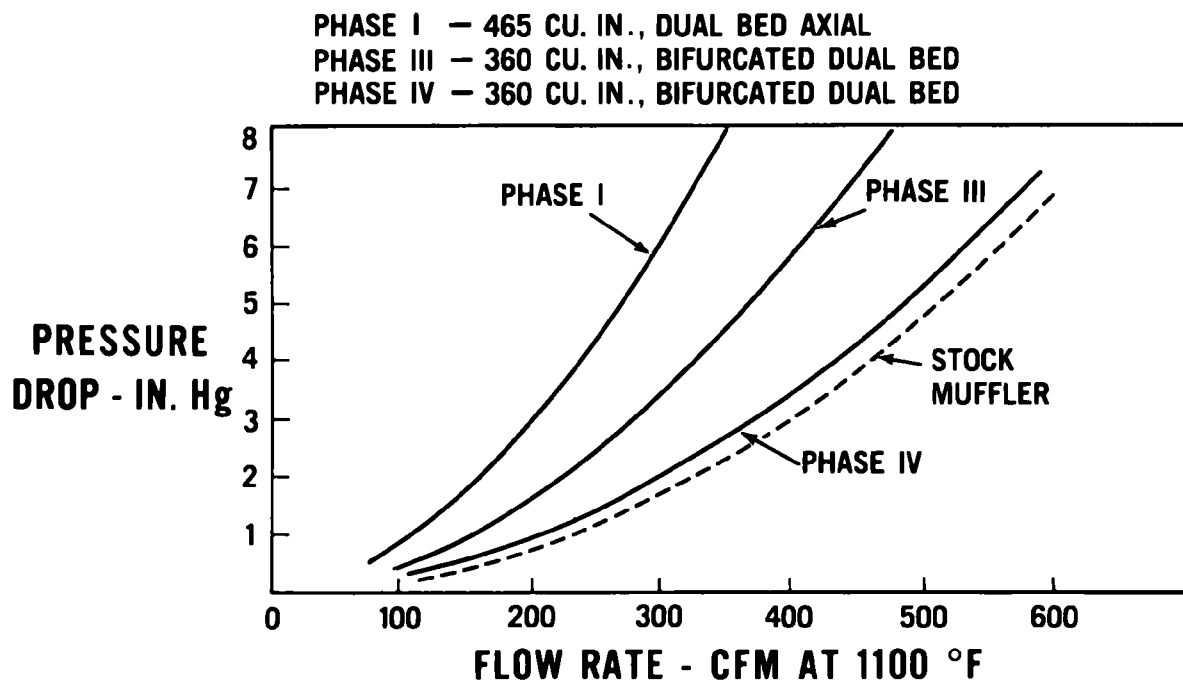


Fig. 4-17. Converter Flow Development (from Ref. 4-24)

This represents a 25.8 percent loss in fuel economy. Approximately 22 percent of that loss is the direct result of mixture enrichment.

Data from a General Motors single-bed converter system driven 69,000 miles indicate a 2.8-5.4 percent loss in fuel economy tests at various driving conditions (Table 4-6, from Ref. 4-30).

Table 4-6. Effect of Catalytic Converter System on Fuel Economy and Performance (from Ref. 4-30)

| Item | With Standard Exhaust Without Secondary Air | With Catalytic Converter System | Reduction in Performance (%) |
|-------------------------|---|---------------------------------|------------------------------|
| Economy, mpg | | | |
| City | 14.3 | 13.9 | 2.8 |
| Highway | 16.1 | 15.6 | 3.1 |
| 30, 50, 70 mph | 22.4, 19.6, 16.0 | 21.2, 19.0, 15.4 | 5.4, 3.0, 3.7 |
| Performance, sec | | | |
| 0-60 mph | 15.4 | 15.9 | 3.2 |
| 0-1/4 mile | 20.5 | 20.7 | 1.0 |

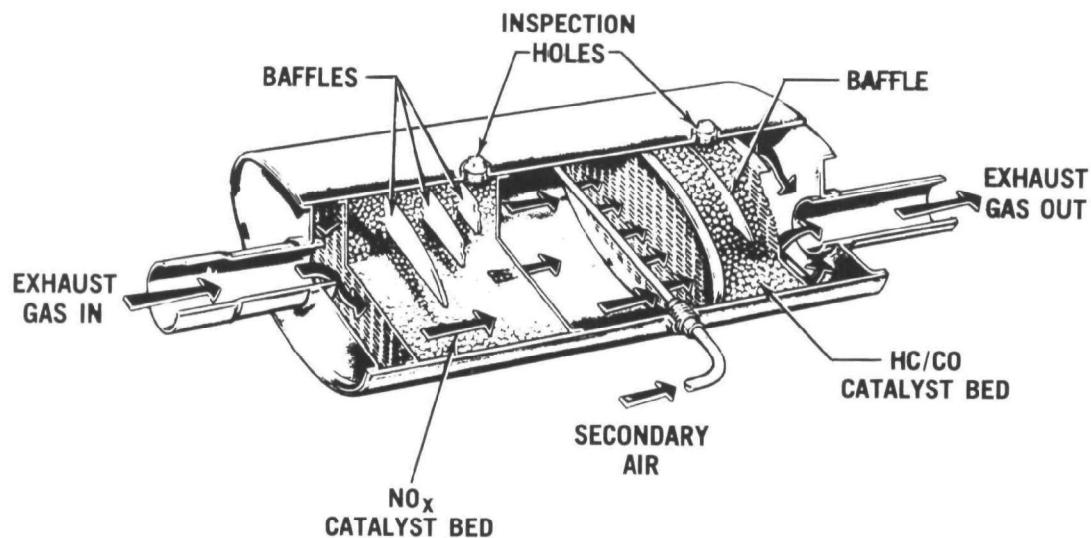


Fig. 4-18. Dual-Bed Axial-Flow Converter (from Ref. 4-24)

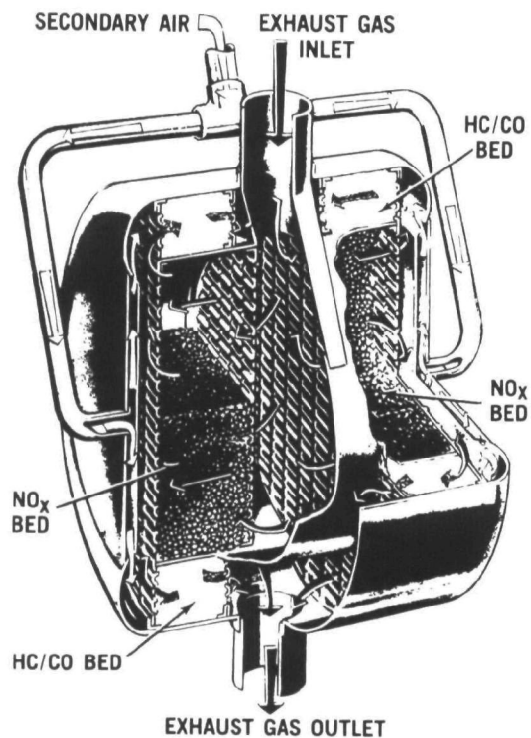


Fig. 4-19. Bifurcated Dual-Bed Catalytic Converter (from Ref. 4-24)

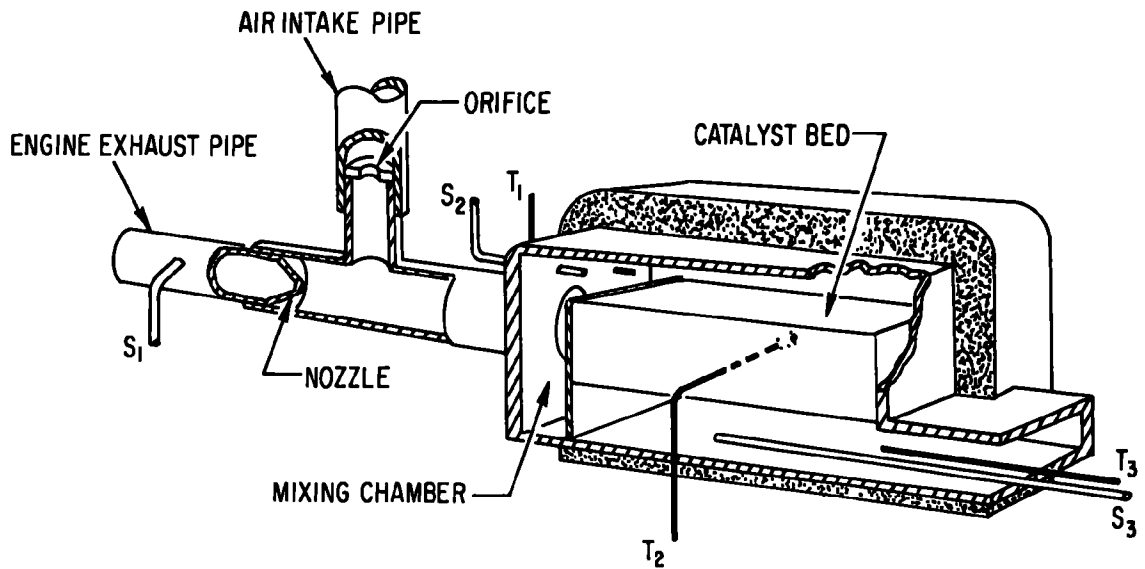


Fig. 4-20. Cutaway Sketch of Oxy-Catalyst Converter (from Ref. 4-22)

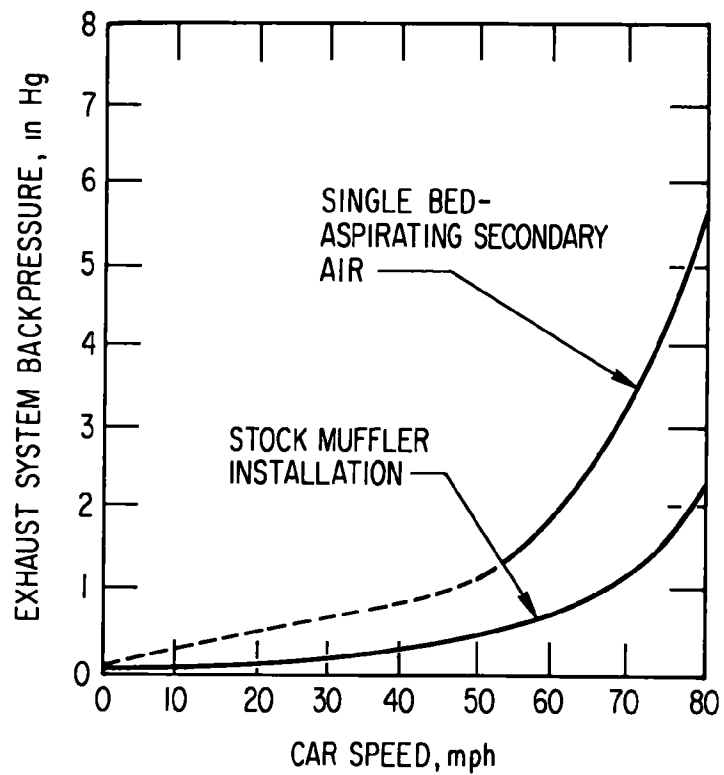


Fig. 4-21. Exhaust System Backpressures-- Road Load Conditions (from Ref. 4-22)

Based on the available information, an estimated 2-4 percent reduction in fuel economy may be attributed specifically to the catalyst bed installation and the presence of the secondary air pump.

4.3 SPECIFIC EMISSION CONTROL SYSTEMS

Various combinations of the foregoing emission control devices have been and are undergoing extensive evaluation by the automakers and other organizations to explore every possible avenue for meeting the 1975-76 emission standards. The four U.S. automobile manufacturers stated to the EPA Administrator in April 1971 (Refs. 4-6, 4-31, 4-32, and 4-33) that at that time they could not meet the standards based on the progress to date, variabilities in production tolerances, etc. Although a great deal of effort has been expended since that time, the automakers still have not demonstrated meeting the emission standards, including the 50,000-mile durability capability.

It is not the purpose of this report to judge the expertise of the auto industry, but rather to review the existing emission control system technology base, and make an assessment as to which general approaches appear promising to meet the 1975-76 standards. To this end, and to provide some order for the numerous control device combinations possible, the emission control systems are discussed in the following generic classes:

1. Catalytic Converter Systems -- those systems primarily based on some form of catalytic converter and not including special warmup devices
2. Thermal Reactor Systems -- those systems primarily based on some form of thermal reactor
3. Combination Systems -- those systems primarily based on some form of thermal reactor in combination with some form of catalytic converter

4.3.1 Catalytic Converter Systems

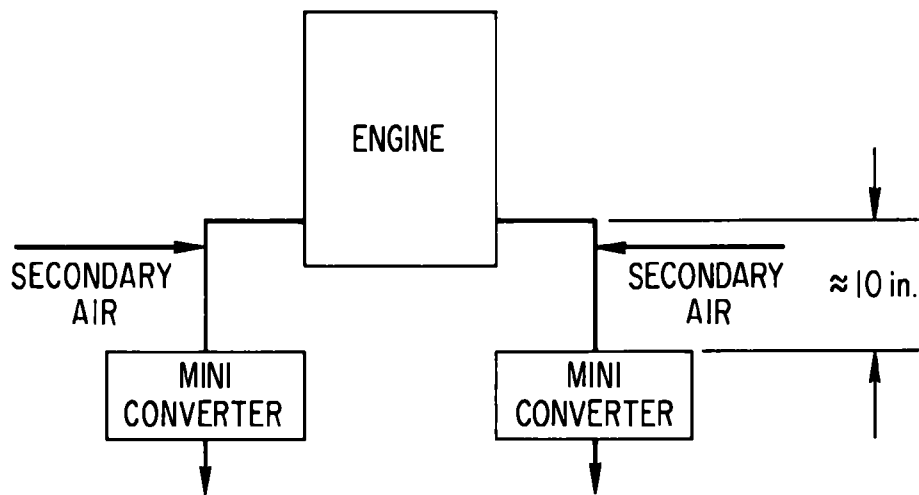
There are four distinctive subclasses of catalytic converter systems:

1. HC/CO Catalytic Converter Alone (no EGR)
2. HC/CO Catalytic Converter plus EGR
3. Dual Catalytic Converter plus EGR
4. Tricomponent Catalytic Converter (no EGR)

4.3.1.1 HC/CO Catalytic Converter Alone (no EGR)

This emission control system concept is characterized by the addition of HC/CO catalytic converter units and secondary air injection (air pumps) to conventional engine systems (no EGR). The available data pertaining to this approach are those provided by Universal Oil Products (UOP) and by Engelhard Industries. The primary goal of these catalyst manufacturers is to develop catalysts for supply to the automakers and, consequently, the bulk of their effort is directed to characterizing catalyst materials with regard to effectiveness and durability and not to developing emission control systems, per se. In their characterization activities, then, the catalyst suppliers have necessarily investigated catalysts with varying amounts of active catalyst material. It is not known whether the emission levels given below correspond to catalysts under serious consideration for use by the automakers, in terms of the amount of active material used in the catalyst and its necessarily attendant cost implications.

In Reference 4-23, UOP described the installation of their "mini-converters" on a domestic V-8 engine (Fig. 4-22). It was stressed that this was a stock vehicle purchased from a local dealer and that carburetion, ignition timing, valve timing, etc., were as delivered from the factory. Typical emission results (from Ref. 4-23) are shown in Tables 4-7, 4-8, and 4-9. Table 4-7 shows CVS test values for a large domestic engine with a normal choke, Table 4-8 shows the same type of results with a faster choke, and Table 4-9 shows results from smaller foreign vehicles. Although CO values are most attractive, HC and NO_x values exceed 1975-76 standards.



MODIFICATIONS TO VEHICLE

- 1 ADDITION OF TWO AIR PUMPS
- 2 ADDITION OF TWO MINI CONVERTERS
- 3 SECONDARY AIR DELAY (10 sec)
- 4 NO CHANGE TO CARBURETION, IGNITION TIMING, etc.

Fig. 4-22. Universal Oil Products Mini-Converter Installation (from Ref. 4-23)

Engelhard (Ref. 4-57) quotes emission levels for their PTX-433 catalytic converter unit (0.2 percent Pt) to be (at the end of 50,000 miles of the AMA driving schedule):

$$\left. \begin{array}{l} \text{HC} = 0.70 \\ \text{CO} = 3.8 \\ \text{NO}_x = 5.0 \end{array} \right\} \text{ gm/mi (single-bag CVS cold start test)}$$

Initial emission values have not been reported by Engelhard.

There are, as yet, no reported data pertaining to fuel economy. Engelhard has reported a 50,000-mile durability test for their PTX catalyst. The test was conducted with an unleaded gasoline having a lead content of approximately 0.03 gm/gal. The catalyst picked up substantial quantities of Pb, Zn, P, and Ba during the test. The Zn and Ba are contaminants Engelhard associates

Table 4-7. 1971 Domestic Engine (350 CID)--Normal Choke,
PZ-195 Catalyst (from Ref. 4-23)

| Converter | CVS-1 Cold Start | | | CVS-1 Hot | | | Comments |
|--------------------------|------------------|-------|---------------------|-----------|------|---------------------|---|
| | HC | CO | NO _x | HC | CO | NO _x | |
| IN Normal Choke | 2.89 | 17.35 | (3.29) NO Only | - | - | - | Average of 2 runs |
| Type 1 | 0.62 | 1.45 | 3.88 | 0.195 | 0.48 | 3.22 | Full air L/R = 1.39/1.33 |
| Type 2 | 0.68 | 1.20 | - | 0.21 | 0.20 | - | Full air |
| Type 2 (2) Type 1 (1) | - | - | - | 0.26 | 1.16 | 1.75 | Full air (both pumps) to 3rd reactor only No air to 5.75 reactors |
| Type 2 (2) Type 1 (1) | 0.59 | 0.96 | (1.80) Est. 2.11 | 0.25 | 1.10 | (1.56) Est. 1.83 | Air to reactors #1 and #2 for 1st 100 sec of cold start Air to reactor #3 only after 100 sec |

Table 4-8. 1971 Domestic Engine (350-CID)--Fast Choke
(from Ref. 4-23)

| Converter | CVS-Cold Start | | | CVS-1 Hot | | | Comments |
|---------------|----------------|------|-------------------|-----------|------|-----------------|---------------------------------|
| | HC | CO | NO _x | HC | CO | NO _x | |
| Type 1 PZ-195 | 0.16 | 1.33 | (2.82) NO Only | 0.035 | 0.25 | - | Fresh catalyst |
| Type 1 PZ-195 | 0.42 | 1.21 | - | 0.18 | 0.28 | - | Aged 16,500 miles |
| Type 3 PZ-195 | 0.51 | 1.94 | 4.74 | 0.14 | 0.28 | - | Fresh catalyst |
| UOP #2303-41 | 0.66 | 3.02 | - | 0.16 | 0.45 | - | Fresh catalyst |
| PTX-5 | 1.15 | 5.77 | - | 0.145 | 0.50 | - | Fresh catalyst |
| PTX-5 | 1.13 | 4.32 | 5.32 | 0.26 | 0.72 | 5.39 | Fresh catalyst |
| Type 1 PZ-195 | 0.25 | 2.58 | 5.08 | - | - | - | Normal choke, 6 cold starts run |

| Vehicle | CVS-1 Cold Start | | | CVS-1 Hot | | |
|---------|------------------|------|-----------------|-----------|------|-----------------|
| | HC | CO | NO _x | HC | CO | NO _x |
| Car A | 1.41 | 3.01 | - | 0.57 | 4.47 | 1.34 |
| Car B | 0.29 | 0.99 | 1.36 | 0.05 | 0.36 | - |
| Car C | 0.40 | 1.20 | - | - | - | - |
| Car C | 0.57 | 2.65 | 1.86 | - | - | - |
| Car C | 0.46 | 3.86 | 1.77 | - | - | - |
| Car D | 0.47 | 1.22 | 1.73 | 0.35 | 0.36 | 1.66 |
| Car D | 0.74 | 1.58 | 2.00 | 0.45 | 0.37 | 1.71 |

Table 4-9. Federal Test Results
for Some Foreign
Vehicles (from
Ref. 4-23)

with motor oil. Engelhard's present position is that the most probable reasons for PTX catalyst deterioration are metal poisons that may be present in the fuel and lubricating oils.

4.3.1.2 HC/CO Catalytic Converter plus EGR

This emission control system concept is illustrated by the Ford Package "B" system (Ref. 4-29). Its major components, shown in Fig. 4-23, include:

1. Dual bifurcated axial-flow converters
2. Single rear bifurcated axial-flow converter
3. Programmed protection system to divert exhaust gas around the first catalyst bed when its temperature exceeds 1350°F
4. Spherical transition metal "pre-attrited" catalyst pellets
5. Secondary air injection just below the exhaust flange
6. Modified distributor with warmup spark retard and reduced part-throttle advance
7. Spacer-entry EGR

Front and rear converters were used in this concept approach because it was felt that it may not be possible to accomplish successful development of transition metal catalysts capable of withstanding temperature excursions above 1400°F. This configurational approach is dependent upon the ability of the normal engine exhaust system to provide adequate rapid warmup of the catalytic converters; hence, the placement of the forward converters is close to the exhaust flange.

4.3.1.2.1 Emission Level Characteristics

Typical emission levels for the Ford Package "B" concept are (Ref. 4-29):

$$\left. \begin{array}{lcl} \text{HC} & = & 0.8 \\ \text{CO} & = & 11.0 \\ \text{NO}_x & = & 1.3 \end{array} \right\} \text{ gm/mi (single-bag CVS cold start test)}$$

Chrysler (Ref. 4-6) reports emission levels of:

$$\left. \begin{array}{l} \text{HC} = 0.24 \\ \text{CO} = 7.2 \\ \text{NO}_x = 2.03 \end{array} \right\} \text{ gm/mi (single-bag CVS cold start test)}$$

for a similar type HC/CO catalytic converter plus EGR system.

4.3.1.2.2 Fuel Economy Results

A fuel economy penalty of 8 percent on the chassis dynamometer is reported for the foregoing Ford Package "B" emission levels.

4.3.1.2.3 System Lifetime Characteristics

No durability or lifetime test data are reported for this concept.

4.3.1.2.4 Effect of Lead Additives

Concept development of the Ford Package "B" system is being made with unleaded fuel. See Section 5 for a discussion of leaded-fuel effects.

4.3.1.3 Dual Catalytic Converter plus EGR

This emission control system concept is illustrated by the Ford Package "C" system (Ref. 4-29). Its major components and operating features, shown in Fig. 4-24, include:

1. IIEC "bifurcated dual-bed" converter (210 in.³ NO_x bed; 150 in.³ HC/CO bed) (see Fig. 4-19)
2. Engine-driven secondary air pump
3. Integral, below-the-throttle EGR system
4. Programmed catalyst protection system
5. Carburetor enriched 5 percent
6. MBT ignition timing with retard during warmup

This system is being explored by Ford in the IIEC Program because it theoretically has the potential for minimal loss in fuel economy as compared with RTR plus EGR and HC/CO catalytic converter plus EGR systems. The minimal dependence on EGR (for NO_x reduction) also allows improvements in vehicle driveability.

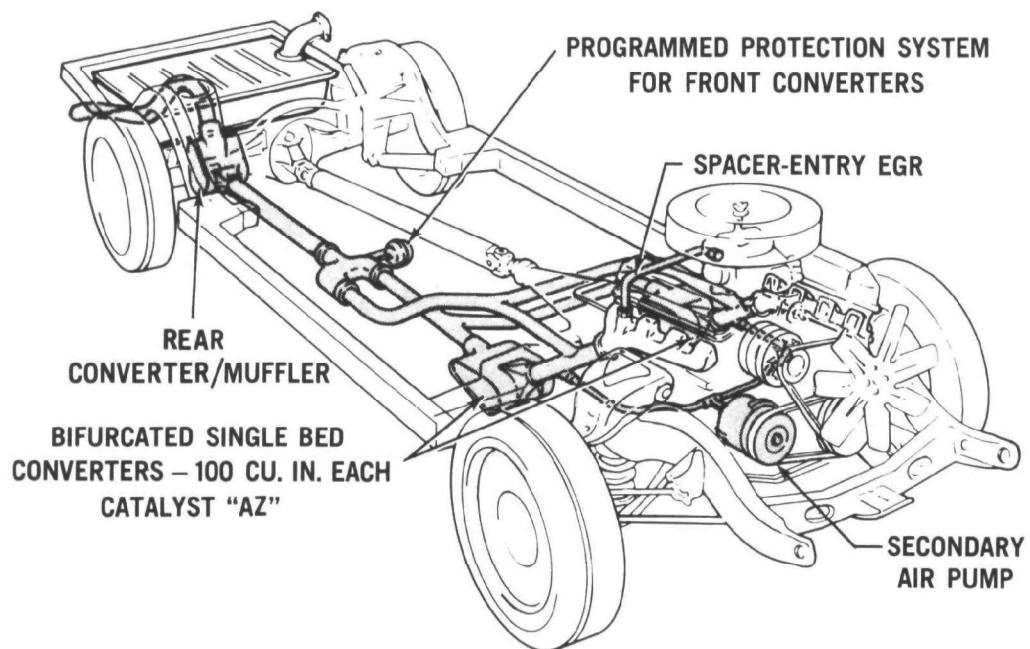


Fig. 4-23. Ford Concept Emission Package "B" (from Ref. 4-29)

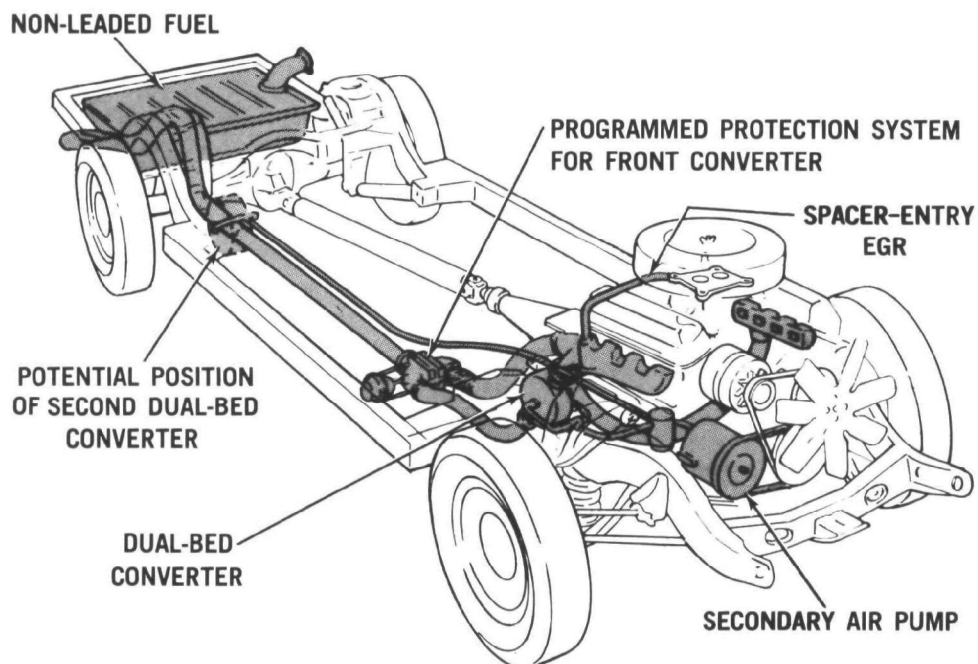


Fig. 4-24. Ford Concept Emission Package "C" (from Ref. 4-29)

Unleaded fuel was established as an absolute necessity with this package because of the observed rapid depreciation in NO_x reduction efficiency of NO_x catalysts operating on leaded fuels (Ref. 4-29). See Section 5 for a discussion of leaded-fuel effects.

4.3.1.3.1 Emission Level Characteristics

Typical emission levels for the Package "C" concept are (Ref. 4-29):

$$\left. \begin{array}{lcl} \text{HC} & = & 0.85 \\ \text{CO} & = & 10.00 \\ \text{NO}_x & = & 0.90 \end{array} \right\} \text{ gm/mi (single-bag CVS-1 cold start tests)}$$

4.3.1.3.2 Fuel Economy Results

A fuel economy penalty of 5 percent was reported for Package "C" (Ref. 4-29) on the CVS-1 test cycle.

4.3.1.3.3 System Lifetime Characteristics

Durability testing and continued development of the major components in this package are reported to be under way by Ford (Ref. 4-29). No data in this regard are reported at this time.

4.3.1.4 Tricomponent Catalytic Converter (no EGR)

In principle, this concept has a three-way catalyst bed for simultaneous reduction of HC, CO, and NO_x and is theoretically extremely attractive. The principal proponent of this approach has been UOP (Ref. 4-23).

UOP provided a 1970 Volkswagen equipped with its catalytic converter to APCO for test evaluation. This vehicle was equipped with a 98 CID engine and automatic transmission. The stock fuel injection was modified to prevent cutoff of fuel during deceleration and the catalytic unit was installed in place of the standard muffler. Results of the tests are shown in Table 4-10 (Ref. 4-34).

Further investigations by UOP determined that optimum nitric oxide conversion is obtained (about 90 percent) within a narrow range of air-fuel ratio on

Table 4-10. Emission Test Results--1970 Volkswagen
with UOP Catalytic Converter (1972
Federal Test Procedure)(from Ref. 4-34)

| Emissions | Emission Levels (gm/mi) | |
|--------------------|-------------------------|--------|
| | Test 1 | Test 2 |
| HC | 2.3 | 1.4 |
| CO | 32 | 10 |
| CO ₂ | 444 | 431 |
| NO _x * | 1.3 | 1.1 |
| NO _x ** | 0.6 | 0.8 |

*NO_x box results reported as NO₂
 **Saltzman results reported as NO₂

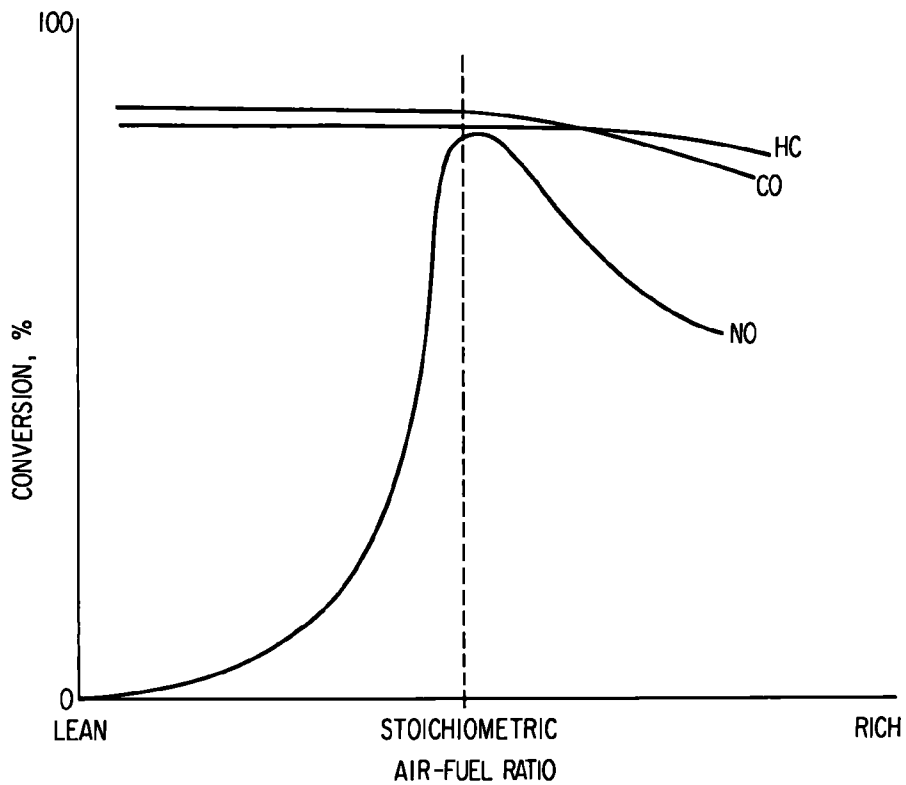


Fig. 4-25. Tricomponent Conversion vs Air-Fuel Ratio
(from Ref. 4-23)

the slightly rich side of stoichiometry, as shown in Fig. 4-25. Fig. 4-25 also shows that conversion of HC, CO, and NO can be attained simultaneously.

Chrysler (Ref. 4-6) recently supplied the following tricomponent catalytic converter data to the EPA Administrator:

| <u>Emission</u> | <u>Emission Levels (gm/mi)</u> | |
|-----------------|--------------------------------|-----------------------|
| | <u>Cold Start 7-Mode</u> | <u>Hot 7-Mode</u> |
| HC | 0.68 | 0.27 |
| CO | 11.50 | 1.50 |
| NO _x | 0.71 | 0.33 |

Chrysler states (Ref. 4-6) that there is not, as yet, an effective three-way catalyst.

American Motors (Ref. 4-35) has tested a prototype three-control catalyst supplied by a catalyst manufacturer and has also provided that same manufacturer with a vehicle for development of a three-component system. These programs did not produce a catalyst with the ability to meet three-component control to the degree necessary for 1975-76. American Motors said that the variability of air-fuel ratio needed for safe, efficient vehicle operation proved to be too large for the catalyst to handle. The proper balance between the "reducing" and the "oxidizing" ability of the engine's exhaust could not be maintained during normal vehicle usage.

No durability or fuel consumption data are available for this conceptual approach. The effects of lead additives are addressed in Section 5.

4.3.2 Thermal Reactor Systems

There are three meaningful subclasses of thermal reactor systems:

1. LTR plus EGR
2. RTR Alone
3. RTR plus EGR

(The LTR Alone system is not considered to be a viable system because of its lack of adequate NO_x control.)

4.3.2.1 LTR plus EGR Concept

This emission control system concept is exemplified by the Ethyl lean reactor design. It consists of a full-size LTR for HC and CO control, an EGR system for NO_x control, and advanced carburetion for engine operation at the selected lean air-fuel ratio (approximately 17.5) provided by a specially developed, high-velocity carburetor. Spark advance characteristics are tailored to provide the best compromise among fuel economy, driveability, and low emissions.

Ethyl has actively pursued and demonstrated this approach with vehicle tests. Its work has been aimed at the development of an emission control system that is not sensitive to fuel additives. Thus all test work reported has been done with fuel containing approximately 3 ml/gal of tetraethyl lead (TEL). In using this fuel, the Ethyl lean reactor system avoids fuel economy penalties brought about by lowering compression ratio to accommodate low-octane fuels. Ethyl states that the retention of a high-compression ratio also makes it possible to operate with good driveability at leaner mixtures than otherwise would be the case, and minimizes problems of EGR with respect to vehicle driveability effects.

4.3.2.1.1 Emission Level Characteristics

The most advanced versions of the Ethyl lean reactor system are now embodied in several Pontiacs and one 1971 Plymouth (Ref. 4-5). Emissions of two of these cars, based on the single-bag CVS test procedures in use prior to July 1971, are shown in Tables 4-11 and 4-12. Similar data obtained with the new (post-July 1971) three-bag CVS test procedure for the 1971 Plymouth are compared with the single-bag data in Table 4-12. As can be seen, HC emissions are 127 percent and CO emissions are 182 percent of the corresponding 1975-76 standards. NO_x emissions are 342 percent of the 1976 standard, but are well below the 1975 standard (3 gm/mi).

Table 4-11. Ethyl Lean Reactor--Emission Data
for 1970 Pontiac (Vehicle 766)
(from Ref. 4-5)

| <u>Vehicle Description</u> | <u>Modifications</u> | | |
|---|---|--|--|
| 1970 Pontiac LeMans 400 CID Engine Automatic Transmission Power Steering Power Brakes | 3-Venturi Carburetor EGR System Exhaust Manifold Reactor Exhaust Port Liners Evaporative Loss Controls Exhaust Cooler Units Particulate Trapping Device Air-Injection Pump (Operates During Choking Period) Transmission Modifications (Modulator and Governor) | | |

| <u>1972 CVS Procedure</u> | | | |
|---------------------------|-----------------------|-----------------------|-----------------------------------|
| <u>Run Date</u> | <u>HC (gm/mi)</u> | <u>CO (gm/mi)</u> | <u>NO_x (gm/mi)</u> |
| 4-5-71 | 0.74 | 7.3 | 1.40 |
| 4-6-71 | 0.75 | 7.0 | 1.60 |
| 4-19-71 | 0.74 | 5.3 | 1.70 |
| 4-20-71 | 0.78 | 6.2 | 1.70 |
| 4-21-71 | 0.84 | 6.2 | 1.48 |
| 4-22-71 | 0.82 | 5.9 | 1.45 |
| 6-3-71 | 0.88 | 6.5 | 1.45 |
| 6-24-71 | 0.73 | 6.8 | 1.40 |
| Avg. | 0.79 | 6.4 | 1.52 |
| 12-18-70 | 0.64 | 9.1 | 1.09 |

| <u>1970 7-Mode Procedure</u> | | | |
|------------------------------|---------------------|-------------------|---------------------|
| <u>Run Date</u> | <u>HC (ppm)</u> | <u>CO (%)</u> | <u>NO (ppm)</u> |
| 4-8-71 | 19 | 0.21 | 226 |
| 4-13-71 | 20 | 0.20 | 200 |
| 4-14-71 | 23 | 0.21 | 197 |
| Avg. | 20.7 | 0.21 | 208 |
| Equivalent gm/mi | 0.26 | 5.0 | 0.81 |

Table 4-12. Ethyl Lean Reactor--Emission Data for
1971 Plymouth (Vehicle 18M-448)
(from Ref. 4-5)

| <u>Vehicle Description</u> | <u>Modifications</u> | | |
|--|--|--|--|
| 1971 Plymouth Fury III 360 CID Engine Automatic Transmission Power Steering Power Brakes Air Conditioning | 3-Venturi Carburetor EGR System Exhaust Manifold Reactor Exhaust Port Liners Evaporative Loss Controls Exhaust Cooler Units | | |

| <u>1972 CVS Procedure (Single-bag tests)</u> | | | |
|--|---------------------|---------------------|---------------------------------|
| <u>Run Date</u> | <u>HC gm/mi</u> | <u>CO gm/mi</u> | <u>NO_x gm/mi</u> |
| 2-26-71 | 1.00 | 8.0 | 1.6 |
| 3-2-71 | 0.74 | 7.3 | 1.7 |
| 3-8-71 | 0.92 | 7.6 | 0.86 |
| 3-24-71 | 0.82 | 10.0 | 1.5 |
| 4-8-71 | 1.00 | 10.0 | 1.23 |
| Avg. | 0.89 | 8.6 | 1.37 |

| <u>1975 CVS Procedure (Three-bag tests)</u> | | |
|---|------|------|
| | 0.52 | 1.37 |

Chrysler (Ref. 4-6) reported similar test results (HC = 0.7, CO = 7.0, NO_x = 1.3) for an LTR plus EGR vehicle using the single-bag CVS test procedures.

With regard to the single-bag CVS test data, Ethyl states that the first 505 seconds of the 1371-second test (36.8 percent of the time) contribute about 78 percent of the HC, 68 percent of the CO, and 48 percent of the NO_x measured in the entire test. Thus, the strong influence of the cold start on HC and CO emissions is evident for this system.

Further improvements which could reduce HC and CO emissions include:

1. Use of a moderate amount of air injection only during the first few minutes of warmup operation to increase exhaust oxidation during the choking period
2. Improvements in heat conservation in the exhaust ports and exhaust port liners (perhaps by addition of flameholders), and improvement in the exhaust reactor design to increase exhaust oxidation
3. Improvements in the intake manifold to promote quicker warmup and the need for less choking during the warmup period
4. Alterations in transmission characteristics to accelerate warmup
5. Use of higher compression ratio to permit still leaner mixtures and better utilization of EGR, and to produce lower exhaust gas volumes with consequent reduction in mass emissions
6. Charcoal absorber traps to reduce HC exhausted during engine startup

The foregoing are logical technical approaches, but until they are incorporated and demonstrated the LTR plus EGR emission control system concept is considered deficient with regard to meeting the 1975-76 HC and CO standards and the 1976 NO_x standard.

4.3.2.1.2 Fuel Economy Effects

Ethyl has reported fuel economy test results for the aforementioned Plymouth and Pontiac lean reactor cars (Ref. 4-5). Two test routes were used to measure fuel economy under consumer driving conditions. Characteristics of the routes are:

1. City and Expressway Route--27.7-mile loop, 10 stops per loop; average speed of 36.7 mph
2. City Route--18.4-mile loop, 40 stops per loop, average speed of 23.4 mph

Table 4-13 compares the results obtained on these test routes with current lean reactor cars and their nonmodified production counterparts. The noted economy losses occurred because of the substantial amounts of EGR used; earlier versions of lean reactor cars without EGR showed little or no loss in fuel economy in comparison with the corresponding nonmodified car.

4.3.2.1.3 System Lifetime Characteristics

An earlier version of an Ethyl modified 1966 Pontiac was driven throughout the United States for over 20,000 miles while being used for a series of demonstrations. Modifications were similar to those in cars now in use except that this car was not equipped with EGR and had a less effective thermal reactor.

Another Pontiac embodying current modifications, among which were EGR and improved thermal reactors, accumulated over 30,000 miles in various types of service including cross-country trips. This car was reported by Ethyl to have demonstrated excellent durability characteristics and emissions stability.

One modified 1970 Pontiac was supplied to CARB in November 1970 for testing and use in general fleet service. Because CARB measured emissions from this vehicle only by the 1970 test procedure, the emission results cannot be directly related to data on other cars obtained by the single-bag 1972 CVS procedure. The California car has the longest uninterrupted history for

Table 4-13. Ethyl Lean Reactor--Fuel Economy Modified and Standard Cars (from Ref. 4-5)

| Item | City Route | City and Expressway |
|---------------------------------|-----------------|---------------------|
| Average Speed | 23 mph | 36 mph |
| Stops per Mile | 2.17 | 0.36 |
| 1971 Plymouth Fury III, 360 CID | | |
| Standard Car | 11.1 mpg | 16.7 mpg |
| Modified Car | | |
| Car A | 11.0 mpg | 14.5 mpg |
| Car B | <u>11.1 mpg</u> | <u>14.7 mpg</u> |
| Economy Loss | 0.5% | 12.6% |
| Avg | | 6.6% |
| 1970 Pontiac LeMans, 400 CID | | |
| Standard Car | 11.5 mpg | 14.9 mpg |
| Modified Car | <u>10.6 mpg</u> | <u>13.5 mpg</u> |
| Economy Loss | 7.8% | 9.4% |
| Avg. | | 8.6% |

Ethyl lean reactor vehicle modifications without changes or updating. The total mileage of this vehicle at the last test point was 12,000 miles: the California test accounts for 8000 miles, and an additional 4000 miles were accumulated during its trip to the West Coast and its preliminary testing period. Emissions of this car have good stability; results are shown in Table 4-14 and plotted in Fig. 4-26.

The basic nature of a lean reactor system would predict less difficulty in obtaining satisfactory durability than would be the case with a rich reactor system. This is because exhaust gas entering the reactor from the lean engine contains about 100 ppm HC, 0.1-0.4 percent CO, and approximately 2-4 percent O₂ (without an air pump). Therefore, little chemical heat is generated in the reactor and its temperature is governed by the degree to

Table 4-14. Ethyl Lean Reactor--Emission Data for Modified Pontiac (No. 761) Supplied to CARB (from Ref. 4-5)

| Date | Approximate Miles in California | Emissions (gm/mi) | | |
|---|---------------------------------|-------------------|------|-----------------|
| | | HC | CO | NO _x |
| 11-19-70 | 0 | 0.60 | 8.34 | 0.72 |
| 1-26-71 | 3,000 | 0.47 | 7.87 | 0.48 |
| 4-1-71 | 6,000 | 0.51 | 8.11 | 0.77 |
| 5-18-71 | 8,000 | 0.42 | 8.8 | 0.79 |
| Note: CARB Laboratory measurements by 1970 equivalent mass method | | | | |

which the sensible heat in the exhaust gas is conserved. This means that the lean reactor operates in a temperature range of 1400°F to 1600°F, even under high-speed turnpike conditions, which is a range that good-quality stainless steels should tolerate well. Moreover, tests by Ethyl (Ref. 4-5) indicate that the lean reactor is not subject to destructive temperature excursions, even with a continuously misfiring spark plug. Thus, durability should not be seriously decreased by situations in which engine malfunctions should occur.

Harmful deposits are also a consideration in system lifetime. However, the more advanced modulating EGR system now used on lean reactor cars was found to be free of such deposits after 12,000 miles of service on the car in CARB service, and was tested successfully for 30,000 equivalent miles on the dynamometer.

Therefore, even though a system life of 50,000 miles has not yet been demonstrated, there appears to be no fundamental reason why it could not be achieved by an LTR plus EGR emission system concept.

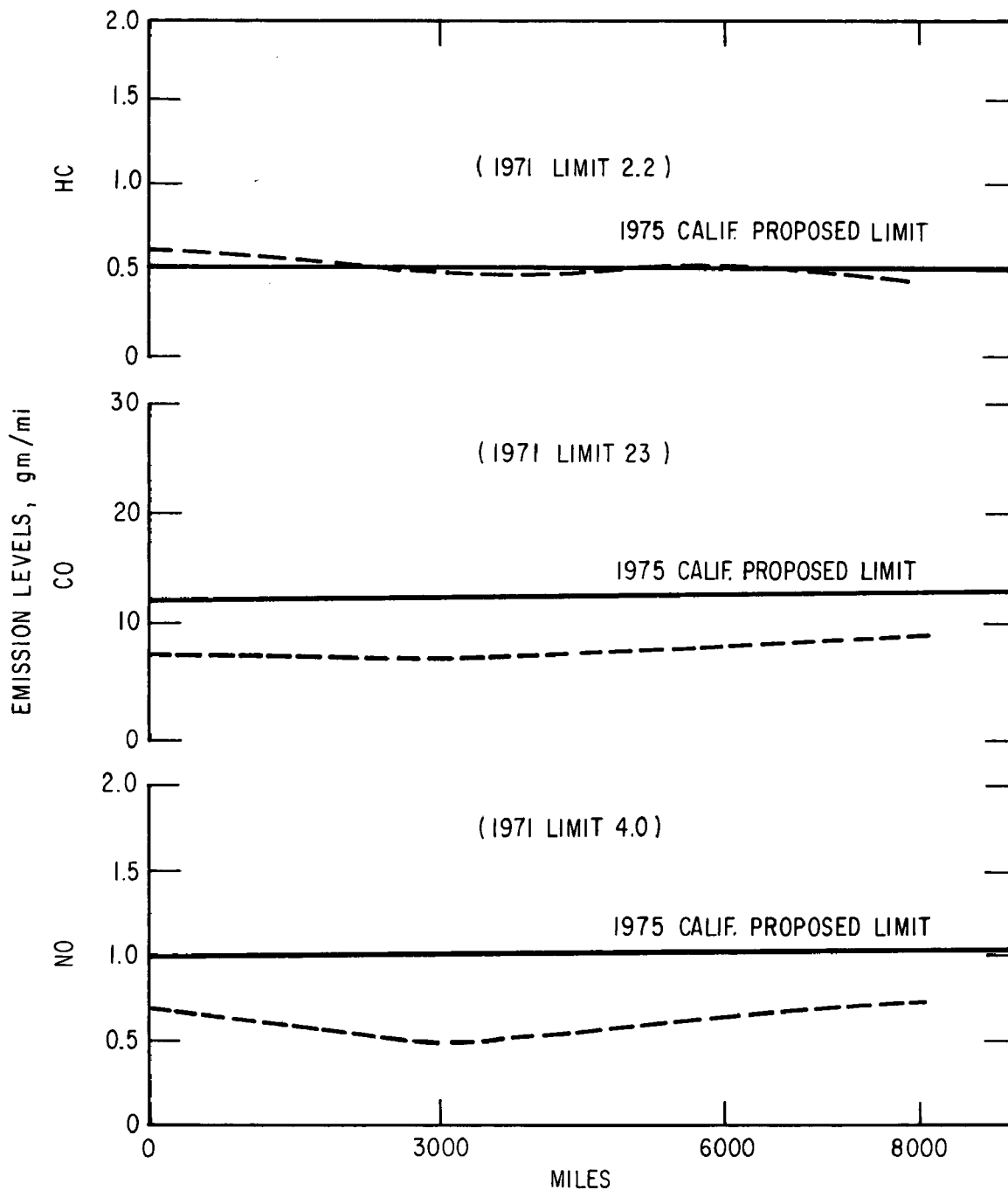


Fig. 4-26. Ethyl Lean Reactor Emissions of Modified Pontiac (No. 761) Supplied to CARB (Measurements by 1970 Equivalent Mass Method) (from Ref. 4-5)

4.3.2.1.4 Effect of Lead Additives

As mentioned above (4.3.2.1), all tests performed by Ethyl with lean reactor cars have been with fully leaded fuels and no adverse effects have been observed on the thermal reactor, per se. Ethyl does recognize that deposits in the EGR system can be expected to result from the decomposition of fuel and lubricant additives, from tars and carbonaceous matter produced during combustion, and from ferrous oxides from exhaust system parts. In addition, water condensate could be an important factor in promoting deposits. Ethyl found (Ref. 4-5) that the utilization of self-cleaning EGR orifice designs (plungers, specially coated surfaces, flexible snap-rings, etc.) in areas susceptible to deposit buildup was a practical method to negate deposit plugging and loss of EGR effectiveness.

4.3.2.2 RTR-Alone Concept

This emission control system concept is exemplified by the Esso Modified Rapid Action Manifold (RAM) thermal reactor design (Ref. 4-2) and the Ford Type J thermal reactor test program (Ref. 4-3). Other RTR performance and durability test programs by Esso, Du Pont, Ford, and other IIEC members are more suitably related to the RTR plus EGR subclass and are discussed in the next section (4.3.2.3).

The RTR-Alone system controls NO_x by fuel-rich carburetion and (in some instances) spark retard. CO and HC, derived from the fuel-rich engine, are mixed and burned with injected secondary air in the reactors and exhaust pipe.

The Esso RAM thermal reactor (Fig. 4-27) consists of a torus made of Type 310 stainless steel. Connecting arms lead exhaust gases from the engine to the torus. The gases flow around the torus and exit through a slot into a central plenum and then into the exhaust pipe. The slot is positioned so that the gases must flow at least half-way around the torus before they can leave, and so that a portion of the circulating gases goes all the way around to mix with the entering engine exhaust. Air is injected into each engine exhaust port and is aimed toward the valve. Most of the thermal reaction

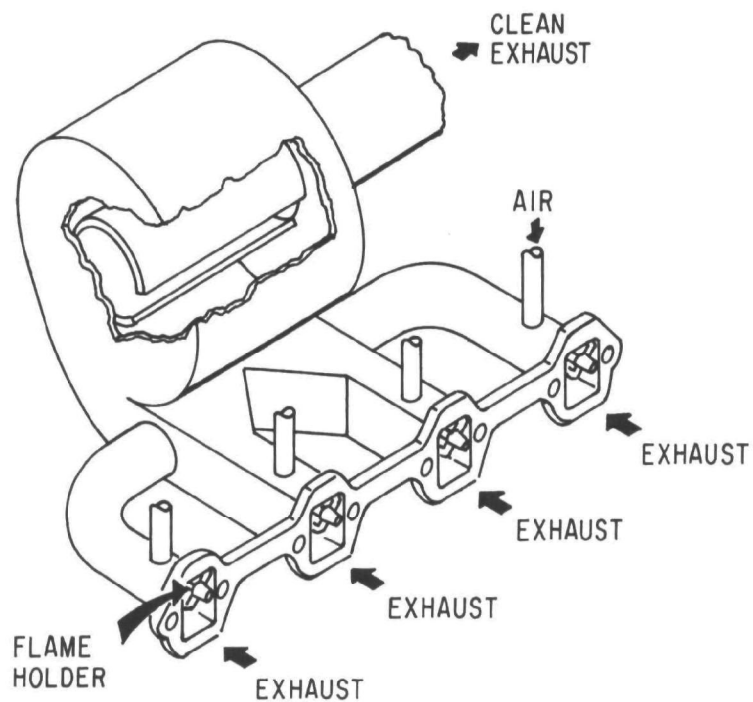


Fig. 4-27. Esso Rapid Action Manifold (RAM) Reactor (from Ref. 4-2)

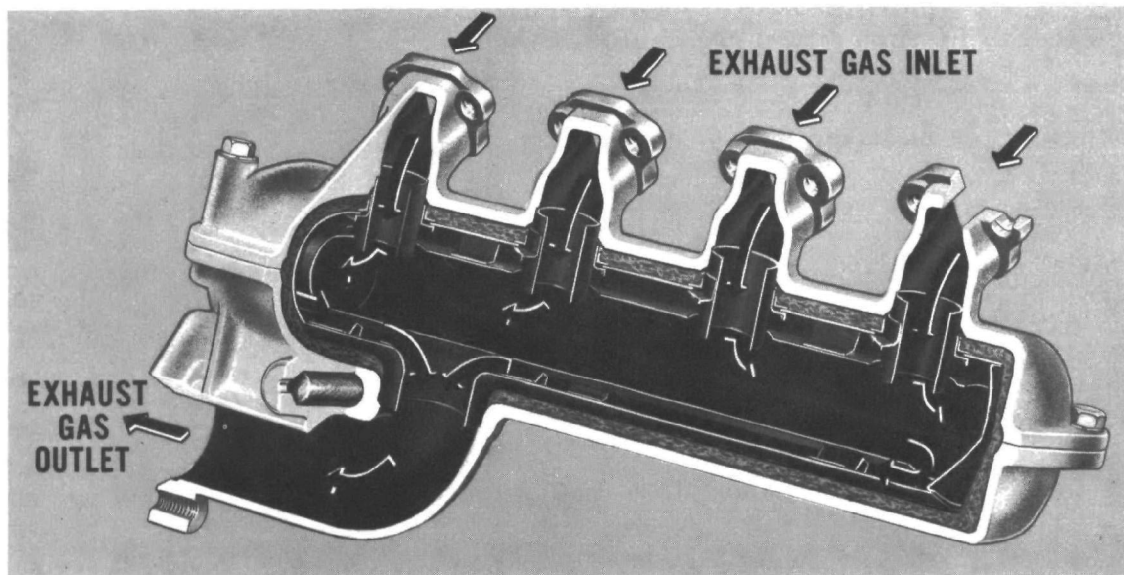


Fig. 4-28. IIEC Type H. Exhaust Manifold Reactor (V-8 Engine)--Small Volume with Concentric Core Design (from Ref. 4-3)

takes place as the gases swirl through the reactor. Any CO or HC not burned in the reactor continues to react in the exhaust pipe after it is heated. Flameholders are located at the exit of each engine exhaust port; they act to stabilize the flame at the exhaust port outlets during startup, when the engine is choked. Once the choke is open there is insufficient fuel to maintain a flame at the flameholders, but by this time the reactor proper is hot and the flame is held there.

The Ford Type J thermal reactor, although not fully described in the literature (Ref. 4-3), is stated to be essentially equivalent to the Type H smaller volume (97 in.³) series of IIEC exhaust manifold reactors (Type H, Ref. 4-3) shown in Fig. 4-28. It is stated that a one-piece shell reactor core was used with thermal growth provisions at the core inlet neck areas (Ref. 4-3). The core was constructed of Inconel 601 material.

4.3.2.2.1 Emission Level Characteristics

Esso test results for the Modified RAM system (Ref. 4-2) are shown below:

| <u>Results/Standards</u> | <u>Emission Levels (gm/mi)</u> | | |
|--------------------------|--------------------------------|-----------|-----------------------|
| | <u>CO</u> | <u>HC</u> | <u>NO_x</u> |
| Modified RAM Results | 4.2 | 0.07 | 1.89 |
| 1975 U.S. Standards | 4.7 | 0.46 | 3.00 |

These are single-bag CVS test data. As indicated, HC and CO values are lower than 1975-76 standards, and NO_x values are higher than 1976 standards (0.4 gm/mi).

The Ford Type J thermal reactor test data (Ref. 4-3) are shown in Fig. 4-29. All emissions (HC, CO, NO_x) are above 1975-76 standards, except for NO_x which is below the 1975 standard of 3 gm/mi (running approximately 0.5 to 0.7 gm/mi).

4.3.2.2.2 Fuel Economy Results

Several tests to measure fuel economy were made by Esso with the Modified RAM system (Ref. 4-2). A 2-hour city driving cycle was used with stop-and-go driving, 28-mph average speed, and cruises up to 45 mph. Some turnpike

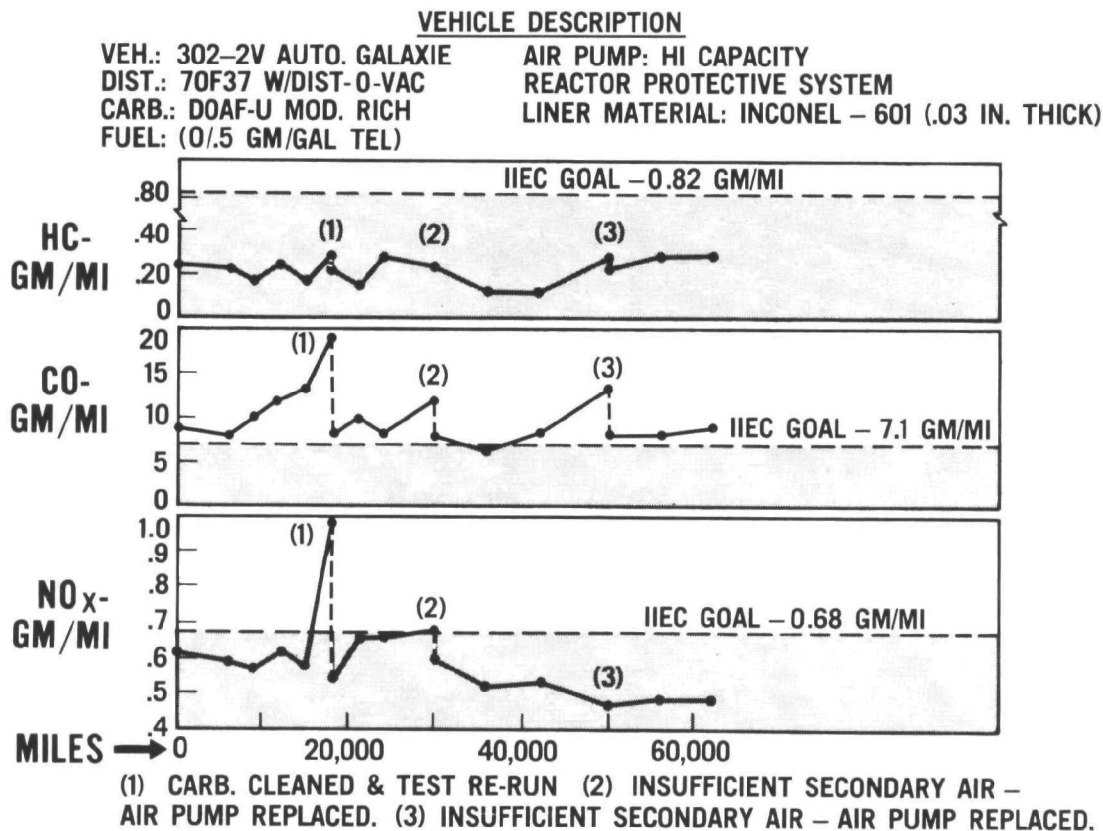


Fig. 4-29. Ford Type J Reactor Durability and Cold Start Emissions Data (from Ref. 4-3)

tests were also made, lasting 1 hour, at an average speed of 58 mph. The results, showing fuel economy compared with the base car with the original carburetor, are given below:

| % Fuel Economy Debit | |
|----------------------|------|
| City Driving | 16.9 |
| Turnpike | 9.5 |

No fuel economy test results were reported (Ref. 4-3) for the Ford Type J thermal reactor tests.

4.3.2.2.3 System Lifetime Characteristics

Esso tests of the Modified RAM concept were demonstrative only; no durability tests have been made. If this concept were tested for durability, a better material than the 310 stainless steel used in the demonstrator model would be required.

The Ford Type J reactor was installed in vehicle for durability testing. As reported in Ref. 4-3, 62,000 miles of heavy-duty operation were accumulated on the reactors at the time of writing (January 1971). Although failures were experienced on ancillary components as mileage was accumulated, the thermal reactor system continued to control emissions to essentially IIEC target levels when all emission component subsystems were operational (see Fig. 4-29 for notation of carburetor and air pump problems). This vehicle was equipped with a reactor overtemperature protection system which limited peak temperatures to 1850°F.

A recent communication (Ref. 4-36) with Ford indicated that 90,000 miles of durability operation has been completed. At test termination, a number of heat cracks in the liner were found and a hole had developed in one small area. Although a loss of performance was observed, the system was still performing relatively well.

4.3.2.3 RTR plus EGR Concept

This emission control system concept is exemplified by the Du Pont thermal reactor system (Ref. 4-8), the Esso RAM thermal reactor (Ref. 4-2), and the Ford Package "A" system (Ref. 4-29). HC and CO emissions are controlled as described in Section 4.3.2.2 for the RTR-Alone concept; EGR is added for NO_x control (see Section 4.2.2) over and beyond that afforded by rich engine operation.

The configurational aspects of the Esso RAM reactor and Ford-type reactors were described in Section 4.3.2.2. The Du Pont-type reactor is of conventional configuration (as shown in Fig. 4-2).

In the case of the Esso RAM system (Ref. 4-2), EGR in the amount of approximately 12 percent of engine intake air was used for maximum NO_x control. It was taken in the vicinity of the muffler, passed through finned tubing for cooling, and introduced into the carburetor above the throttle plates. EGR was not used at throttle positions below 20-25 mph cruise because it increased CO and HC emissions. Also, it was not used during warmup because it prevented

a flame from being established quickly. The use of EGR resulted in about a 50-percent decrease in NO_x emissions from the level achieved by fuel-rich engine operation.

The EGR system utilized in the Du Pont thermal reactor system concept (Ref. 4-8) is basically similar to that used by Esso. Recirculation is shut off at (1) idle to give smooth engine operation, and (2) at WOT conditions to prevent loss in maximum vehicle performance. The recirculation rate employed has been varied, with the most recent Du Pont system employing an approximately 18 percent recycle rate.

The EGR system utilized on the Ford concept emission Package "A" design (Ref. 4-29) is a below-the-throttle recycle injection system, with recycle pickup taken before the muffler. The particular rate of recycle is not given.

4.3.2.3.1 Emission Level Characteristics

Esso test results for the RAM system (Ref. 4-2) are shown below:

| <u>Emission Levels (gm/mi)</u> | | |
|--------------------------------|-----------|-----------------------|
| <u>CO</u> | <u>HC</u> | <u>NO_x</u> |
| 3.7 | 0.08 | 0.72 |

These are single-bag CVS test data. As indicated, the CO value is slightly below the 1975-76 standard, the HC value is considerably below the 1975-76 standard, and the NO_x level exceeds the 1976 standard.

More recent single-bag and three-bag CVS tests were reported by EPA (Ref. 4-37) to give the following emission value ranges for a RAM-equipped 1971 Ford LTD:

| <u>Test Type</u> | <u>Emission Levels (gm/mi)</u> | | |
|------------------|--------------------------------|-----------|-----------------------|
| | <u>CO</u> | <u>HC</u> | <u>NO_x</u> |
| Single-bag tests | 3.80-5.90 | 0.14-0.20 | 0.60-0.65 |
| Three-bag tests | 3.19-4.76 | 0.10-0.11 | 0.67 |

The most recent Du Pont thermal reactor system is quoted by Du Pont (Ref. 4-8) to have the following emission levels (single-bag CVS test procedure):

$$\left. \begin{array}{l} \text{HC} = 0.05 \\ \text{CO} = 9.20 \\ \text{NO}_x = 0.52 \end{array} \right\} \text{ gm/mi}$$

The Ford Package "A" single-bag CVS test results were (Ref. 4-29):

$$\left. \begin{array}{l} \text{HC} = 0.30 \\ \text{CO} = 9.00 \\ \text{NO}_x = 1.40 \end{array} \right\} \text{ gm/mi}$$

Chrysler Corporation (Ref. 4-6) reported single-bag CVS laboratory test data emission values for the RTR plus EGR concept of:

$$\left. \begin{array}{l} \text{HC} = 0.23 \\ \text{CO} = 13.80 \\ \text{NO}_x = 0.45 \end{array} \right\} \text{ gm/mi}$$

4.3.2.3.2 Fuel Economy Results

Tests were made by Esso to measure fuel economy for the RAM system. They were run as described for the Modified RAM system in Section 4.3.2.2.2. Specific results, showing fuel economy compared with the base car with the original carburetor, are given below:

| <u>% Fuel Economy Debit</u> | |
|-----------------------------|------|
| City Driving | 22.4 |
| Turnpike | 17.4 |

The recent Du Pont thermal reactor system (described above) is stated (Ref. 4-8) to have a 21-percent fuel economy loss under city-suburban driving conditions.

The Ford Concept "A" system (Ref. 4-29) had a 20-percent fuel economy loss on the chassis dynamometer, and an 18-percent loss under city-suburban driving conditions.

Chrysler (Ref. 4-6) estimated a fuel economy penalty of approximately 30 percent for the RTR plus EGR concept evaluated by them.

4.3.2.3.3 System Lifetime Characteristics

Esso tests of the RAM concept were demonstrative only; no durability tests have been made.

The Ford Package "A" concept also was demonstrative only. However, the durability test program for the Ford Type J reactor (Section 4.3.2.2.3) would be equally applicable to the reactor portion of the Package "A" concept. As mentioned, the final results of this durability program have not been published or released by Ford.

Du Pont supplied six cars to CARB in the fall of 1970 for its evaluation in a two-year program. These cars were 1970 Chevrolets with 350 CID engines and automatic transmissions, and were equipped with the Du Pont particulate-trapping system as well as thermal reactor and EGR. The six test cars, along with six production vehicles for comparison, were assigned to the State Motor Pool in California for normal driving service by state employees. In June 1971, the average of the odometer readings of the six vehicles was 17,954 miles. As the vehicles had about 3000 miles of operation prior to incorporation of the emission control system, about 15,000 miles of durability testing of the emission control system were actually logged.

Near the end of August 1971, a failure of a timing chain occurred in one of the six test vehicles. The failure was described as an elongation of the timing chain, which eventually caused a hole to be rubbed in its cover. None of the six vehicles in the control fleet was affected.

Du Pont (Ref. 4-38) states that similar wear was observed in three of the six CARB test cars. Symptoms of similar wear had been previously detected in three reactor vehicles tested by Du Pont. Timing chain pins, cam followers, rocker arms, and valve guides were affected. Du Pont is convinced that the wear problem is due to the lapping action of small (0.02-0.05 micron) metal

oxide particles mixed in the engine oil. These small particles come from the reactor core and find their way through the EGR line to the lubrication system (presumably by entering the intake valve ports and then passing through the piston rings and/or exhaust valve guides).

Severe oxidation of the reactor core 310 stainless steel material was demonstrated in Du Pont tests of two reactors which lost 0.5 pound of core weight (23 percent) after 20,000 miles of testing. Du Pont feels that the wear problem could be overcome by using a material such as Inconel 601 in the reactor core. Since oxidation of any part of the exhaust system is a potentially similar hazard, a more complete solution would be to use an EGR gas source upstream of the thermal reactor.

Because of these problems, the CARB test program has been discontinued. Du Pont plans (Ref. 4-39) to concentrate on the development of an improved thermal reactor emission control system, rather than retrofit current devices. New systems may include (1) Esso-type RAM features, (2) air injection modulation, (3) spark advance adjustment, and (4) fuel injection (for more precise air-fuel ratio control).

Durability tests of EGR alone for a similar type EGR system were conducted by Esso (Ref. 4-13) for NAPCA. In this test program, the EGR system was evaluated in three 1969 Plymouths and three 1969 Chevrolets over 52,000 miles under city-suburban driving conditions simulated on a tape-controlled mileage accumulation dynamometer. No major problems were reported. Engine wear and cleanliness were considered normal for the mileage and driving regime. These results appear to bear out Du Pont's contention that the CARB test program failure was related to the thermal reactor core oxidation process.

4.3.2.3.4 Effect of Lead Additives

As noted in Ref. 4-29, Ford changed to the use of a low-lead (0.5 gm/gal) fuel because of concurrent supporting program efforts showing severe corrosion of

material specimens when exposed to high-temperature exhaust gas from an engine operated on fuel containing 3 gm/gal of TEL (more fully reported in Ref. 4-29).

Du Pont studies (Ref. 4-8) indicate that the presence or absence of lead has no effect on corrosion or oxidation of high-temperature materials, such as Inconel 601, at the temperatures at which RTR's normally operate; i.e., between 1700°F and 1900°F.

The presence of lead in gasoline, and particularly the combination of lead and phosphorous, causes deterioration of the reactor core at localized points where the exhaust gases coming in from the engine impinge on the interior surfaces. This deterioration, termed erosion, was reported in Refs. 4-40 and 4-41. Erosion was shown to be caused by lead, and it was accelerated when lead and phosphorous were combined. It was also shown that erosion is subject to partial control by changing the reactor geometry to minimize gas impingement. Further, it was shown (Ref. 4-41) that a nickel-chromium alloy such as Universal Cyclops Uniloy 50/50 (50 percent Ni, 50 percent Cr) has exceptionally good resistance to erosion. Since erosion is quite localized, Du Pont concludes that small patches of Uniloy 50/50 could be inserted at the erosion points to protect the core, which would be of a less expensive material such as Inconel 601.

4.3.3 Combination Systems

There are four meaningful subclasses of combination systems:

1. LTR plus HC/CO Catalytic Converter plus EGR
2. RTR plus HC/CO Catalytic Converter plus EGR
3. RTR plus Dual Catalytic Converter plus EGR
4. RTR plus NO_x Catalytic Converter plus RTR

(The LTR plus Dual Catalytic Converter plus EGR concept is not considered a feasible approach as a reducing atmosphere is required for all known NO_x catalysts.)

4.3.3.1 LTR plus HC/CO Catalytic Converter plus EGR

This emission control system concept is exemplified by the General Motors "1975 Experimental System" (Ref. 4-31). The major new components of this low-emission concept vehicle (shown in Fig. 4-30) include:

1. Improved carburetor with altitude compensation and power choke (electronic fuel injection may be used in some models)
2. Exhaust gas recirculation (into intake manifold)
3. HC/CO catalytic converter
4. Air injection pump
5. Unitized ignition system

Although not specifically illustrated in Fig. 4-30, it is understood (Ref. 4-42) that the system includes the General Motors Air Injection Reactor (A.I.R.) system, wherein slightly lean (A/F approximately 15-16.5) carburetion plus

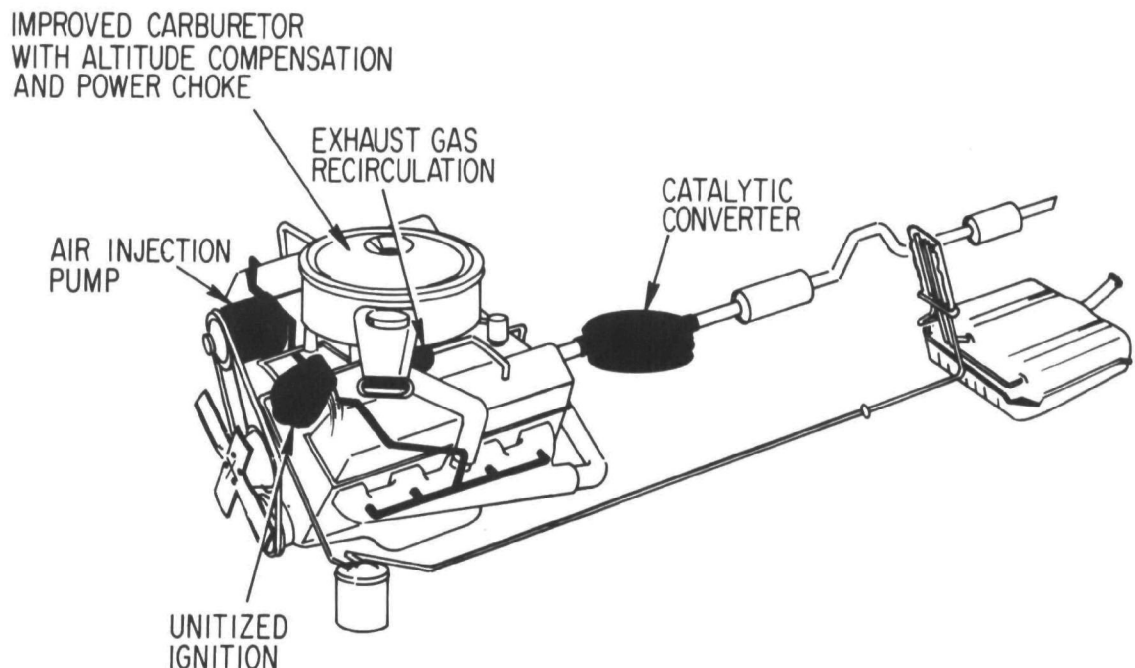


Fig. 4-30. General Motors 1975 Experimental Emission Control System (from Ref. 4-31)

air injection into the exhaust manifold serves as a "low-grade" LTR to provide rapid warmup of the catalytic converter. After warmup, the air injection is directed to the catalytic converter.

4.3.3.1.1 Emission Level Characteristics

Emission test values for the General Motors proposed 1975 system (Ref. 4-31) are:

$$\left. \begin{array}{l} \text{HC} = 0.54 \\ \text{CO} = 9.20 \\ \text{NO}_x = 1.00 \end{array} \right\} \text{ gm/mi (CVS cold start single-bag tests)}$$

More recent three-bag CVS data reported by General Motors (Ref. 4-43) for this type of system are:

$$\left. \begin{array}{l} \text{HC} = 0.40 \\ \text{CO} = 5.50 \\ \text{NO}_x = 0.95 \end{array} \right\} \text{ gm/mi}$$

American Motors (Ref. 4-35) is currently testing, and has in the past two years tested, three basic catalyst types for the control of HC and CO in a configuration similar to the General Motors approach delineated above. Typical baseline (zero vehicle and system miles) emission levels are:

| <u>Catalyst</u> | <u>Emissions (gm/mi)</u> | | <u>Vehicle</u> |
|---------------------|--------------------------|-----------|---|
| | <u>HC</u> | <u>CO</u> | |
| Platinum-monolithic | 0.04 | 2.35 | 3000-lb Javelin; single-bag CVS tests |
| Base metal-bead | 0.11 | 3.29 | 3500-lb standard car; three-bag CVS tests |
| Platinum-bead | 0.45 | 2.96 | 3500-lb standard car; single-bag CVS tests |

EGR was used to give NO_x levels of 3 gm/mi.

4.3.3.1.2 Fuel Economy Results

General Motors has not indicated the fuel economy characteristics of their proposed 1975 system (Ref. 4-31), except to indicate a goal of approximately 10 percent loss in fuel economy.

4.3.3.1.3 System Lifetime Characteristics

General Motors (Ref. 4-31) has emphasized that its advanced emission control concepts are experimental, and that durability and/or lifetime characteristics are not well defined at this point in time. Although the Corporation is attempting to develop catalytic converters for useful lifetimes of 50,000 miles, initial converters placed in service in some 1974 models may have a recommended replacement interval of approximately 25,000 miles (Ref. 4-43).

4.3.3.1.4 Effect of Lead Additives

Previous comments with regard to the effect of lead additives on thermal reactors and EGR systems were given in Section 4.3.2.2.4. With respect to HC/CO catalytic converters, the following position was recently taken by General Motors (Ref. 4-44):

Lead seriously affects catalyst life; all of some 300 catalysts tested in cars were affected by lead; there is some regenerative property, but very little.*

4.3.3.2 RTR plus HC/CO Catalytic Converter plus EGR

This emission control system concept is exemplified by the Ford "Combined Concept Emission Package" (Ref. 4-29). In this type of system, the thermal reactor acts as a "preheater" for the HC/CO catalytic converters. Carburetor enrichment and EGR are utilized for NO_x control.

The major components and features of this Ford combined "maximum

*This refers to the case of using unleaded gas after the catalyst has been exposed to leaded fuels

effort" low-emission concept vehicle (the A-B system), shown in Fig. 4-31, include:

1. Two 97 in.³ IIEC Type H reactors (with center core)
2. Two noble metal catalytic converters
3. Reactor inlet and outlet sheet metal liners
4. Modified cylinder heads with exhaust port liners
5. One engine-driven secondary air pump (16 in.³ displacement)
6. Below-the-throttle EGR system
7. Production-type carburetor with richer calibration
8. Production distributor with modified curve
9. More spark retard during warmup (until engine water temperature reaches 120°F)
10. Modified crankcase ventilation
11. Prototype reactor protective system to limit maximum core temperature to 1850°F
12. Unleaded fuel requirement

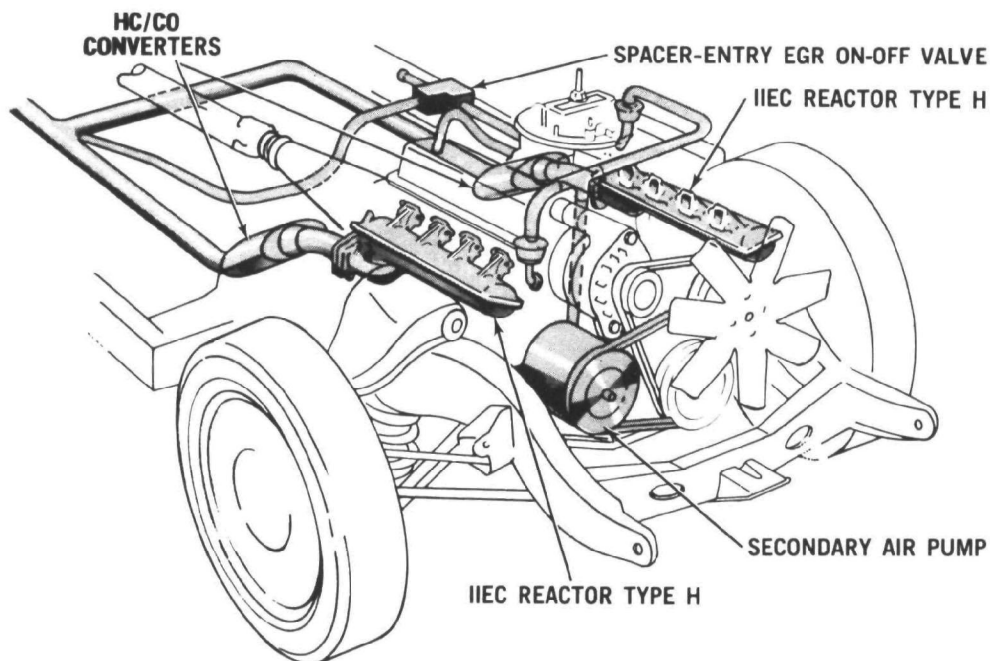


Fig. 4-31. Ford Combined Maximum Effort/Low-Emission Concept Vehicle (from Ref. 4-29)

4.3.3.2.1 Emission Level Characteristics

The average emission data from ten separate cold start CVS single-bag tests of the Ford combined "maximum effort" vehicle at low mileages are given below along with the low and high value ranges:

| <u>Test Data</u> | <u>Emissions (gm/mi)</u> | | |
|------------------|--------------------------|-----------|-----------------------|
| | <u>HC</u> | <u>CO</u> | <u>NO_x</u> |
| Average | 0.28 | 3.4 | 0.76* |
| Low | 0.11 | 1.7 | 0.51 |
| High | 0.53 | 6.7 | 1.02 |

*NO_x emission levels were measured using a nondispersive infrared instrument for NO and a nondispersive ultraviolet instrument for NO₂.

More recent data from Ford (Ref. 4-45) for a similar system with a higher EGR flow rate are:

$$\left. \begin{array}{l} \text{HC} = 0.25 \\ \text{CO} = 2.95 \\ \text{NO}_x = 0.55 \end{array} \right\} \text{ gm/mi (three-bag CVS tests)}$$

4.3.3.2.2 Fuel Economy Results

At the level of emissions shown, the Ford "maximum effort" test vehicle had a 27-percent loss in fuel economy over baseline vehicles for a city-suburban driving schedule. Limited testing was conducted on this vehicle to minimize the significant fuel economy losses. When the fuel economy loss (on the CVS chassis dynamometer test) was reduced from approximately 25 percent to about 10 percent by running less rich, HC and CO emissions increased only slightly, and NO_x emission levels increased from the 0.72-gm/mi level to the 1.3-gm/mi level. Figure 4-32 shows NO_x emission levels from a series of CVS cold starts as they relate to the fuel economy loss (on the chassis dynamometer) over a baseline vehicle. For all tests, HC and CO emission levels were below 0.4 and 4.0 gm/mi, respectively.

4.3.3.2.3 System Lifetime Characteristics

Ford also emphasizes that their advanced emission control concepts are

experimental and that durability and/or lifetime characteristics are not well defined at this point in time (Ref. 4-33).

4.3.3.2.4 Effect of Lead Additives

Previous comments with regard to the effect of lead additives on thermal reactors and EGR systems were given in Section 4.3.2.3.4. With respect to HC/CO catalytic converters, the following statements were recently made by Ford (Ref. 4-46):

Lead-free gasoline is mandatory; one tankful of gasoline containing 3 gm/gal of lead seriously impairs catalyst performance (although some catalysts have some recuperative power); trace-lead (0.015 gm/gal) is probably tolerable; phosphorus, chlorine, bromine, and sulfur are also detrimental.

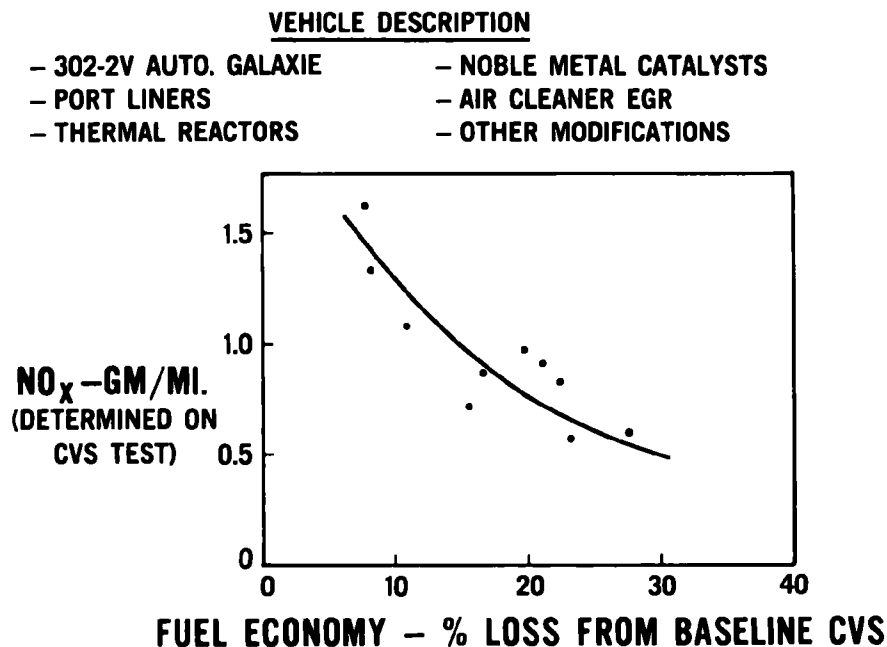


Fig. 4-32. Ford Maximum Effort Vehicle-- NO_x Emissions vs Fuel Economy (from Ref. 4-29)

4.3.3.3 RTR plus Dual Catalytic Converter plus EGR

This emission control system concept is exemplified by an experimental General Motors system (Ref. 4-31) and by experimental test systems of Ford (Ref. 4-45) and the American Oil Company (AMOCO) (Ref. 4-47).

The General Motors system consists essentially of the 1975 proposed control system plus a quick-heat manifold and fast choke, as well as the addition of a NO_x catalytic converter for NO_x control (Fig. 4-33, Ref. 4-31). In addition, the engine is run rich (A/F approximately 14-15) to provide the necessary reducing atmosphere for the NO_x catalytic converter. Emission test results are:

$$\left. \begin{array}{l} \text{HC} = 0.2 \\ \text{CO} = 4.0 \\ \text{NO}_x = 0.6 \end{array} \right\} \text{ gm/mi (single-bag CVS tests)}$$

More recent three-bag CVS test results reported by General Motors (Ref. 4-43) indicate emission bands (composites of several tests) as follows:

$$\left. \begin{array}{l} \text{HC} = 0.2-0.3 \\ \text{CO} = 2.5-6.0 \\ \text{NO}_x = 0.35-0.85 \end{array} \right\} \text{ gm/mi}$$

No specific details are available on the Ford test vehicle, although it is presumably similar to the Ford combined concept package (Fig. 4-31) except for the use of a dual catalytic converter instead of an HC/CO catalytic converter. Emission test results reported at low mileage with a fresh catalyst are:

$$\left. \begin{array}{l} \text{HC} = 0.27 \\ \text{CO} = 2.24 \\ \text{NO}_x = 0.60 \end{array} \right\} \text{ gm/mi (three-bag CVS tests)}$$

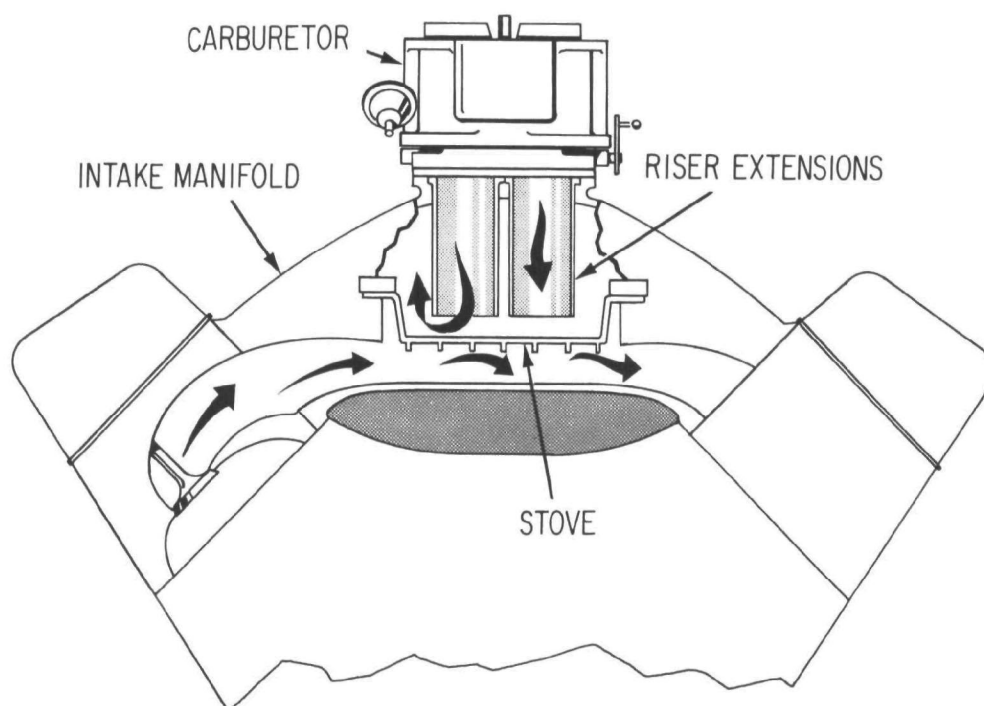


Fig. 4-33. General Motors Quick-Heat Manifold and Fast Choke Configuration (from Ref. 4-31)

Similar emission data are reported by AMOCO (Ref. 4-47). In this case, two different dual catalytic converter configurations were evaluated in vehicle tests. The three-bag CVS test emission data are (based on two tests of each configuration):

| <u>Configuration</u> | <u>Emission Levels (gm/mi)</u> | | |
|---|--------------------------------|-----------|-----------------------|
| | <u>HC</u> | <u>CO</u> | <u>NO_x</u> |
| Pelletized NO _x catalyst plus pelletized HC/CO catalyst (fresh catalyst; no mileage) | 0.26 | 1.72 | 0.55 |
| Monolithic NO _x catalyst plus monolithic HC/CO catalyst (at 100 miles) | 0.38 | 2.07 | 0.68 |

Although only laboratory, low-mileage data on this concept are available, it is a logical approach to achieving lower NO_x levels at reasonable fuel consumption penalties (<10 percent) and, in principle, is merely the replacement of a single-bed HC/CO catalytic converter with a dual-bed HC/CO/NO_x converter or the addition of a NO_x catalytic converter to a system already

incorporating an HC/CO converter. Although not openly reported, it is known that this emission control system concept is under intensive evaluation by the automotive industry with respect to its potential for meeting the stringent 1976 NO_x standards.

Comments regarding the effects of lead additives in gasoline are deferred to Section 5.

4.3.3.4 RTR plus NO_x Catalytic Converter plus RTR

This emission control system concept is exemplified by one American Motors (Ref. 4-35) experimental system. American Motors tests of this system showed it to meet the required levels of HC, CO and NO_x simultaneously, at zero mile conditions. It utilizes an exhaust manifold reactor operating rich, with sufficient secondary air injection to increase the sensible energy content of the exhaust gas and remain "reducing." This exhaust is fed through an NO_x catalyst followed by additional secondary air and another thermal reactor. Zero-mile emission levels as tested in a 4500-pound Jeep vehicle with a 360 CID engine were:

$$\left. \begin{array}{l} \text{HC} = 0.01 \\ \text{CO} = 2.44 \\ \text{NO}_x = 0.37 \end{array} \right\} \text{ gm/mi (CVS 3-bag data)}$$

The nominal air-fuel ratio was 12:1, and no EGR was employed. The first thermal reactor was unbaffled with a stainless steel liner. The second thermal reactor is located in a compartment directly behind the NO_x catalyst bed. It is stated that the exhaust gas temperature from the second RTR is approximately 1800°F, which is felt to be too hot for safe vehicle operation.

It is believed that the fast warmup intake manifold with a timed choking mechanism could possibly lower CO to provide increased margin. Lack of system durability experience, severe installation problems, very high fuel consumption (estimated 25 percent SFC penalty) are current problem areas and these preclude serious consideration of this system by American Motors at this time.

4.3.3.5 Stratified Charge Engine

A prototype stratified charge engine installed in a one-quarter-ton light truck was recently tested in the EPA test center in Willow Run, Michigan, and met the 1976 emission standards at an inertia weight of 3000 pounds. However, the power-to-weight ratio of this vehicle was not sufficiently high to meet all the acceleration requirements of the dynamometer driving cycle. Fourteen tests were conducted in the period of August 30 to September 14, 1971, with the following average emission results (1975 CVS-3 procedure) (Ref. 4-48):

| <u>Emission</u> | <u>Emission Levels (gm/mi)</u> |
|-----------------|--------------------------------|
| HC | 0.37 |
| CO | 0.93 |
| NO _x | 0.33 |

This system also included a thermal reactor, EGR, and an HC/CO catalytic converter. The engine incorporates a different combustion chamber design and fuel injection directly into the chamber, and requires specially designed spark plugs. Ford, the developer of this engine, has stated that it is still experimental and that there is no chance that it could be mass produced and certified by 1976. It should be noted that the emission levels given above are for low-mileage, laboratory conditions and were accomplished in a light-weight vehicle (~3000 pounds) with a low power-to-weight ratio not typical of current passenger cars.

On this basis, then, the stratified charge engine will not be further evaluated in this study. Since this system incorporates a catalytic converter, the findings of this study relative to the lead effects on catalytic devices would be applicable if this system were to be adopted.

4.3.4 Summary of Specific Emission Control Systems

4.3.4.1 Comparison of Emission Levels with 1975-76 Standards

In organizing and evaluating the emissions data, it is necessary to contend with the problems imposed by the changes that have been made in the Federal

test procedures for emissions testing. The 7-mode, 7-cycle procedure (FTP) defined in the Federal Register of June 1968 (Ref. 4-49) was changed to the single-bag CVS technique (CVS-1) described in the Federal Register of July 15, 1970 (Ref. 4-50). Following this change, a new three-bag CVS weighted-average procedure (CVS-3), applicable to 1975-76 systems, was defined in July 1971 (Ref. 4-51). These changes are found to have a substantial impact on the resultant emission levels measured for certain systems. In general, it is not possible to convert FTP to CVS-1 data because of the differences in emphasis on the cold start emission contribution, because of differences in the driving cycle, and because of differences in the test instrumentation. A similar set of constraints applies to the conversion of CVS-1 to CVS-3 data.

As only CVS data is regarded as representative of system performance in relation to the goals presently established for 1975-76 systems, the available CVS data previously given in Section 4.3 are summarized in Table 4-15. Except for the RTR plus NO_x Catalytic Converter plus RTR concept (Table 4-15C), no emission control system has demonstrated meeting 1976 concurrent (HC, CO, and NO_x) emission standards, whether by CVS-1 or CVS-3 test procedures. With regard to the data in Table 4-15, the following observations can be drawn.

1. In general, the catalytic-converter-only or catalytic-converter-plus EGR systems do not appear meaningful for meeting 1975-76 standards. This apparently results from CVS cold start effects and the lack of provision for rapid "warmup" capability of the catalyst converter. There are some instances, however, where catalytic-converter-only systems meet the HC and CO values with a fresh catalyst.
2. The LTR plus EGR system has yet to demonstrate meeting 1975-76 HC and CO standards. Proposed changes to the thermal reactor (flameholders, etc.) might help, and the addition of an HC/CO catalytic converter would certainly enhance the HC and CO picture for the lean thermal reactor approach. As lean operation precludes the use of an NO_x catalyst, this approach is limited to EGR NO_x reduction levels and is not capable of meeting 1976 NO_x emission levels on this basis.
3. RTR systems (noncatalyst), e.g., the Esso RAM system, are well below 1975-76 HC standards and approach (met in one case) 1975-76

Table 4-15A. Summary of Emission Control System Emission Data--Catalytic Converter Systems (Laboratory, Low-Mileage Tests)

| CVS Cold-Start Emissions (gm/mi) | | | Single-Bag (CVS-1) (Pre-July 1971) | | | Three-Bag (CVS-3) (Post-July 1971) | | | Reference |
|---|---------|---------|---------------------------------------|-----------------|------------------|---------------------------------------|-----|------------------|-----------|
| | | | HC | CO | NO _x | HC | CO | NO _x | |
| System Type | Fed Std | 1975-76 | 0.46 | 4.7 | 3.0 _x | 0.41 | 3.4 | 3.1 _x | |
| | | | 0.4 | | | 0.4 | | | |
| HC/CO Catalytic Converter Only (No EGR) | | | | | | | | | |
| UOP Tests | | | | | | | | | |
| U S 1971 Domestic V-8 (Normal Choke) | | | 0.59 to 0.68 | 0.96 to 1.45 | 2.11 to 3.88 | | | | |
| U S 1971 Domestic V-8 (Fast Choke) | | | 0.16 to 0.51 | 1.21 to 2.58 | 4.74 to 5.08 | | | | |
| Some Foreign Vehicles | | | 0.29 to 1.41 | 0.99 to 3.86 | 1.36 to 2.0 | | | | |
| Engelhard Tests | | | | | | | | | |
| PTX-433 Catalyst (0.2% Pt) | | | 0.70 | 3.80 | 5.0 | | | | |
| HC/CO Catalytic Converter + EGR | | | | | | | | | |
| Ford Package "B" | | | 0.80 | 11.0 | 1.3 | | | | |
| Chrysler | | | 0.24 | 7.2 | 2.03 | | | | |
| Dual Catalytic Converter + EGR | | | | | | | | | |
| Ford Package "C" | | | 0.85 | 10.0 | 0.90 | | | | |
| Tricomponent Catalytic Converter | | | | | | | | | |
| APCO Tests of UOP System (1970 VW) | | | 1.4 to 2.3 | 10 to 32 | 0.6 to 1.3 | | | | |

Table 4-15B. Summary of Emission Control System Emission Data--Thermal Reactor Systems (Laboratory, Low-Mileage Tests)

| CVS Cold-Start Emissions (gm/mi) | | | Single-Bag (CVS-1) (Pre-July 1971) | | | Three Bag (CVS-3) (Post-July 1971) | | | Reference |
|-------------------------------------|------------------|---------|---------------------------------------|---------|-----------------|---------------------------------------|------|-----------------|-----------|
| | | | HC | CO | NO _x | HC | CO | NO _x | |
| System Type | Fed Std, 1975-76 | 0.46 | 4.7 | 3.0 | 0.41 | 3.4 | 3.1 | 0.4 | Reference |
| LTR plus EGR | | | | | | | | | |
| Ethyl Corporation | | | | | | | | | |
| Pontiac | | 0.64 | 6.4 | 1.52 | | | | | 4-5 |
| Plymouth | | 0.89 | 8.6 | 1.37 | 0.52 | 6.2 | 1.37 | | 4-5 |
| Chrysler | | 0.70 | 7.0 | 1.30 | | | | | 4-6 |
| RTR Alone | | | | | | | | | |
| Modified RAM | | 0.07 | 4.2 | 1.89 | | | | | 4-2 |
| Ford Type J Reactor | | 0.1-0.3 | 6-12 | 0.5-0.7 | | | | | 4-3 |
| RTR plus EGR | | | | | | | | | |
| RAM | | | | | | | | | |
| Esso Tests (Chev) | | 0.08 | 3.7 | 0.72 | | | | | 4-2 |
| EPA Tests (1971 Ford LTD) | | | | | | | | | 4-37 |
| (a) | | 0.20 | 5.9 | 0.65 | | | | | |
| (b) | | 0.20 | 3.8 | 0.60 | | | | | |
| (c) | | 0.14 | 4.8 | 0.60 | | | | | |
| (d) | | 0.10 | 4.54 | 0.67 | 0.11 | 4.76 | 0.67 | | |
| (e) | | 0.14 | 4.77 | 0.63 | 0.10 | 3.19 | 0.67 | | |
| Recent Du Pont System | | 0.05 | 9.2 | 0.52 | | | | | 4-8 |
| Ford Package "A" | | 0.30 | 9.0 | 1.40 | | | | | 4-29 |
| Chrysler | | 0.23 | 13.8 | 0.45 | | | | | 4-6 |

Table 4-15C. Summary of Emission Control System Emission Data--
Combination Systems (Laboratory, Low-Mileage Tests)

| CVS Cold-Start Emissions (gm/mi) | | Single-Bag (CVS-1) (Pre-July 1971) | | | Three-Bag (CVS-3) (Post-July 1971) | | | Reference |
|---|-------------------|---------------------------------------|------|-----------------|---------------------------------------|-----------|-----------------|-----------|
| | | HC | CO | NO _x | HC | CO | NO _x | |
| | | 0.46 | 4.7 | 3.0 | 0.41 | 3.4 | 3.1 | |
| System Type | Fed Std - 1975-76 | 0.4 | | | 0.4 | | | |
| LTR plus HC/CO Catalytic Converter plus EGR | | | | | | | | |
| G M "1975 Experimental System" ^a | | 0.54 | 9.2 | 1.0 | 0.40 | 5.5 | 0.95 | 4-31/4-43 |
| American Motors | | | | | | | | 4-35 |
| Platinum-Monolithic, Air-injection Reactor | | 0.40 | 2.35 | 3.0 | | | | |
| Base Metal-bead Air-injection Reactor | | | | | 0.11 | 3.29 | 3.0 | |
| Platinum-bead, Air-injection Reactor | | 0.45 | 2.96 | 3.0 | | | | |
| RTR plus HC/CO Catalytic Converter plus EGR | | | | | | | | |
| Ford Combined Concept Package | | | | | | | | |
| "Maximum Effort" Tests | | 0.28 | 3.4 | 0.76 | | | | 4-29 |
| "Improved Fuel Economy" Tests | | ~0.3 | ~3.5 | 1.3 | | | | 4-29 |
| High-rate EGR System | | | | | 0.25 | 2.95 | 0.55 | 4-45 |
| RTR plus Dual Catalytic Converter plus EGR | | | | | | | | |
| G M "1975 System" plus Quick-heat Manifold and Fast Choke plus NO _x Catalytic Converter ^b | | 0.2 | 4.0 | 0.6 | 0.2to 0.3 | 2.5to 6.0 | 0.35to 0.85 | 4-31/4-43 |
| Ford Dual Bed Catalyst System | | | | | 0.27 | 2.24 | 0.60 | 4-45 |
| AMOCO Vehicle Tests | | | | | | | | 4-47 |
| Pelletized Catalysts | | | | | 0.26 | 1.72 | 0.55 | |
| Monolithic Catalysts | | | | | 0.38 | 2.07 | 0.68 | |
| RTR plus NO _x Catalytic Converter plus RTR | | | | | | | | |
| American Motors (Jeep with 360 CID, no EGR) | | | | | 0.01 | 2.44 | 0.37 | 4-35 |

^aGeneral Motors A I R System, l e , "low-grade" LTR, lean (A/F = 15-16.5) operation

^bGeneral Motors A I R System, l e , "low-grade" RTR, rich (A/F = 14-15) operation

^aGeneral Motors A I R System, i e , "low-grade" LTR, lean (A/F = 15-16.5) operation

^bGeneral Motors A I R System, i e , "low-grade" RTR, rich (A/F = 14-15) operation

- CO levels. NO_x levels are determined by combined air-fuel ratios and EGR reduction effects, and although significantly low (approximately 0.7 gm/mi), do not meet 1976 NO_x standards.
- Combined systems, incorporating some form of thermal reactor (whether it be a "full-size" reactor or a "low-grade" reactor, e.g., General Motors A.I.R. system) for catalyst bed warmup under cold start conditions, appear to offer the means for eventually meeting the 1976 standards for all three emission constituents (HC, CO, and NO_x). Even in this case, a NO_x catalyst bed would be required to meet NO_x standards.
 - Without a NO_x catalyst, both the RTR plus EGR and "low-grade" RTR plus HC/CO catalytic converter plus EGR concepts, offer a somewhat similar potential for concurrent emission reduction (approaching 1975-76 HC and CO standards and achieving NO_x levels higher than the 1976 standard).

It is emphasized that the foregoing observations are based on experimental laboratory data only. If, as the various automakers have suggested, levels of approximately 50 percent of the 1975-76 standards have to be achieved to account for the variation of production tolerances, test reproducibility, degradation with accumulated mileage effects, etc., then it would appear that the emission control systems proposed and evaluated to date will not meet the 1975-76 emission standards.

4.3.4.2 Lifetime/Durability Effects

As detailed in Section 4.3 for each specific emission control system discussed, there are no meaningful lifetime or durability data available for any combined emission control system seriously being considered for implementation by the U.S. automakers.

The approximately 90,000-mile durability test of a thermal reactor by Ford (Ref. 4-36) is certainly significant, but did not even include an EGR system, let alone a catalytic converter.

Engelhard (Ref. 4-57) has reported a 50,000-mile (AMA driving schedule) durability test of their PTX-433 catalytic converter unit; again EGR was not incorporated.

At this point in time, then, overall emission control system durability and lifetime remain simply as goals, with little or no demonstrated capability.

4.3.4.3 Fuel Economy Effects

As indicated in Sections 4.2 and 4.3 there is a wide variability in the SFC values reported for the various emission control systems. The primary factor, however (as shown in Section 4.2.2.3), is the combined effect of air-fuel ratio and EGR flow rate utilized to control NO_x to different levels. Over and above this basic effect is the variation in method of reporting SFC effects. For the same emission control system, different results are obtained with different driving cycles and/or dynamometer test procedures.

A general correlation for a number of the systems examined in Section 4.3 is presented in Figure 4-34, where the SFC increase (over the baseline vehicle without the specific emission control system) is shown as a function of the NO_x level achieved. This general correlation is nearly the same as the Ford/IIEC estimate of Ref. 4-29 (presented herein as Fig. 4-32, Section 4.3.3.2.2).

As can be seen in Fig. 4-34, both non-catalytic-converter systems (LTR + EGR, RTR + EGR) and HC/CO catalytic-converter systems (HC/CO catalytic converter + EGR, RTR + EGR + HC/CO catalytic converter) comprise the general correlation. This is as would be expected, since the NO_x level realized is related only to conditions present in the engine cylinder (i.e., air-fuel ratio and percentage EGR) and not to any external device or condition. As these data points represent test configurations employing operating parameters (air-fuel ratio, EGR rate) selected to produce minimum NO_x levels, the shape of the general correlation curve conforms to (again, as would be expected) the limiting envelope of SFC versus NO_x reduction capability previously shown in Fig. 4-13.

Also shown in Fig. 4-34 that relationship of SFC increase versus NO_x level estimated to occur if a NO_x catalyst at 75-percent conversion efficiency were added to a system characterized by the general correlation line and if this addition did not influence other parts of the system (75 percent selected as a typical number; representative values for NO_x catalysts now under development are not available).

As can be noted, extremely high fuel consumption penalties occur if NO_x levels below approximately 1 gm/mi are achieved, unless an NO_x catalyst is used. Even then, SFC increases of approximately 7-8 percent are envisioned at NO_x levels of approximately 0.4 gm/mi.

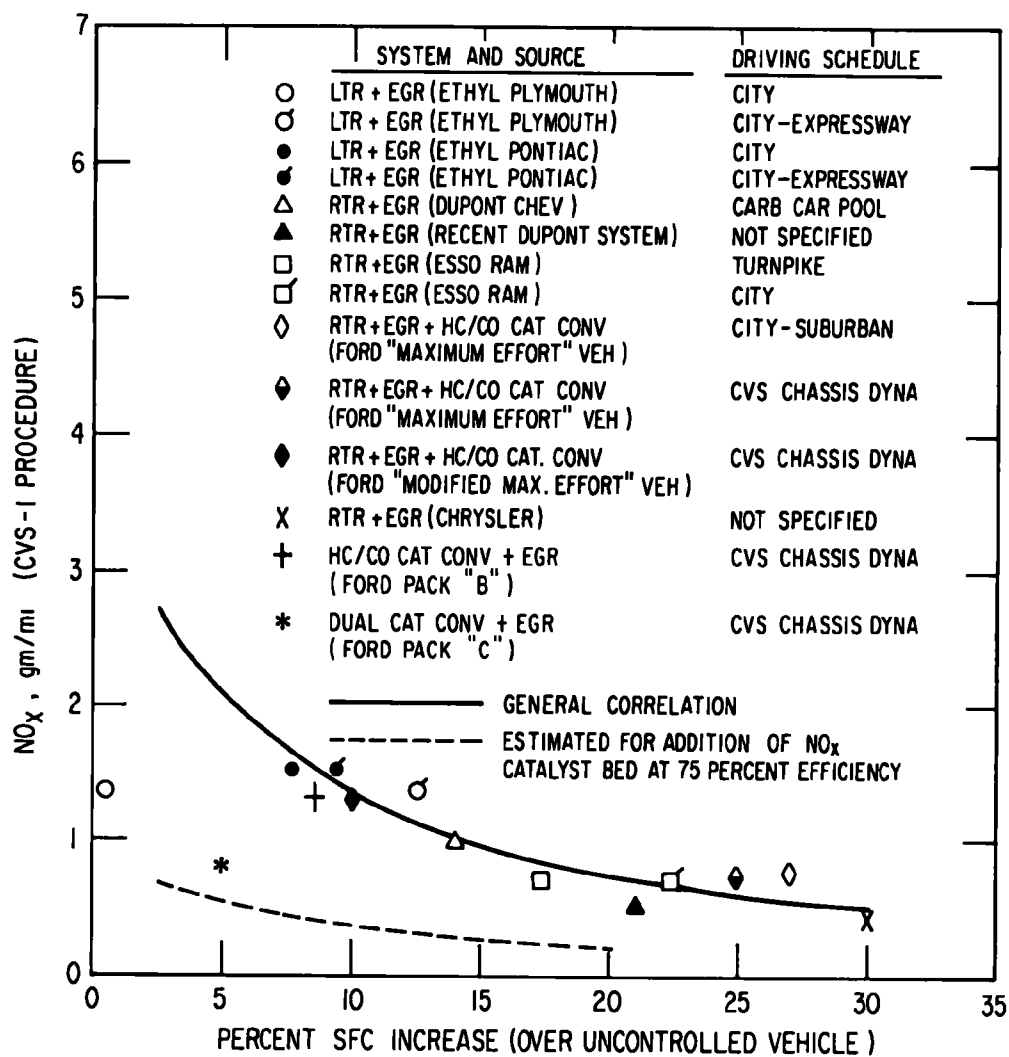


Fig. 4-34. NO_x vs SFC Increase

REFERENCES

- 4-1. Exhaust Manifold Thermal Reactor Development at Du Pont, Petroleum Chemicals Division, Du Pont de Nemours & Co., Wilmington, Delaware (20 January 1971).
- 4-2. R. J. Lang, "A Well Mixed Thermal Reactor System for Automotive Emission Control," SAE Paper No. 710608 (June 1971).
- 4-3. A. Jaimee, D.E. Schneider, A.I. Rozmanith, and J.W. Sjoberg, "Thermal Reactor Design, Development and Performance," SAE Paper No. 710293 (January 1971).
- 4-4. Air Injection Pump Horsepower Requirements for V-8 Engines, Drawing No. 3210665, American Motors Corporation (4 September 1969).
- 4-5. The Ethyl Lean Reactor System, Ethyl Corporation Research Laboratories, Detroit (1 July 1971).
- 4-6. Chrysler Corporation, Letter in response to a request from the Administrator, Environmental Protection Agency, Subject: Regarding Emission Control (1 April 1971).
- 4-7. K. Matsumoto and H. Nohira, "Oxides of Nitrogen from Smaller Gasoline Engines," SAE Paper No. 700145 (January 1970).
- 4-8. Effect of Lead Antiknocks on the Performance and Costs of Advanced Emission Control Systems, Du Pont de Nemours & Co., Wilmington, Delaware (15 July 1971).
- 4-9. W.F. Deeter, et al., "An Approach for Controlling Vehicle Emissions," SAE Paper No. 680400 (May 1968).
- 4-10. Y. Kaneko, et al., "Small Engine Concept Emission Vehicles," SAE Paper No. 710296 (January 1971).
- 4-11. W. Glass, et al., "Evaluation of Exhaust Recirculation for Control of Nitrogen Oxides Emissions," SAE Paper No. 700146 (January 1970).
- 4-12. W. Glass, D.S. Kim and B.J. Kraus, "Synchrothermal Reactor System for Control of Automotive Exhaust Emissions," SAE Paper No. 700147 (January 1970).
- 4-13. G.S. Musser, et al., "Effectiveness of Exhaust Gas Recirculation with Extended Use," SAE Paper No. 710013 (January 1971).

REFERENCES (cont.)

- 4-14. Demonstration of the Technological Feasibility of Controlling Oxides of Nitrogen from Vehicular Exhaust, Progress Report No. 2, California Air Resources Board (May 1969) Federal Grant No. 68A0605D).
- 4-15. Demonstration of the Technological Feasibility of Controlling Oxides of Nitrogen from Vehicular Exhaust, Progress Report No. 5, California Air Resources Board (April 1970) (Federal Grant No. 68A0605D).
- 4-16. Demonstration of the Technological Feasibility of Controlling Oxides of Nitrogen from Vehicular Exhaust, Progress Report No. 6, California Air Resources Board (July 1970) (Federal Grant No. 68A0605D).
- 4-17. Project CI: Du Pont Reactor Vehicles, 4th Progress Report, California Air Resources Board (18 June 1971).
- 4-18. F.W. Bowditch (Director, Automotive Emission Control, General Motors Corporation), Letter to the Administrator, Environmental Protection Agency, Subject: Comments on Notice of Proposed Rule-Making for NO_x on 1973 New Motor Vehicles, Federal Register of 27 February 1971, Vol. 36, No. 40 (28 April 1971).
- 4-19. H. K. Newhall, "Control of Nitrogen Oxides by Exhaust Recirculation --A Preliminary Theoretical Study," SAE Paper No. 670495 (1967).
- 4-20. S. Ohigashi, et al., "Heat Capacity Changes Predict Nitrogen Oxides Reduction by Exhaust Gas Recirculation," SAE Paper No. 710010 (January 1971).
- 4-21. "Study of Catalytic Control of Exhaust Emissions for Otto Cycle Engines," Stanford Research Institute (April 1970).
- 4-22. G. J. Nebel and R. W. Bishop, "Catalytic Oxidation of Automobile Exhaust Gases," SAE Paper 29-R (January 1959).
- 4-23. T. V. De Palma, "The Application of Catalytic Converters to the Problems of Automotive Exhaust Emissions," Paper presented at the Interpetrol Congress, Rome, Italy (24 June 1971).
- 4-24. G. H. Meguerian, "NO_x Reduction Catalysts for Vehicle Emission Control," SAE Paper No. 710291 (January 1971).
- 4-25. "IIEC, A Cooperative Research Program for Automotive Emission Control," SAE Publication SP-361 (1971).

REFERENCES (cont.)

- 4-26. M. Shelef, K. Otto and H. Gandhi, "The Heterogeneous Decomposition of Nitric Oxide on Supported Catalysts, Atmosphere Environment, Vol. 3, Pergamon Press (1969), pp 107-122.
- 4-27. Personal discussion with representatives of the Universal Oil Products Company, July 1971.
- 4-28. E.E. Hancock, R.M. Campau and R. Connolly, "Catalytic Converter Vehicle System Performance: Rapid Versus Customer Mileage," SAE Paper No. 710292 (January 1971).
- 4-29. R.M. Campau, "Low Emission Concept Vehicles," SAE Paper No. 710294 (January 1971).
- 4-30. H.W. Sworchert, "Performance of a Catalytic Converter on Nonleaded Gasoline," SAE Paper No. 690503 (May 1969).
- 4-31. Progress and Programs in Automotive Emissions Control, Progress Report to the Environmental Protection Agency, General Motors Corporation (12 March 1971).
- 4-32. American Motors Corporation, Letter in response to a request from the Administrator, Environmental Protection Agency, Subject: Regarding Requirements of the Clean Air Act (2 April 1971).
- 4-33. H. L. Misch (Vice President--Engineering, Ford Motor Company), Statement to the Environmental Protection Agency (6 May 1971).
- 4-34. J. C. Thompson, Exhaust Emissions from a Passenger Car Equipped with a Universal Oil Products Catalytic Converter, Air Pollution Control Office, Environmental Protection Agency (December 1970).
- 4-35. C.E. Burke (American Motors Corporation), Letter to The Aerospace Corporation (29 September 1971).
- 4-36. B. Simpson (Ford Motor Company), Letter to The Aerospace Corporation (15 September 1971).
- 4-37. Telephone conversation with H. Gompf, Environmental Protection Agency (12 October 1971).
- 4-38. R. C. Butler (Du Pont de Nemours & Co.), Letter to Office of Air Programs, Environmental Protection Agency (30 August 1971).

REFERENCES (cont.)

- 4-39. Telephone conversation with J. Mikita, Du Pont de Nemours & Co. (September 1971).
- 4-40. E.N. Cantwell, et al., "A Progress Report on the Development of Exhaust Manifold Reactors," SAE Paper No. 690139 (January 1969).
- 4-41. W. J. Barth and E.N. Cantwell, "Automotive Exhaust Manifold Thermal Reactors--Materials Considerations," Presented before the Division of Petroleum Chemistry, Inc., 161st Meeting of the American Chemical Society, Los Angeles, California (28 March - 2 April 1971).
- 4-42. Telephone conversation with F. Bowditch, General Motors Corporation (September 1971).
- 4-43. Personal discussion with representatives of the General Motors Corporation (September 1971).
- 4-44. Personal discussion with representatives of the General Motors Corporation (30 June 1971).
- 4-45. Telephone conversation with B. Simpson, Ford Motor Company (October 1971).
- 4-46. Personal discussion with representatives of the Ford Motor Company (1 July 1971).
- 4-47. J. H. Somers (Office of Air Programs, Environmental Protection Agency), Letter to the Aerospace Corporation, Subject: Discussion with Dr. G. Meguerian (7 October 1971).
- 4-48. "Army Motor Vehicle Meets 1976 Emission Levels," Environmental News (Press Release), Environmental Protection Agency, Washington, D. C. (24 September 1971).
- 4-49. "Standards for Exhaust Emissions, Fuel Evaporative Emissions, and Smoke Emissions Applicable to 1970 and Later Vehicles and Engines," Federal Register, Vol. 33, No. 108, Part II (4 June 1968).
- 4-50. "Control of Air Pollution from New Motor Vehicles and New Motor Vehicle Engines," Federal Register, Vol. 35, No. 136 (1 July 1970).

REFERENCES (cont.)

- 4-51. "Control of Air Pollution from New Motor Vehicles and New Motor Vehicle Engines," Federal Register, Vol. 36, No. 128 (2 July 1971).
- 4-52. Consequences of Removing Lead Antiknocks from Gasoline, A Status Report, No. AC-10, Ethyl Corporation, Detroit (August 1970).
- 4-53. E. N. Cantwell, et al., "Recent Developments in Exhaust Manifold Reactor Systems," Presented at a meeting of the Automobile Division, Institution of Mechanical Engineers, Paper No. ADP-13, London, England (11 May 1970).
- 4-54. E. N. Cantwell (Du Pont de Nemours & Co.), Letter to The Aerospace Corporation (12 August 1971).
- 4-55. S. Lawrence and J. Wisdom, "Emission Control by Exhaust Manifold Reactor--An Initial Study for Small Engines," Presented at a meeting of the Automobile Division, Society of Mechanical Engineering, Paper No. ADP-13(A)/70, London, England (11 May 1970).
- 4-56. D. Hirschler (Ethyl Corporation), Letter to The Aerospace Corporation (August 1971).
- 4-57. Engelhard Industries, Inc., Letter to The Aerospace Corporation (13 October 1971).

SECTION 5

GENERAL ASSESSMENT OF EFFECTS OF LEAD ADDITIVES ON EMISSION CONTROL DEVICES/SYSTEMS

In Sections 4.2 and 4.3, various comments, statements, and/or positions relative to the effect of lead additives in gasoline were reported where they were pertinent to a particular device/system under discussion. The purpose of this section is to examine the relevant data and make a general assessment of the effects of lead additives on the various emission control devices/systems.

5.1 CATALYTIC CONVERTERS

Degradation of the performance of catalytic converters employed as pollution control devices on automobiles run on leaded and unleaded gasoline is observed to occur much more rapidly with leaded gasoline. Degradation may occur either by loss of catalytic activity, or physical attrition, or both. The lead component of gasoline thus clearly constitutes a catalyst "poison," which acts through a variety of chemical and mechanical toxicity mechanisms that are not mutually exclusive.

Even though numerous theoretical and laboratory investigations have been performed on catalyst poisoning, the complex composition of exhaust gas, the wide range and number of engine operating parameters, and the many types and configurations of catalytic materials, make it very difficult to arrive at generalizations regarding the most likely mechanisms. Nevertheless, a review of these mechanisms has indicated that lead, sulfur, and phosphorus compounds would have a deleterious effect on catalysts. Experimental data with prototype catalysts, run with actual automotive exhausts under realistic operating conditions, are therefore most meaningful in assessing the effects of lead. These are discussed in this section. A brief discussion of possible catalyst poisoning mechanisms can be found in Appendix B.

5.1.1 Summary of Experimental Data

5.1.1.1 Laboratory Tests

The available data on lead effects are primarily for HC and CO oxidation catalysts. To date, NO_x reduction catalysts have been studied much less fully.

Tests conducted by the Studebaker-Packard Corporation (Ref. 5-21) on an HC/CO catalytic converter, using leaded and unleaded gasoline, indicate rapid deterioration of catalyst effectiveness with leaded gasoline (Fig. 5-1).

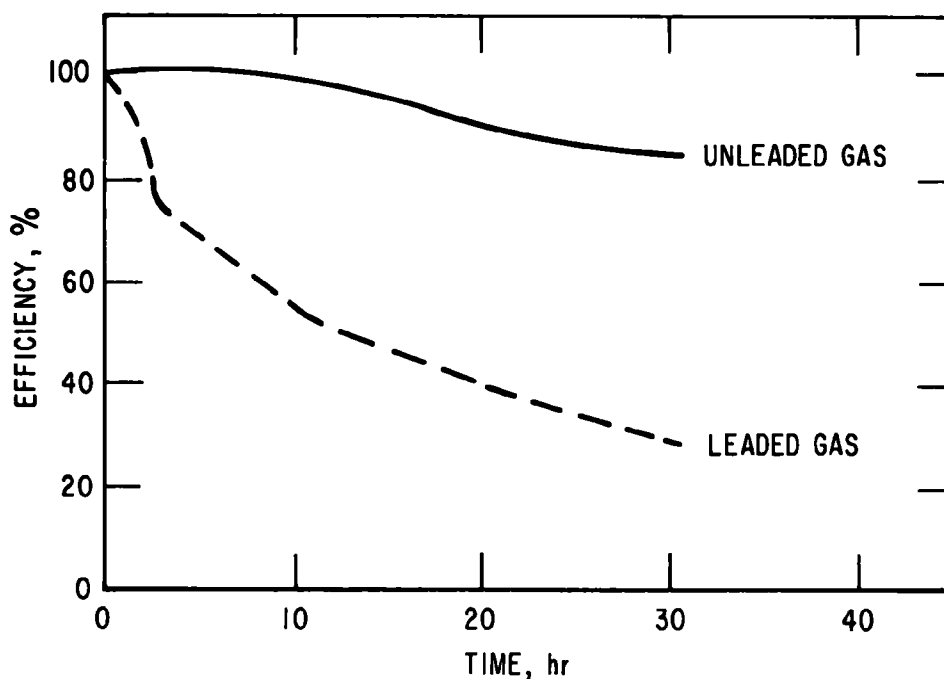


Fig. 5-1. Catalyst Life--Leaded vs Unleaded Gasolines
(from Ref. 5-21)

At the Bureau of Mines, Hofer, et al., studied an alumina (Al_2O_3) catalyst, and chromia (Cr_2O_3), manganic sesquioxide (Mn_2O_3), and urania (U_3O_8)

catalysts supported on alumina, using gasoline containing 3 ml/gal/ of TEL (Ref. 5-1). Test results from that study are listed in Table 5-1. As a criterion for loss in catalytic activity, they used the rise in catalyst temperature T_a required for oxidation of 80 percent of four selected hydrocarbons tested individually. In these tests the catalysts were exposed to engine exhaust for periods of approximately 340 hours, except for the Al_2O_3 catalyst which was exposed for 126 hours. The lead deposits were in the form of the sulfate ($PbSO_4$), oxysulfate ($PbSO_4 \cdot PbO$), and chloro-bromide $[Pb(Cl, Br)_2]$. About half the lead contained in the fuel appeared to be deposited on the catalyst. The data show no increase in activation temperature with unleaded fuel, whereas with leaded fuel a significant rise occurs. Effects of lead poisoning on the HC oxidation efficiency of platinum (Pt) and vanadium pentoxide (V_2O_5) catalysts are summarized in Fig. 5-2 (Ref. 5-2). The data indicate that these catalysts are adversely affected by lead compounds; V_2O_5 is more resistant to lead poisoning than Pt.

Catalyst deactivation as affected by TEL, motor mix (TEL plus scavengers) and bromoethane (C_2H_5Br , similar to a scavenger) is illustrated in Fig. 5-3 for a copper oxide-chromia (CuO/Cr_2O_3) NO_x catalyst (Ref. 5-3). Deactivation with TEL was very rapid initially, but after about 20 hours it decreased at a lower rate. Deactivation with bromoethane was very fast, and after 60 hours the catalyst was almost inactive. The effect of motor mix was intermediate between that of TEL and bromoethane. This shows that lead and scavengers are detrimental to this catalyst.

Composition changes in this copper oxide-chromia catalyst upon deactivation with motor mix in the fuel, as determined by electron-probe microanalyses, are shown in Fig. 5-4 (Ref. 5-3). Lead was concentrated about 15 microns thick at the pellet surface. Copper appeared to remain immediately behind lead, whereas chromium tended to migrate toward the center of the pellet. No such segregation was observed in fresh catalysts or catalysts aged in the absence of lead. Because of this change in composition during deactivation by lead in the fuel, restoration of catalyst activity appears unlikely. Thus,

Table 5-1. Effect of TEL on Catalytic Activity (from Ref. 5-1)

| Catalyst | T _a (°C) Before Exposure To Exhaust | T _a (°C) After Exposure To Exhaust | Concentration of TEL (cc/gal) |
|--|--|---|-------------------------------|
| Al ₂ O ₃ | 506 | 529 | 3 |
| Mn ₂ O ₃ /Al ₂ O ₃ | 375 | 600 | 3 |
| U ₃ O ₈ /Al ₂ O ₃ | 420 | 600 | 3 |
| Cr ₂ O ₃ /Al ₂ O ₃ | 325 | 430 | 3 |
| Cr ₂ O ₃ /Al ₂ O ₃ | 325 | 325 | 0 |

Note. Period of exposure of catalyst to exhaust was ~340 hours, except for plain Al₂O₃ which was 126 hours

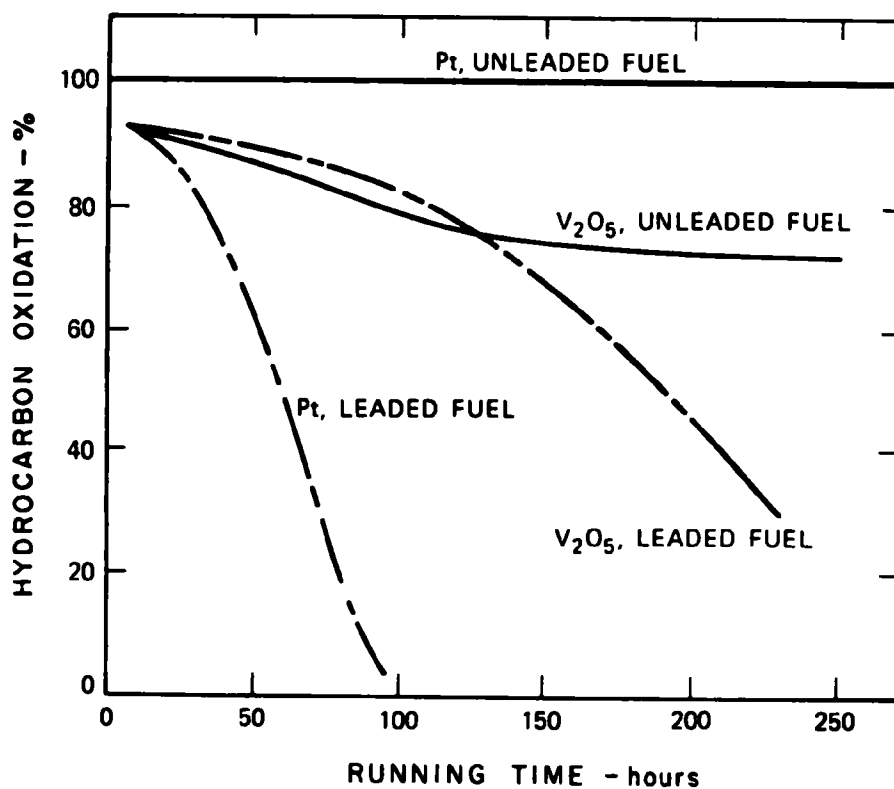


Fig. 5-2. Effect of TEL on Catalyst Efficiency for HC Oxidation (from Ref. 5-2)

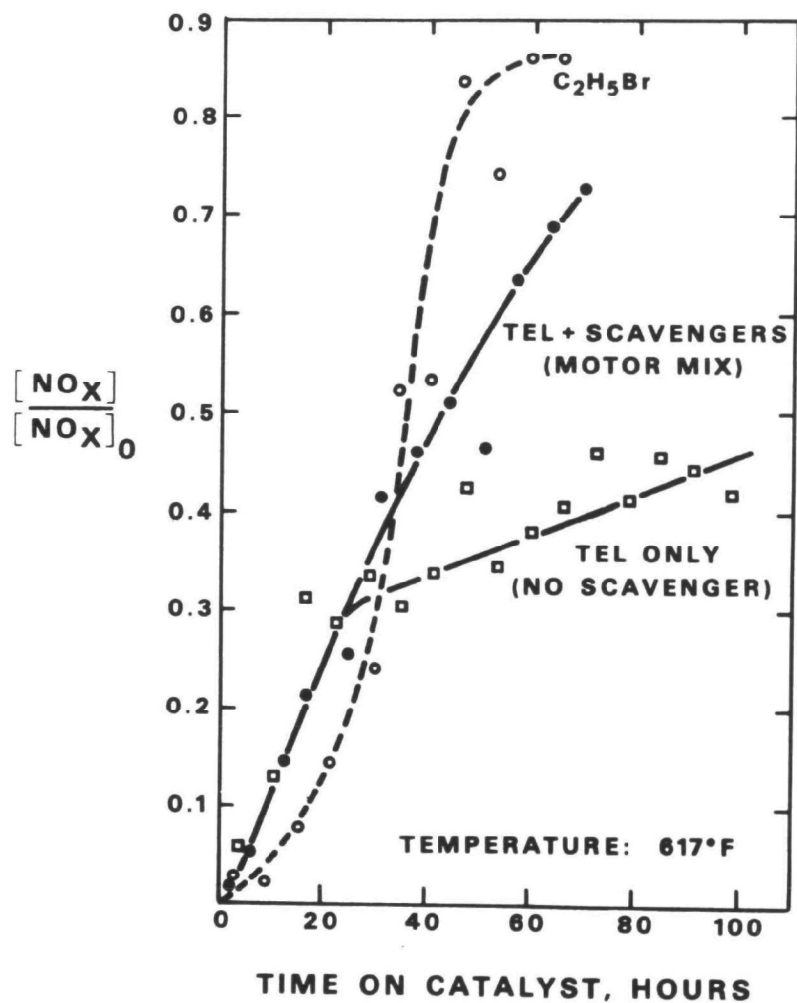


Fig. 5-3. NO_x Catalyst ($\text{CuO}/\text{Cr}_2\text{O}_3$) Deactivation by Lead (from Ref. 5-3)

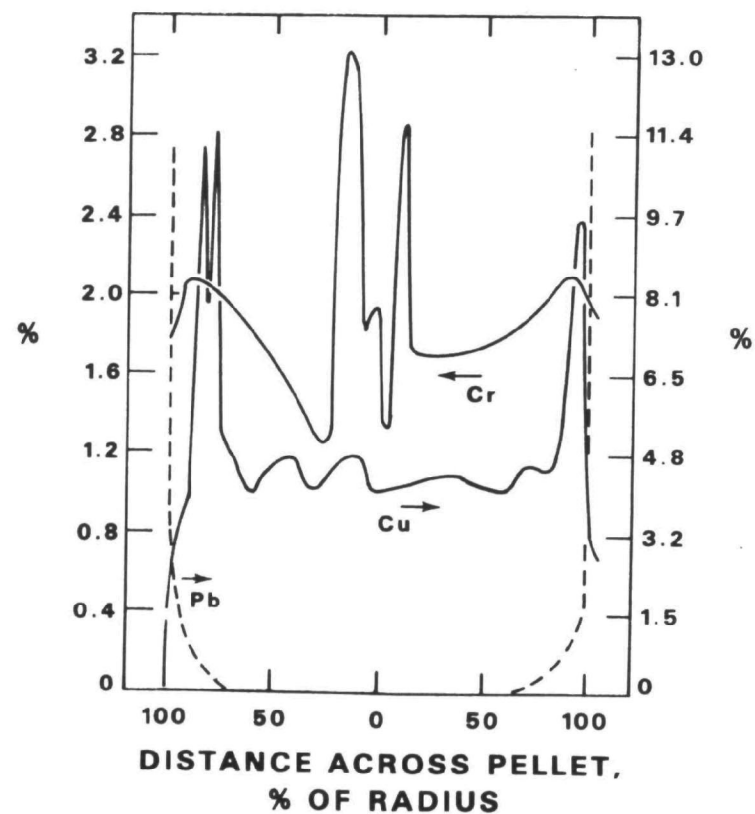


Fig. 5-4. NO_x Catalyst ($\text{CuO}/\text{Cr}_2\text{O}_3$) Pellet Composition Profile (Upon De-Activation with Motor Mix in the Fuel) (from Ref. 5-3)

NO_x catalysts of this type will require the use of unleaded gasolines exclusively.

A comparative study of a number of catalysts (Ref. 5-2) showed that in the case of a palladium/alumina (Pd/Al₂O₃) catalyst, the efficiency for HC oxidation was 62 percent for an unleaded catalyst and 42 percent for the leaded catalyst (equivalent to approximately 10,000 miles of road use). For CO oxidation, however, there was no deleterious effect of lead; that is, the conversion figure remained at 97 percent. This is inconsistent with other data denoting the effects of lead on catalyst conversion efficiency.

Laboratory test data for noble metal and transition metal oxide catalysts are presented in Figs. 5-5 to 5-8 (Ref. 5-4). Catalyst BH (Fig. 5-5) has been evaluated with low-lead (0.5 gm/gal) fuel. As indicated, this catalyst retained sufficient activity to meet IIEC goals for at least 50,000 miles. It should be noted that the IIEC goals represent higher emission levels than the Federal standards for 1975-76.

Transition metal oxide catalyst data are shown in Figs. 5-6 through 5-8. Catalyst G is similar to catalyst BH except it is smaller in diameter. It has been evaluated with leaded, low-lead, and unleaded fuels. The data and model predictions indicate that this catalyst will stay below IIEC HC and CO emission levels for 50,000 miles with unleaded fuel, about 15,000 miles with low-lead fuel, and about 6000 miles with fully leaded fuel.

Catalyst AJ is an improved, extruded version of the composition used in Catalyst G. Again, increased performance is noted with decreasing lead level.

Catalyst BI is also a transition metal oxide catalyst similar to Catalyst AJ; however, an additional transition metal oxide component was added to further improve catalyst stability. As shown in Fig. 5-8, similar trends are observed.

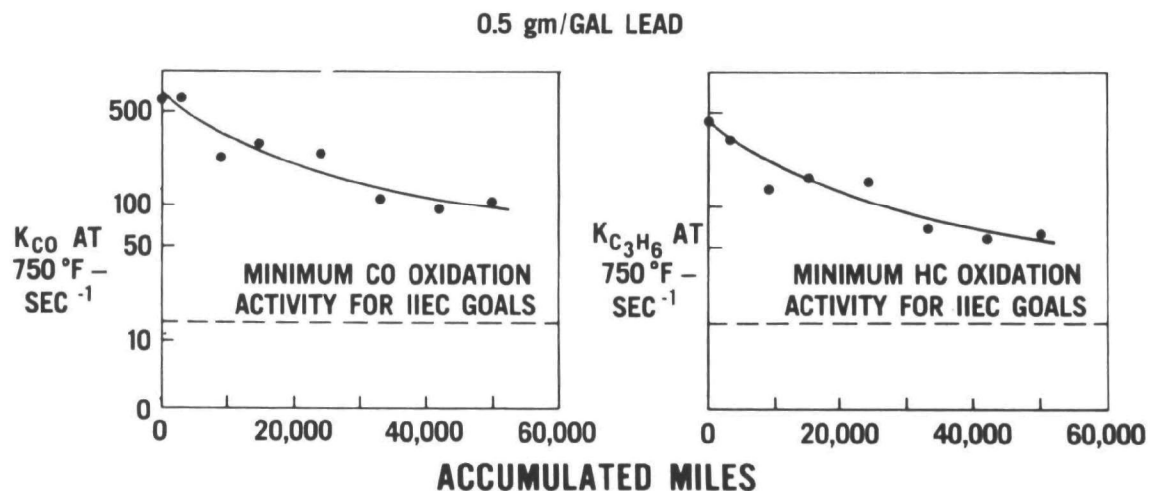


Fig. 5-5. Effect of Lead Content in Fuel on Catalyst Type "BH" Oxidation Activity (from Ref. 5-4)

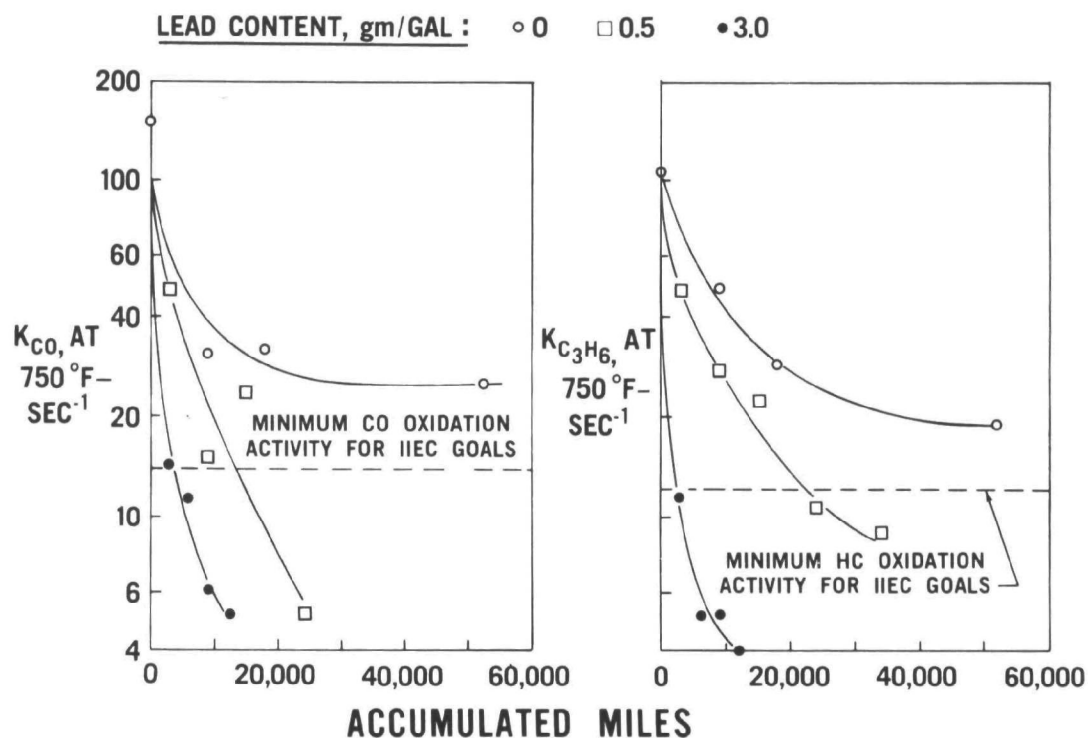


Fig. 5-6. Effect of Lead Content in Fuel on Catalyst Type "G" Oxidation Activity (from Ref. 5-4)

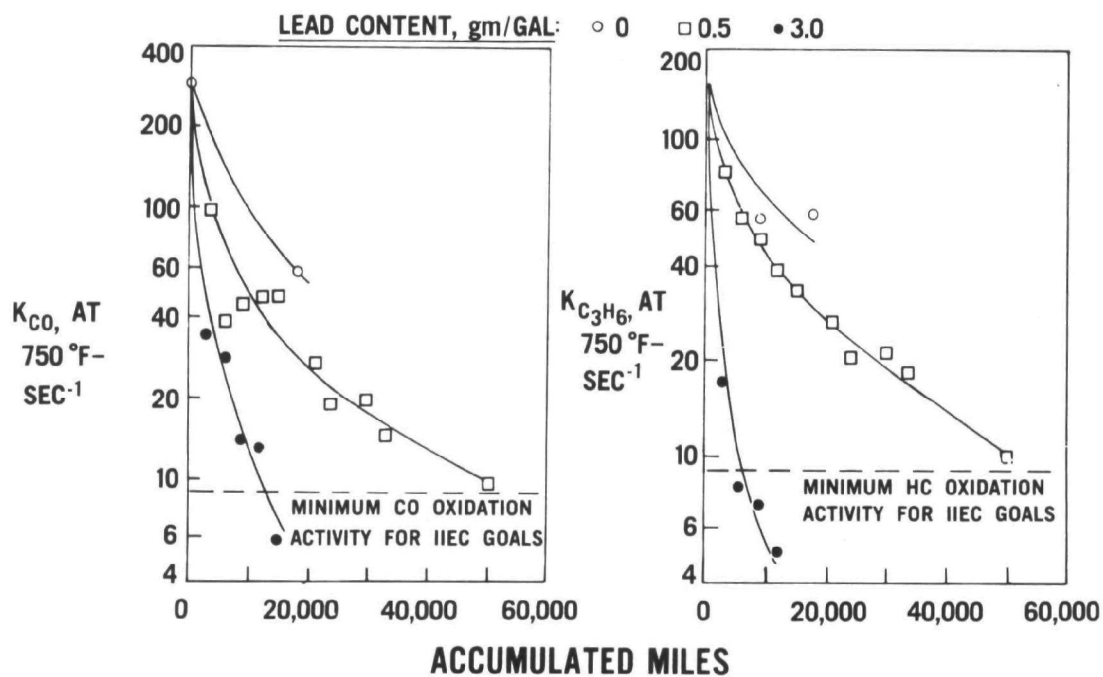


Fig. 5-7. Effect of Lead Content in Fuel on Catalyst Type "AJ" Oxidation Activity (from Ref. 5-4)

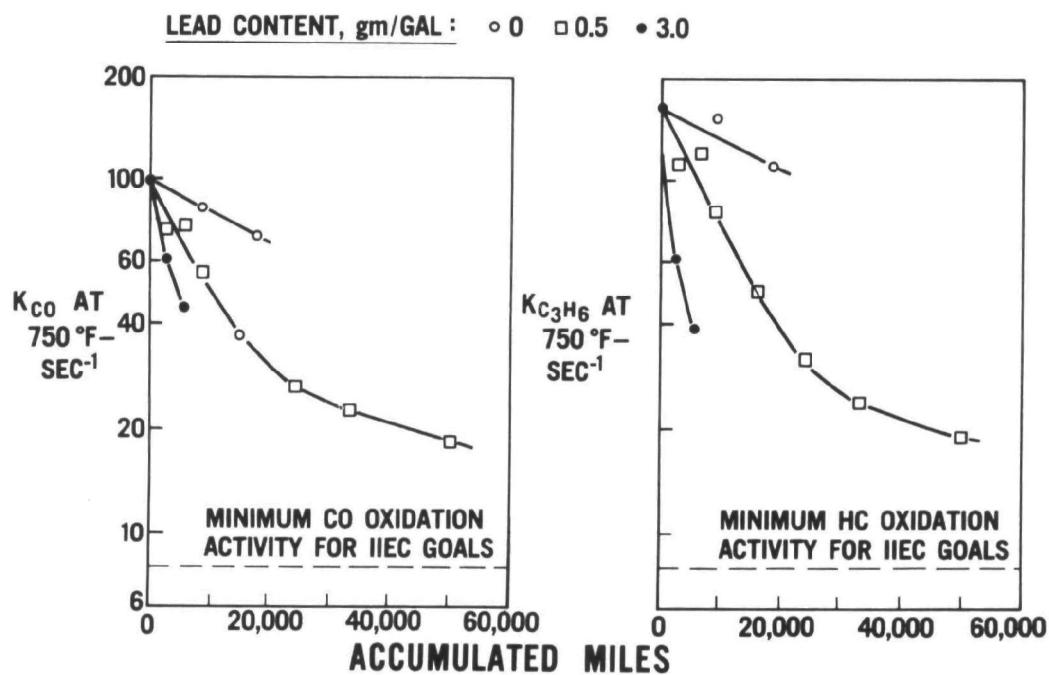


Fig. 5-8. Effect of Lead Content in Fuel on Catalyst Type "BI" Oxidation Activity (from Ref. 5-4)

Some catalyst manufacturers are pursuing the development of lead-tolerant catalysts. Although some success has been reported, test data are not available in sufficient quantity and under the appropriate vehicle operating conditions to present an evaluation of these systems at this time.

It is emphasized that the foregoing are projections of catalyst performance; vehicle tests which simulate typical customer vehicle usage are necessary to verify these predictions and establish catalyst durability.

5.1.1.2 Vehicle Tests

Catalyst half-life data obtained by Ford from a fleet test program are shown in Fig. 5-9 (Ref. 5-5). As indicated, catalyst half-life decreases with increasing lead content in the gasoline. American Cyanamid fleet tests (Ref. 5-6) showed similar trends.

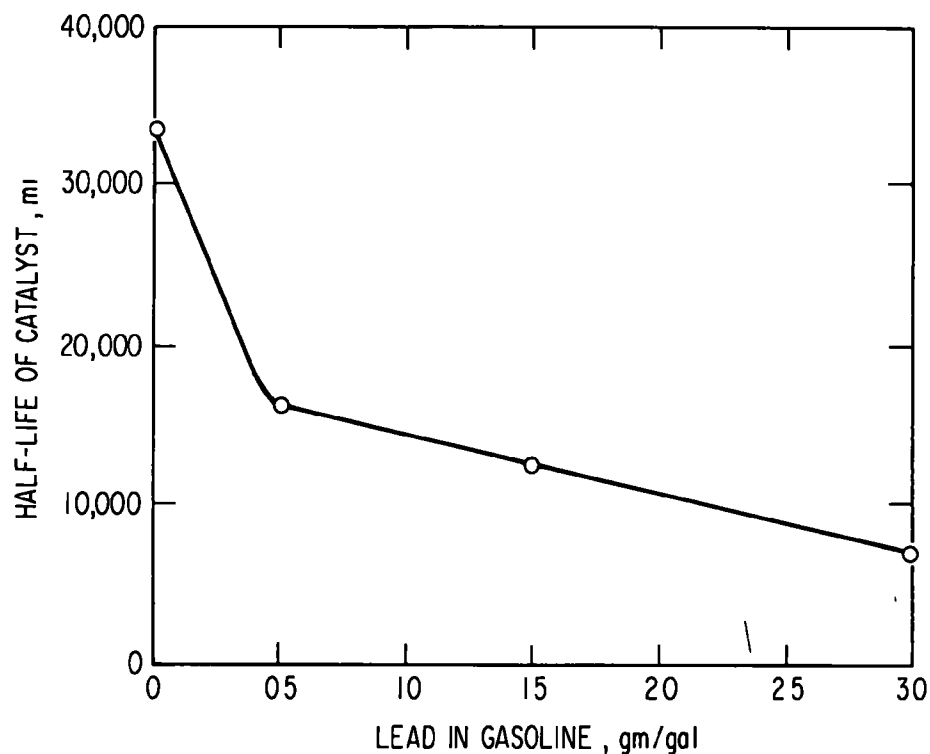


Fig. 5-9. Effect of Lead on Catalyst Life (from Ref. 5-5)

Data obtained from Universal Oil Products Company (UOP) are shown in Fig. 5-10 (Ref. 5-7). Catalyst conversion efficiency decreases very rapidly with leaded fuel and very little when unleaded fuel is used.

Ford (Ref. 5-5) has conducted a road test program on a $\text{CuO/V}_2\text{O}_5$ catalyst to determine the effects of TEL on HC and CO oxidation effectiveness.

About 18,000 road miles were accumulated for four pairs of cars, using 0.05, 0.5, 1.5, and 3.0 ml/gal of TEL, respectively. HC conversion was adversely affected by the presence of TEL in the fuel, and the half-life for HC conversion was estimated to be 33,000 miles for unleaded fuel and 7500 miles for fuel having a concentration of 3 ml/gal of TEL. However, CO conversion efficiency was the same for leaded and unleaded fuels.

The average efficiency based on a cold start is shown in Fig. 5-11. The curves clearly illustrate the detrimental effect of TEL in the fuel. Similar results were obtained at 30-mph cruise (Fig. 5-12). Because these data were taken with a hot catalyst bed, the initial HC conversion efficiency of the catalyst was higher.

The average amounts of CO removed during cold start tests are indicated in Fig. 5-13. Although the efficiency gradually deteriorated from the initial 80 percent value, there are no trends to indicate a lead effect on the rate of deterioration.

Data published by Ford (Ref. 5-8) are presented in Figs. 5-14 and 5-15 which show the results obtained on the 302 CID engine group, in which two vehicles were operated on fuel containing 3 ml/gal of TEL and two on commercially available unleaded fuel over similar driving cycles with base metal catalysts on alumina support.

Figures 5-16 and 5-17 show the results obtained on the 390-428 CID engine groups, in which two vehicles were operated on leaded fuel and two on unleaded fuel. Both engine groups, when operated on unleaded fuel, have

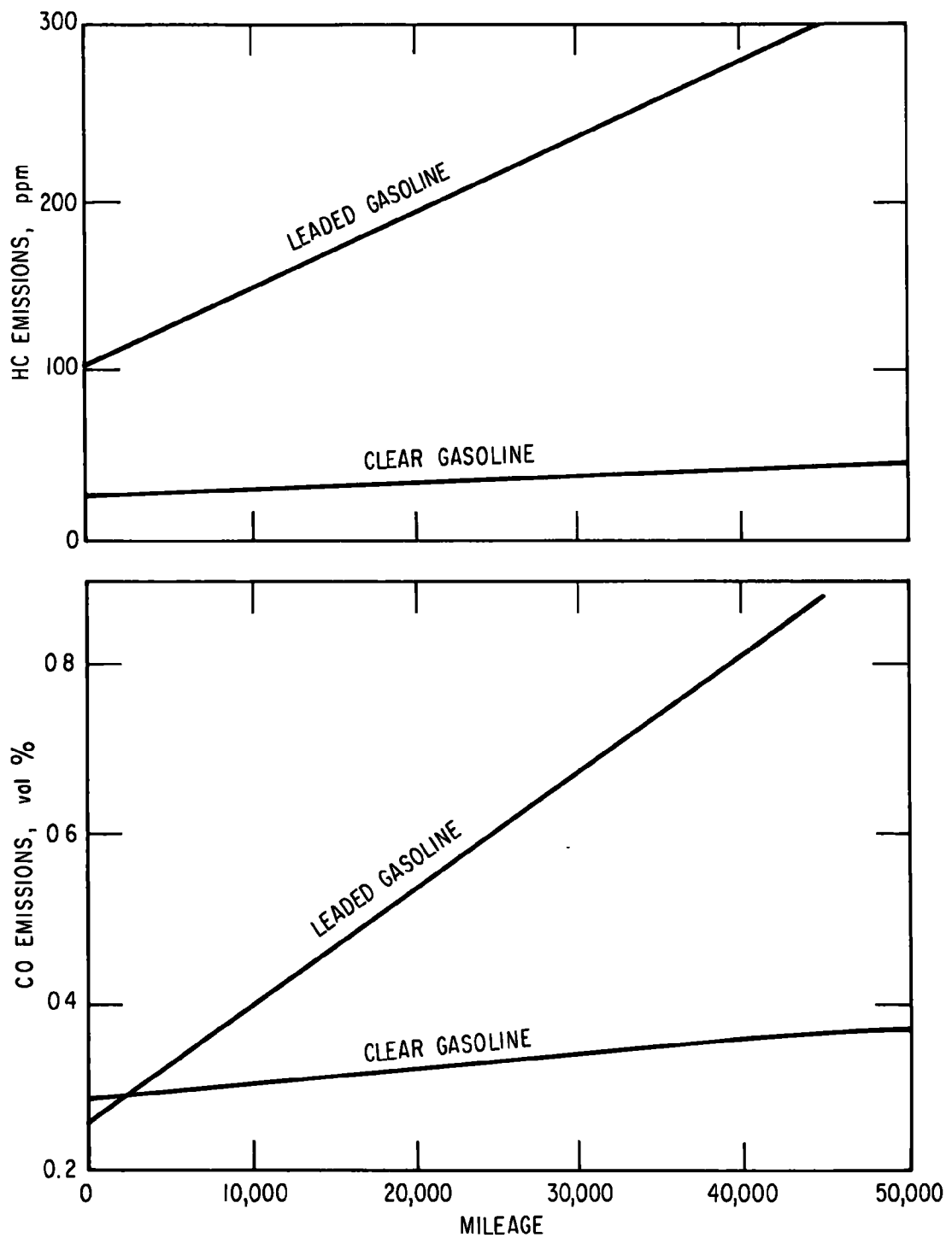


Fig. 5-10. Typical Vehicle Emissions with a Catalytic Converter
(from Ref. 5-7)

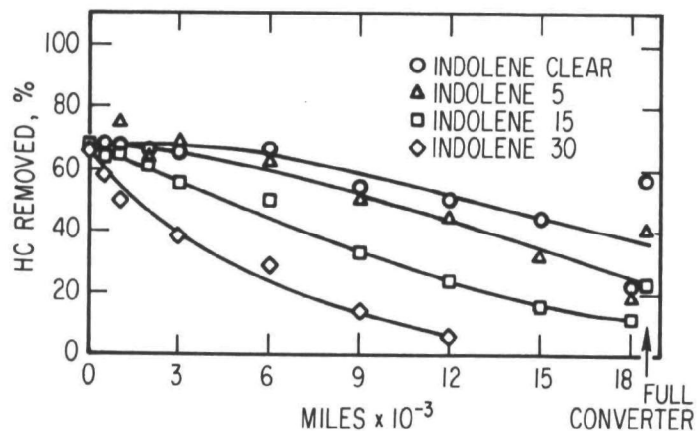


Fig. 5-11. Catalyst Efficiency-- Cold Start NDIR HC Data (Average of Two Vehicles) (from Ref. 5-5)

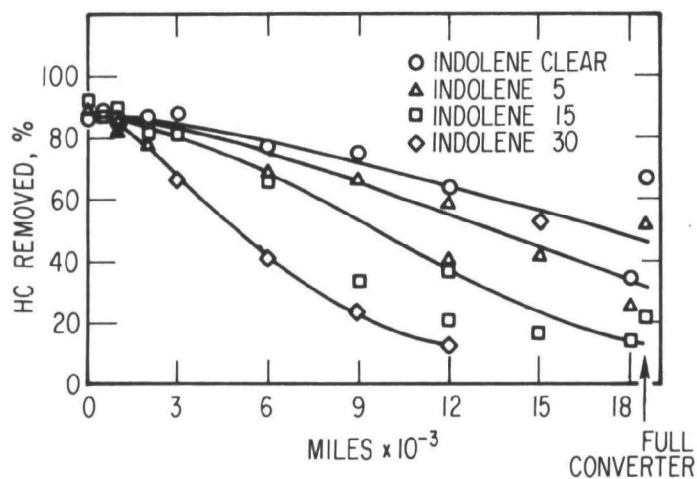


Fig. 5-12. Catalyst Efficiency-- Cruise 30 FID HC Data (Average of Two Vehicles) (from Ref. 5-5)

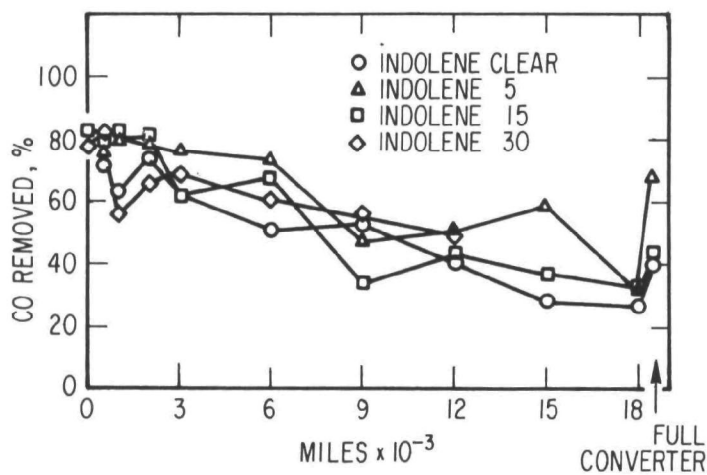


Fig. 5-13. Catalyst Efficiency-- Cold Start CO Data (Average of Two Vehicles) (from Ref. 5-5)

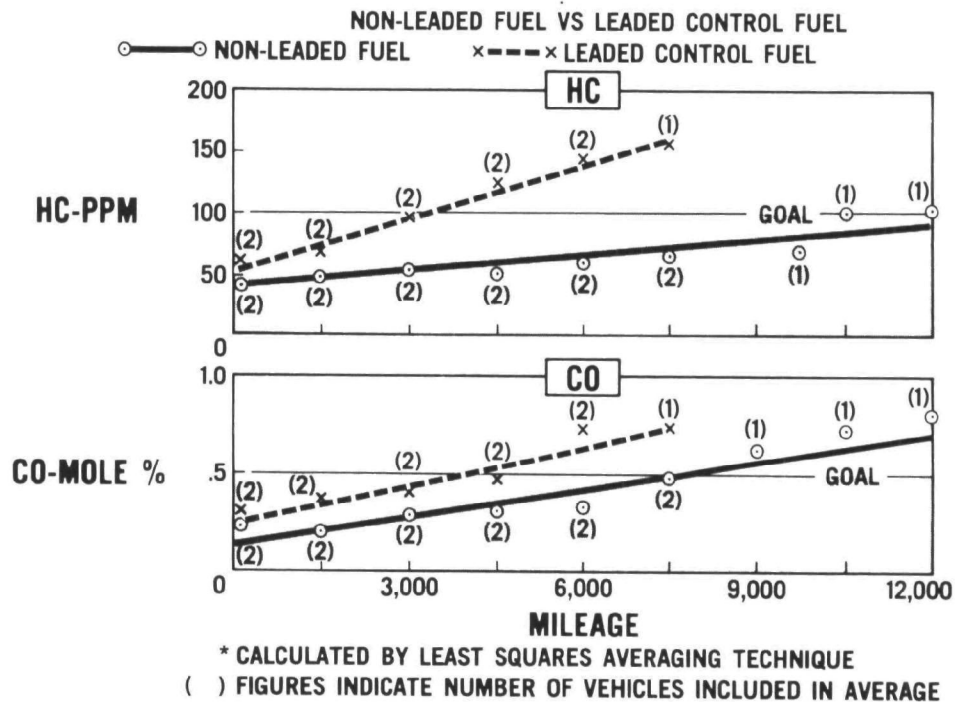


Fig. 5-14. Ford 24-Car Fleet Tailpipe HC/CO Emissions* (302 CID Engine) (from Ref. 5-8)

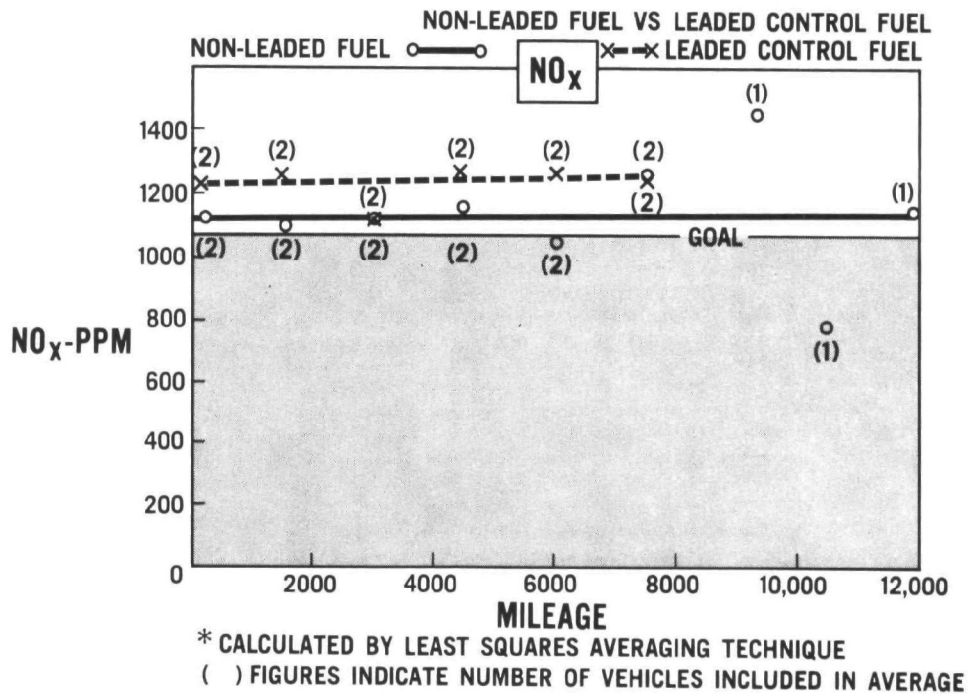


Fig. 5-15. Ford 24-Car Fleet Tailpipe NO_x Emissions* (302 CID Engine) (from Ref. 5-8)

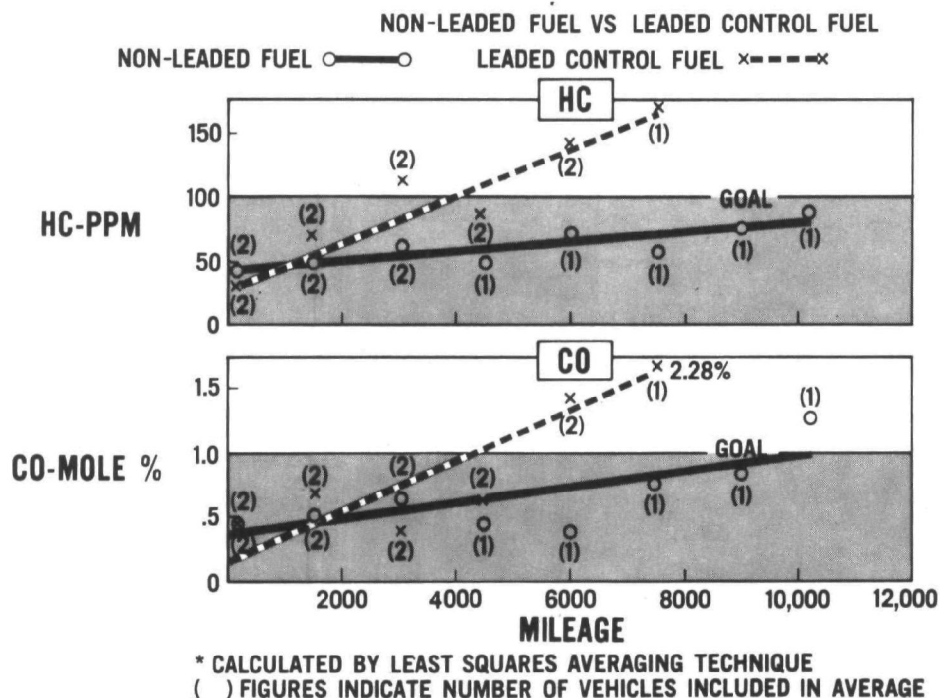


Fig. 5-16. Ford 24-Car Fleet Tailpipe HC/CO Emissions*
(390 and 428 CID Engines) (from Ref. 5-8)

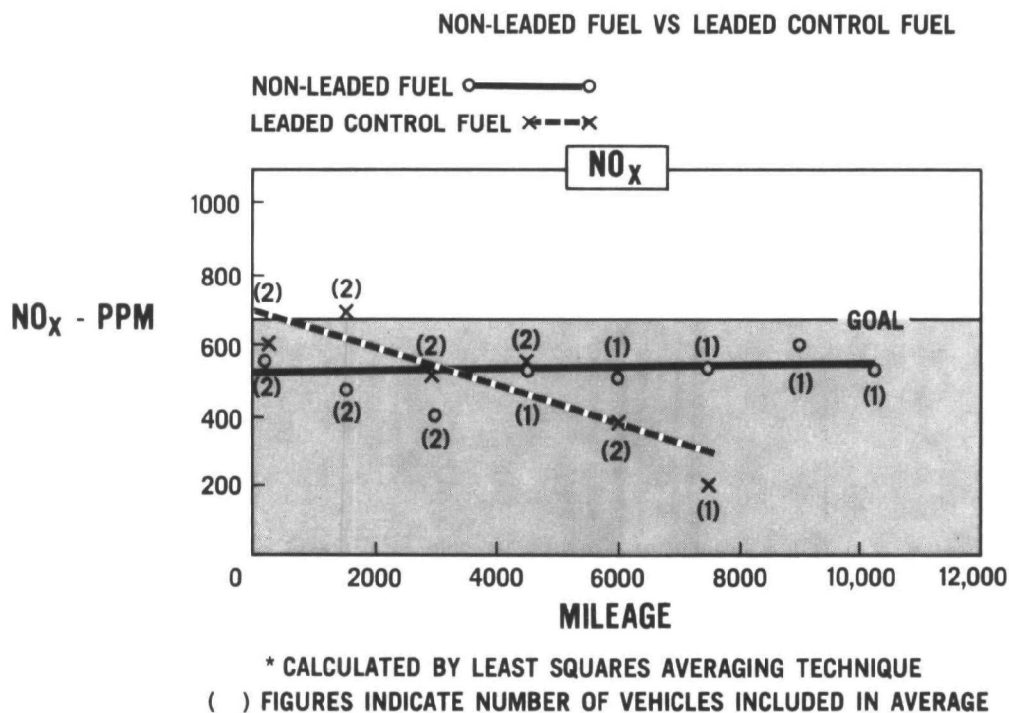


Fig. 5-17. Ford 24-Car Fleet Tailpipe NO_x Emissions*
(390 and 428 CID Engines) (from Ref. 5-8)

better emission control compared with the vehicles on leaded fuel. The findings are essentially in agreement with previous Ford fleet testing (Ref. 5-5). It should be noted (Fig. 5-17) that NO_x reductions for leaded gasoline show anomalous results because of unscheduled carburetor enrichment due to filter clogging.

Other evidence for the deleterious effects of lead is indirect. Schwochert (Ref. 5-9) reports excellent results with a supported noble metal catalytic converter tested with unleaded fuel. At the end of a 50,000-mile road test, HC and CO conversion efficiencies of approximately 70 percent were obtained. This represents better performance than noted elsewhere for leaded gasoline.

5.1.2 Maximum Allowable Lead Levels

The available data with respect to lead additives in gasoline and their effect on catalytic converter performance and durability indicate that lead levels of 0.5 gm/gal and greater would have deleterious effects and that vehicles with such emission control devices would be unable to meet emission standards after extremely short operational times. It has been stated by some of the automakers that one tankful of fuel containing 3 gm/gal of lead would severely harm the catalyst system. A catalyst manufacturer has stated that, based on its test experience, one tankful of 3-gm/gal leaded fuel would be very deleterious if the catalyst had been operated for extended mileage, but that this effect would not be immediately apparent when the catalyst was fresh (zero mileage conditions). In any event, it is clear that even one tankful of gasoline could greatly shorten the durability capability of catalysts for meeting emission standards. Similarly, all automakers and domestic catalyst manufacturers state that the use of 0.5-gm/gal leaded fuel on a continuous basis is unacceptable.

All the available data indicate that unleaded gasoline is required for emission control systems using catalytic converters that would also have acceptable durability characteristics to meet the emission standards of 1975-76.

Unleaded gasoline, however, does contain very small amounts of lead resulting from current (and foreseeable) refinery and distribution practices. Therefore, it is very important to have specifications that limit the maximum permissible amount of lead in unleaded gasoline. The American Society for Testing and Materials (ASTM) has under consideration a proposed revision to their standard specifications for gasoline (ASTM Designation: D 439-70) in which they have selected the value of 0.07 gm/gal of lead for unleaded gasoline. This value, which is not official at this time, was influenced in part by the level given in Interim Federal Specification VV-G-001690 (Army-MR). This specification defines unleaded gasoline as follows:

Unleaded gasoline shall be defined as gasoline to which the addition of lead compounds is not permitted. Lead compounds present shall not exceed that amount which results from contamination when good refinery and distribution practices are followed, and shall not exceed 0.07 gm/gal.

This Federal specification was developed by Army representatives and a task force which included representatives from petroleum and automotive companies.

It should be noted, however, that with respect to catalyst performance and durability, most of the data available for unleaded gasoline did not identify the precise level of lead contained in the gasoline. The automakers and catalyst manufacturers have stated that their experimental work has been done with unleaded gasoline containing lead in the range of about 0.02-0.06 gm/gal, and that most of the development work was with lead levels of 0.02-0.03 gm/gal. It was difficult to ascertain that any data are available for lead levels between 0.06 and 0.5 gm/gal.

Since the proposed ASTM maximum level of 0.07 gm/gal of lead was apparently based on refinery and distribution considerations, rather than catalyst life considerations, it would appear that this specification bears further investigation to ensure that the lead content is reduced to that amount which is

compatible with obtaining a 50,000-mile useful lifetime. In this connection, many of the automakers and catalyst manufacturers have stated that the ASTM value of 0.07 gm/gal is probably too high. Some of the automakers have expressed opinions that on the basis of limited data 0.05 gm/gal may be a reasonable limit. Engelhard (Ref. 5-22) has stated that, based on the performance data with its catalyst, the maximum lead content in gasoline should be 0.03 gm/gal. Ford (Ref. 5-23) stated that although they did not have an accurate quantitative answer with respect to the maximum lead level for acceptable catalyst life, the Engelhard limit of 0.03 gm/gal might be reasonable.

It should also be emphasized that at the lead levels of unleaded fuels used, no automaker has stated to date that 50,000 miles of operation at satisfactory emission levels has been achieved. It is not known whether this durability/lifetime deficiency is related to the lead level (0.02-0.03 gm/gal), to other trace elements in the gasoline, or to other catalyst properties.

As can be seen from the above, substantive data to precisely determine the maximum permissible lead content compatible with catalytic converters are not available. In order to establish a meaningful maximum lead level, the characteristics of durability versus lead content must be established for catalysts capable of meeting the 50,000-mile requirement. The maximum lead level selected should also consider the feasibility and economics of providing gasoline at this lead level.

5.1.3 Summary

Fleet and laboratory test data show that HC and CO conversion efficiencies of base metal catalysts are adversely affected by the presence of TEL in the fuel.

It was found that scavengers in the fuel contribute significantly to deactivation via depletion of the active component from the surface of the catalyst. The rate of deactivation increases with increasing amounts of TEL in the fuel.

Substantive data to establish an upper lead level compatible with catalytic converters are not available.

5.2 THERMAL REACTORS

This section summarizes the relevant experimental data illustrating the effects of lead additives on thermal reactors. The data base for the discussion includes vehicle testing by Du Pont and by Ethyl, and laboratory material studies conducted under the IIEC Fuel Composition Effects Project and the NASA/Lewis Materials Evaluation program.

5.2.1 Erosion/Corrosion Effects

Thermal reactor durability or effective lifetime may be significantly affected by erosive and/or corrosive deterioration caused by the presence of lead compounds in the exhaust gas. The problem has been the subject of recent intensive investigations. The symptoms of erosion are generally exhibited as a deterioration of the baffles and reactor core surface in localized areas opposite the valve ports. Du Pont (Ref. 5-10) has analyzed the erosive behavior of a number of thermal reactor material candidates with various fuels. Its study has shown that erosion is chemical rather than mechanical in nature and is affected by TEL. Of the alloys tested, Uniloy 50/50 (50 percent Cr, 50 percent Ni) was found to be the most resistant to attack. Uniloy 50/50 erosion rates are regarded by Du Pont as being acceptable for normal passenger car service. Since the thermal reactor erosion tends to be localized, Du Pont proposes to insert small patches of Uniloy 50/50 at the erosion points and use a less expensive material for the reactor core.

Du Pont (Ref. 5-10) concludes that the mechanism of corrosion is primarily oxidation and that the presence of phosphorus in the fuel accelerates corrosive attack (Fig. 5-18). Inconel 601 and Armco 18 SR were determined to be promising corrosion-resistant materials for reactor applications.

Fuel composition effects on thermal reactor durability were investigated in an IIEC materials evaluation program (Ref. 5-11). The materials tested (as core specimens in a vehicle reactor) included ferritic (nickel-free) and

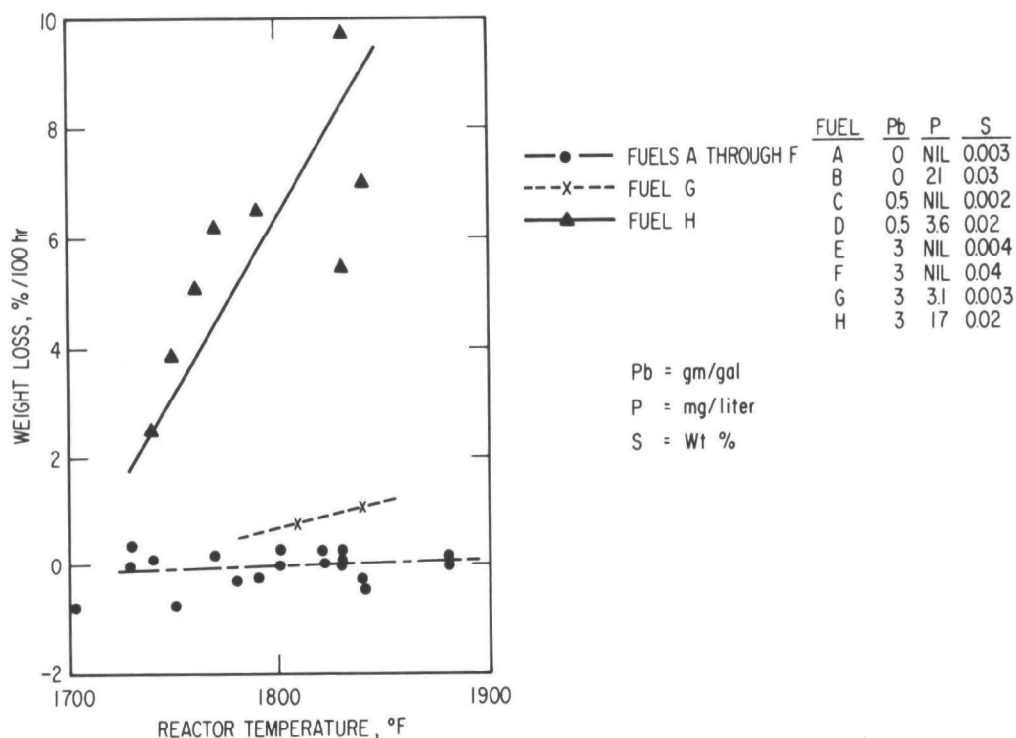


Fig. 5-18. Effect of Fuel Additives on Corrosion Weight Loss of Inconel 601 (from Ref. 5-10)

austenitic stainless steels, high-nickel alloys, and various coatings on low-cost materials. Tests of OR-1, a low-cost nickel-free alloy candidate, showed that with leaded fuel, halides and phosphorus contribute heavily to metal deterioration at elevated temperatures (Fig. 5-19). Leaded gasoline without phosphorus showed considerably less erosion. Thus, the halides and phosphorus are major contributors to material loss. The OR-1 material, as well as other low-cost candidates, exhibited good corrosion resistance with low-lead (0.5 gm/gal) or unleaded fuels. On the basis of these and other similar results, the study concluded that operation with unleaded or low-lead fuels was required to achieve satisfactory reactor life. Accordingly, 0.5-gm/gal fuel was used in all of the Ford/IIEC durability vehicle test work. The low-cost alloy steels, however, were ultimately rejected for reactor use

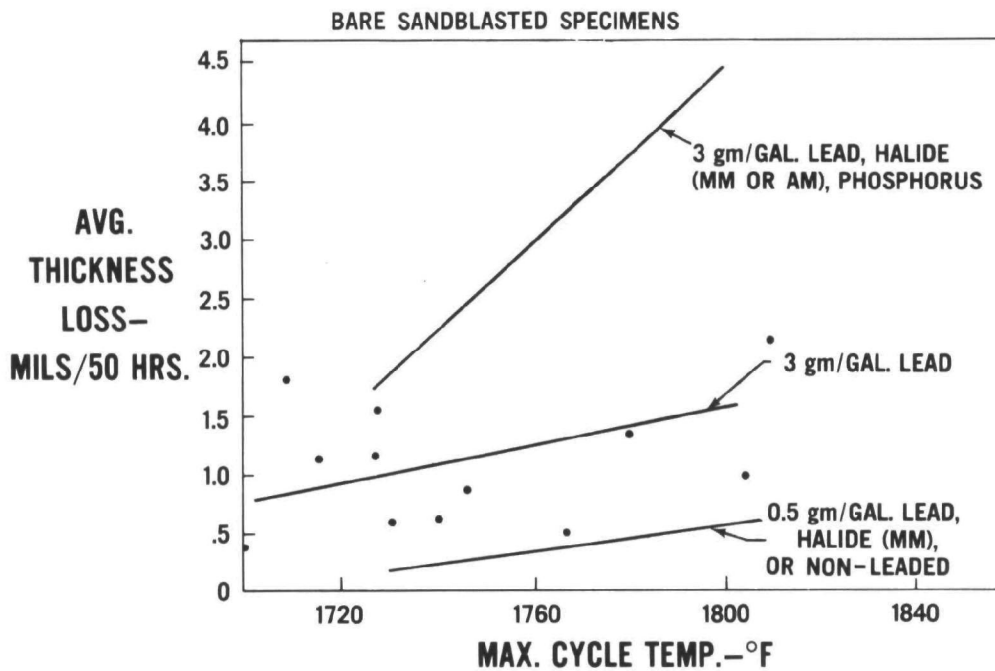


Fig. 5-19. Effect of Fuel Variables on Average Thickness Losses of OR-1 Alloy During Continuous Thermal Cycling (from Ref. 5-11)

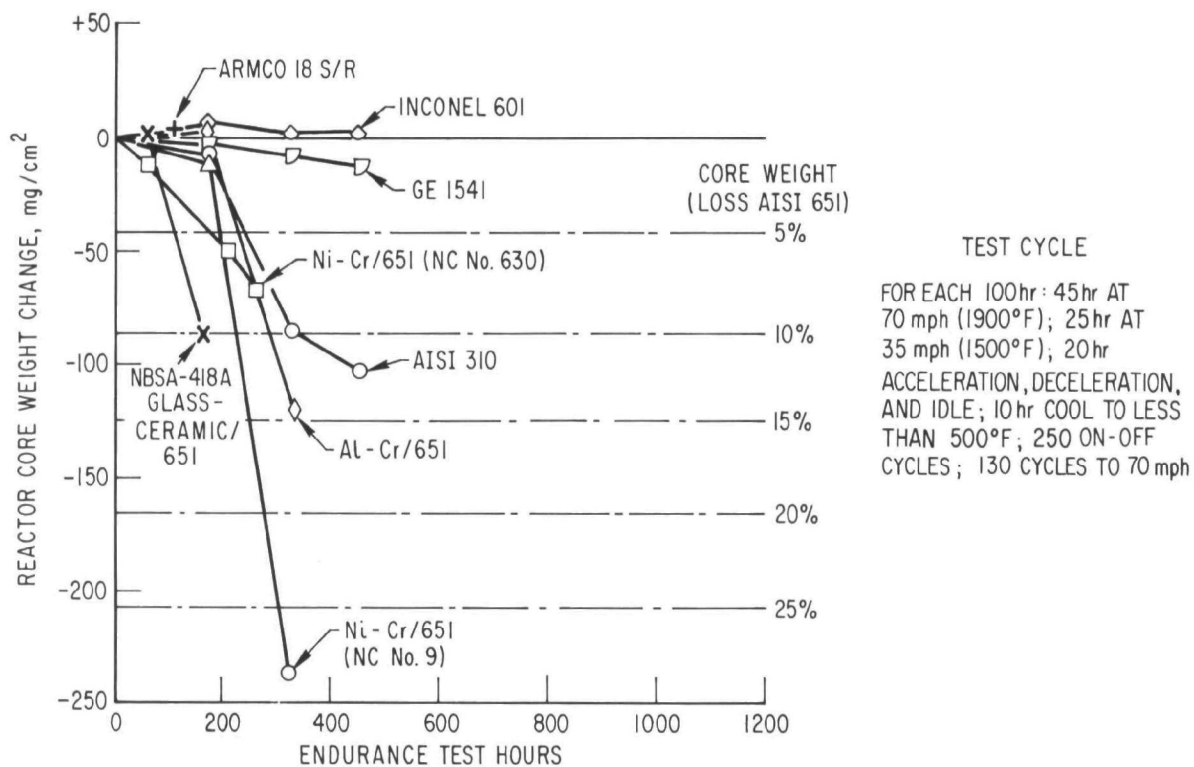


Fig. 5-20. Weight Change of Test Reactor Cores in Engine Dynamometer Endurance Test (from Ref. 5-12)

because of poor high-temperature strength. The most promising reactor materials were all intermediate-cost nickel-alloy steels.

The NASA/Lewis Research Center has been conducting a thermal reactor materials evaluation and development program for EPA (Ref. 5-12). Coupon screening, core testing, and full-scale thermal reactor endurance testing (by Teledyne-Continental) have led to the identification of two materials which appear to be suitable for rich reactor operation with leaded fuels. These are GE 1541 (15 Cr-4Al-1Y) and Inconel 601. Armco 18 SR may also be a candidate.

Recently, the fuel used for endurance testing in the NASA program was switched from leaded to unleaded gasoline. No change in the weight loss of GE 1541 or Inconel 601 was observed (Ref. 5-12). However, lead effects may have been encountered with Dow-Corning 9458, a glass-ceramic core material candidate which blistered and spalled in coupon testing using leaded gasoline. When this material was tested in a core configuration using unleaded gasoline, no deleterious effects were observed. Endurance test results for various thermal reactor material candidates are shown in Fig. 5-20.

The available data on materials testing with leaded fuels indicate that corrosion effects due to lead halides and/or phosphate compounds in the exhaust are temperature related. Figure 5-19, for example, suggests that, at temperatures approaching 1700°F, corrosive weight loss rates are not sensitive to fuel composition. There is, therefore, a rational basis for the Ethyl claim that the lead composition of fuel has no impact on the Ethyl Lean Reactor, which operates at temperatures below 1700 °F even under high-speed turnpike conditions (Ref. 5-13). Ethyl has found that 430 stainless steel (with zero nickel content) has a useful life in their lean reactor of about 30,000 miles of road service. The same material has a life of only 17 hours when tested on the dynamometer at 100-mph vehicle speed with retarded spark to increase temperature. Under the same dynamometer conditions, a duplicate reactor

fabricated of 310 stainless steel (20 percent nickel) showed no deterioration for more than 200 hours (equivalent of 20,000 miles). Therefore, Ethyl concludes that 310 stainless steel should provide a tenfold improvement over the 30,000-mile road service obtained with 430 stainless steel.

5.2.2 Emission Level Effects

Test data published by Du Pont (Ref. 5-10) show that lead has no effect on the emissions of the Du Pont reactor. A 1970 Du Pont reactor vehicle (350 CID Chevrolet of the type supplied to CARB) with 17,000 miles of operation using conventional leaded gasoline was cleaned (combustion chamber deposits removed) and equipped with new plugs and points. The car was then operated for 6000 miles with unleaded gasoline on a chassis dynamometer. Emission tests conducted before and after operation with unleaded fuel produced the results plotted in Fig. 5-21. Du Pont regards these data as proof that operation with or without leaded fuel has no significant effect on thermal reactor emission levels. This is supported by additional test data from a Du Pont Type I reactor which was operated for 100,000 miles with leaded gasoline. A small increase in HC emissions (10 percent) and CO emissions (20 percent), compared with the initial values, was observed. Diagnostic tests by Du Pont indicated that these minor effects were due primarily to changes in carburetor metering. It is noted that data reported by CARB in the Du Pont reactor vehicle fleet test program show slightly increasing HC, CO, and NO_x emissions with mileage accumulation.

5.2.3 Summary

Lead has been shown to enhance, by varying degrees, the corrosion of a number of alloys. The effect of lead in thermal reactors is that of being one more detrimental factor over and above the already severely corrosive environment.

Based on laboratory data, leaded fuels with a TEL content of up to 0.5 gm/gal do not significantly increase the rate of corrosion of the better oxidation-resistant materials above that obtained with unleaded fuels.

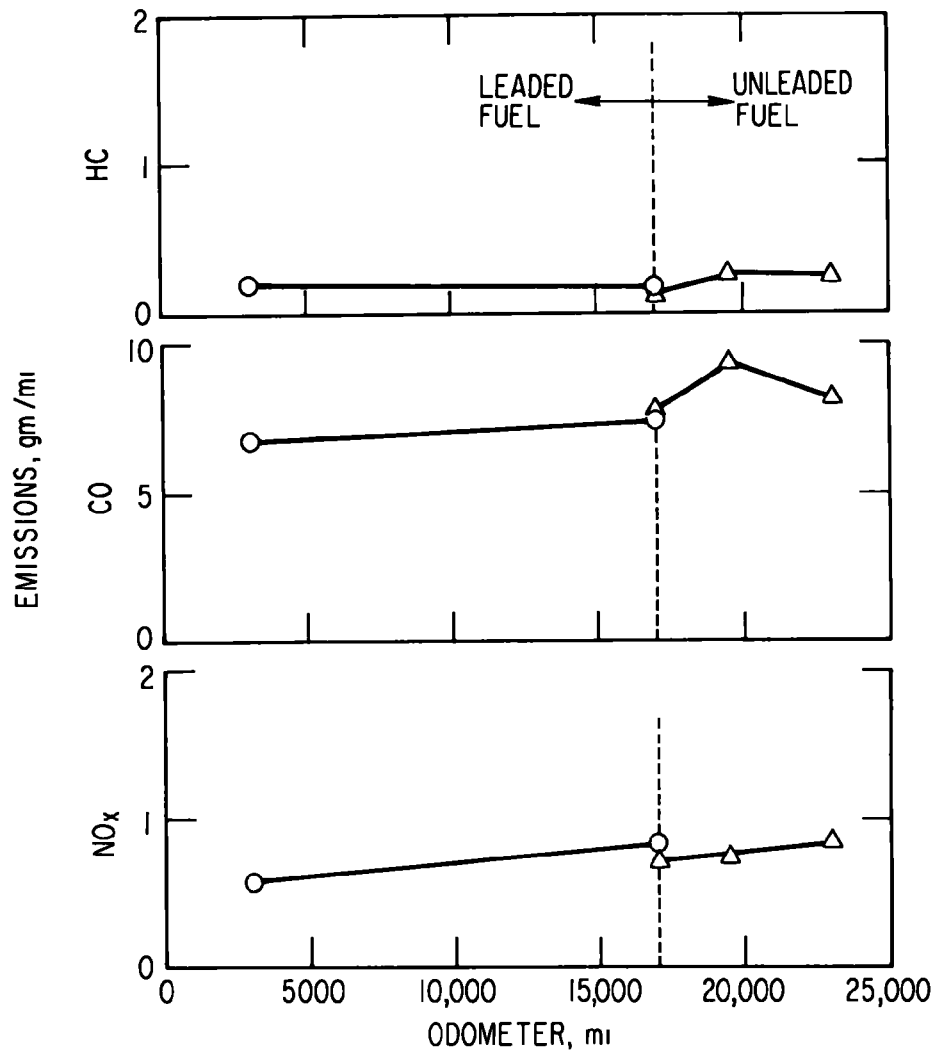


Fig. 5-21. Du Pont Type V Thermal Reactor--HC, CO, and NO_x Emissions with Leaded and Unleaded Fuel (from Ref. 5-10)

Some alloys should be able to meet the 100,000-mile durability requirements. However, as this degree of durability has not yet been achieved without material failures, with or without lead, firm conclusions must await further testing.

It appears that the durability requirements could be met with the Ethyl Lean Reactor using leaded fuel.

Fuel composition may have a significant effect on reactor material durability at the temperature levels associated with rich reactor operation. High-nickel-content alloys appear to be required in order to achieve satisfactory durability. The combined presence of lead and phosphorus additives has an accelerating influence on the corrosive deterioration of a number of different metallic alloys.

5.3 EXHAUST GAS RECIRCULATION (EGR) SYSTEMS

With the exception of the RTR Alone, RTR plus NO_x Catalytic Converter plus RTR, and Tricomponent Catalytic Converter concepts, all generic emission control system approaches described in Section 4.3 utilize EGR for some measure of NO_x control.

All of the available data relating to potential effects of lead additives in gasoline on EGR systems are experimental in nature. Therefore, this section will briefly summarize the more significant findings to date and the projected plans for EGR systems in this regard.

5.3.1 Relevant Technology Discussion

Nearly all of the reported test data were based on the use of fully leaded gasoline (exceptions noted below). No low-lead (0.5 gm/gal) data were available.

The most significant data base for EGR system durability effects is the extended-use program conducted by Esso (Ref. 5-14) for NAPCA. In this test program, an EGR system previously developed (Ref. 5-15) was evaluated on three 1969 Plymouths and three 1969 Chevrolets over 52,000 miles under city-surburban driving conditions simulated on a tape-controlled mileage accumulation dynamometer. No major problems were reported. There was no decrease in NO_x reduction efficiency over the 52,000 miles. Engine wear and cleanliness were considered normal for the mileage and driving regime. In addition, the EGR system was found to be compatible with commonly

employed air injection and engine modification systems used for HC and CO control.

In the aforementioned Esso EGR extended-use program with a fully leaded fuel, it was noted that throttle plate deposits occurred. Analysis of the deposits indicated the main components were lead chlorides and lead bromides. Despite the throttle plate deposits with leaded fuel, however, the NO_x control effectiveness was unaffected. Control tests of a vehicle with unleaded fuel indicated essentially no throttle plate deposits.

Ford (Ref. 5-16) has published data (shown as Fig. 5-22) which indicate that the use of leaded fuel does lead to decreased EGR system efficiency. It is stated that deposits affect flow characteristics by changing critical dimensions or by preventing control valve seating (thereby altering the programmed rate of recycle flow and changing the NO_x reduction efficiency).

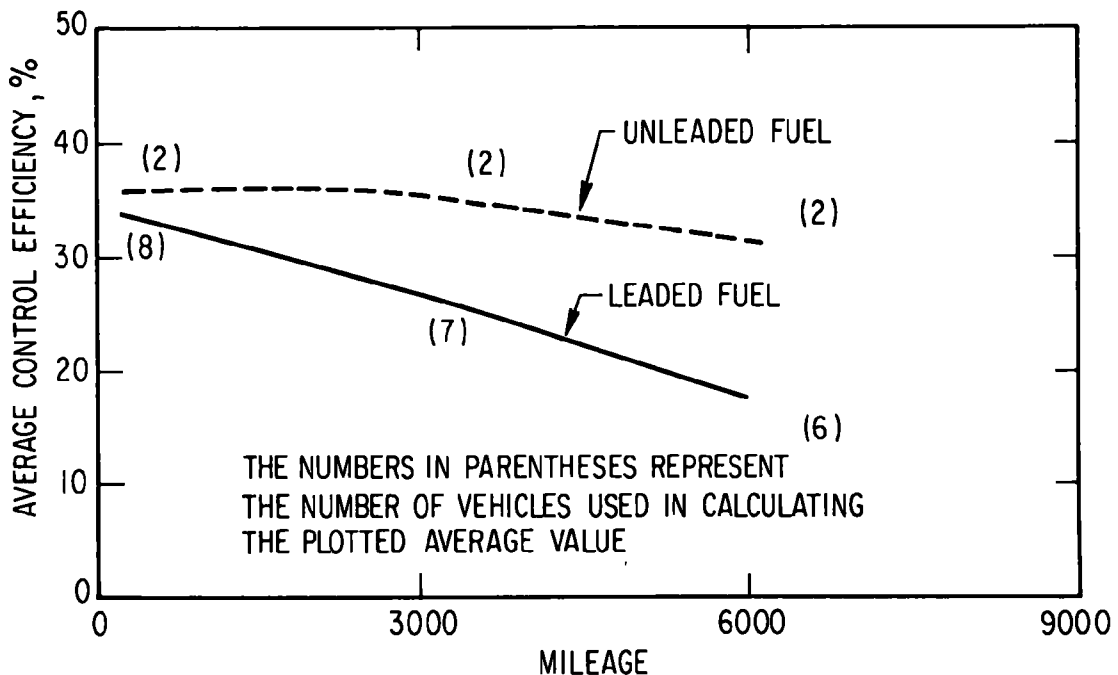


Fig. 5-22. Effect of Leaded Fuel on the Control Efficiency of Air Cleaner EGR Systems (302 CID Engine)
(from Ref. 5-16)

The Esso EGR tests utilized above-the-throttle recycle injection with rather large (approximately 1/2 inch) flow orifices for approximately 15-17 percent EGR flow rate. The orifice size in the Ford air-cleaner injection systems (Fig. 5-22) is not stated in the reference.

The limited amount of test data in Ref. 5-14 pertaining to EGR NO_x reduction in the same vehicle, using both leaded and unleaded gasoline, indicates the same nominal level of NO_x reduction for both fuels.

5.3.2 1973-74 EGR Systems

During visits by The Aerospace Corporation to General Motors, Ford, Chrysler, and American Motors (Refs. 5-17 to 5-20), all four companies stated that EGR was necessary and would be employed to meet the 1973-74 emission standards for NO_x (3 gm/mi).

There was a general consensus that lead could cause deposit and life problems in the EGR system. The degree of the effect would be dependent upon the EGR tap-off location and injection orifice size used, i.e., the smaller the hole size the more likely clogging could or would occur.

Ford referred to previously published data (Fig. 5-22, from Ref. 5-16) which indicated a decrease in effectiveness to 0.15 at 6000 miles from 0.35 initially when a leaded fuel was used (7 to 10 percent EGR flow rate).

American Motors expects to use approximately 10 percent EGR in 1973 for most models, particularly with V-8 engines and/or large vehicles. Its current test information shows that this results in a substantial increase in intake manifold, EGR system, combustion chamber, and exhaust valve seat deposit buildup. The deposit is presumed to be largely lead, although its exact composition has not been identified. The deposit may be responsible for the increased tendency to burn exhaust valves, increased valve leakage, and EGR system plugging. It is felt that these problems are proportional to the amount of lead additive in the fuel at a given recirculation rate. These severe problems of deposit buildup were only identified by American Motors.

5.3.3 1975-76 EGR Systems

It appears that in general (Refs. 5-17 to 5-20), the 1975-76 EGR systems will be similar to those finally selected for the 1973-74 cars, except for possible orifice size changes to accommodate increased EGR flow rates and associated necessary EGR control modifications.

5.3.4 Summary

The foregoing brief discussion and assessment of relevant EGR technology indicate the following, with respect to lead additives:

1. The presence of lead additives in gasoline does not, per se, significantly affect the NO_x reduction performance or basic durability of EGR systems, based on the very little test data available.
2. The presence of lead additives in gasoline can result in deposits in EGR orifices, throttle plate areas, etc. The actual severity of such deposits, in terms of NO_x reduction efficiency, etc., would appear to be strongly related to the particular type of EGR system employed as well as to control orifice sizes used, and/or to the utilization of self-cleaning designs (plungers, specially coated surfaces, flexible snap-rings, etc.) in areas susceptible to deposit buildup.
3. Lead-free or low-lead gasoline is not, therefore, required for the implementation of EGR systems, per se.

REFERENCES

- 5-1. L.J.E. Hofer, J.F. Schultz and J.J. Feenan, Bureau of Mines Report No. RI 6243 (1963).
- 5-2. R.S. Yolles, H. Wise and L.P. Berriman, Study of Catalytic Control of Exhaust Emissions for Otto Cycle Engines, Final Report SRI Project PSU-8028, Stanford Research Institute (April 1970).
- 5-3. G.H. Meguerian, "Nitrogen Oxide--Formation, Suppression and Catalytic Reduction," PD 23, Paper 3, American Oil Company, Research and Development Dept., Whiting, Indiana.
- 5-4. K.I. Jagel and F.G. Dwyer, "HC/CO Oxidation Catalysts for Vehicle Exhaust Emission Control," SAE Paper No. 710290 (January 1971).
- 5-5. E.E. Weaver, "Effects of Tetraethyl Lead on Catalyst Life and Efficiency in Customer Type Vehicle Operation," SAE Paper No. 690016 (January 1969).
- 5-6. R.M. Yarrington and W.E. Bambrick, "Deactivation of Automobile Exhaust Control Catalyst," APCA Journal 20, No. 6 (June 1970), p. 398.
- 5-7. R.R. Allen and C.G. Gerhold, "Catalytic Converters for New and Current (Used) Vehicles," Paper presented at the Fifth Technical Meeting, West Coast Section of the Air Pollution Control Association, San Francisco, California (8-9 October 1970).
- 5-8. E. E. Hancock, R.M. Campau and R. Connolly, "Catalytic Converter Vehicle System Performance: Rapid Versus Customer Mileage," SAE Paper No. 710292 (January 1971).
- 5-9. H.W. Schwochert, "Performance of a Catalytic Converter on Non-leaded Gasoline," SAE Paper No. 690503 (May 1969).
- 5-10. W.J. Barth and E.N. Cantwell, "Automotive Exhaust Manifold Thermal Reactors--Materials Considerations," Presented before the Division of Petroleum Chemistry, Inc., 161st Meeting of the American Chemical Society, Los Angeles, California (28 March-2 April 1971).
- 5-11. A. Jaimee, "Thermal Reactor--Design, Development and Performance," SAE Paper No. 710923 (January 1971).

REFERENCES (cont.)

- 5-12. R.E. Oldrieve and P.L. Stone, Letter Report on the Current Status of the NASA/Lewis Program for Evaluation and Development of Materials for Automobile Thermal Reactors, Materials and Structures Division, NASA/Lewis Research Center, Cleveland (30 April 1971).
- 5-13. The Ethyl Lean Reactor System, Ethyl Corporation Research Laboratories, Detroit (1 July 1971).
- 5-14. G.S. Musser, et al., "Effectiveness of Exhaust Gas Recirculation with Extended Uses," SAE Paper No. 710013 (January 1971).
- 5-15. W. Glass, et al., "Evaluation of Exhaust Recirculation for Control of Nitrogen Oxides Emissions," SAE Paper No. 700146 (January 1970).
- 5-16. H.L. Misch (Vice President--Engineering, Ford Motor Company), Testimony before the California Air Resources Board, Sacramento, California (4 March 1970).
- 5-17. Personal discussion with representatives of the General Motors Corporation (30 June 1971).
- 5-18. Personal discussion with representatives of the Ford Motor Company (1 July 1971).
- 5-19. Personal discussion with representatives of the Chrysler Corporation (29 June 1971).
- 5-20. Personal discussion with representatives of the American Motors Corporation (29 September 1971).
- 5-21. D.L. Davis and G.E. Onishi, SAE Paper No. 486F (March 1962).
- 5-22. Engelhard Industries, Inc., Letter to The Aerospace Corporation (13 October 1971).
- 5-23. Personal discussions with representatives of the Ford Motor Company (30 September 1971).

**6. FEASIBILITY/IMPLICATIONS
OF LEAD TRAPS/EXHAUST
SCRUBBERS**

SECTION 6

FEASIBILITY AND IMPLICATIONS OF LEAD TRAPS AND EXHAUST GAS SCRUBBER DEVICES

Although lead is not compatible with catalytic converters, it is not clear that it has to be removed from gasoline for this reason alone. A variety of chemical scrubbers which efficiently convert volatile lead halides to nonvolatile compounds that are nontoxic to catalysts are being developed and might be used. However, most of these scrubbers require periodic maintenance that involves the replacement of certain chemicals. This shifts the maintenance problem from more frequent replacement of the catalyst, which would be required if no scrubber were used, to replacement of chemicals.

An investigation conducted to determine the feasibility and cost of chemical or mechanical lead traps upstream and downstream of emission control devices culminated in the collection of information from seven organizations with a total of eight devices carried to various stages of development. The techniques employed by these devices were found to fall into two basic categories. The first technique is capable of removing lead in the gaseous as well as particulate form at exhaust manifold temperatures, so that the exhaust is held sufficiently hot for further catalytic treatment to control NO_x , HC, and CO emissions. The second technique requires that exhaust gases be cool enough for a sufficient amount of lead to be in particulate form for collection. A detailed treatment of lead traps and exhaust gas scrubber technology is presented in Appendix C.

A study of the physical characteristics of exhausted lead compounds at the efficient operating temperatures of catalytic reactors indicated that lead would exist in the vapor state; thus, only those devices utilizing the first technique were considered practical for use in this application. With the exception of the Atomics International molten carbonate lead trap device, all techniques required that lead exist in the particulate form for collection and

removal. As a consequence, the Atomics International device was the only lead trap candidate that could be considered as practicable for use upstream of catalytic reactors.

The Atomics International lead trap device was developed on the basis that lead halides which are mildly acidic can be expected to react chemically with a basic alkali carbonate. Thus, a molten carbonate salt was evolved for scrubbing gaseous and particulate lead compounds from automobile exhausts. This device has undergone considerable development and testing and the results suggest that a molten carbonate lead trap design could be installed upstream of a catalytic reactor and have the potential for removing 90 percent of the lead, essentially all the sulfur oxides, and in excess of 80 percent of all particulates over the entire operating range of the automobile. In addition, the molten carbonate device compares favorably to standard mufflers with regard to engine noise attenuation and backpressures in the exhaust system. During 7-mode cycling tests, a prototype design of the molten carbonate process achieved operating temperatures of 1000°F in slightly more than 2 minutes, with gas temperature drops across the device never exceeding 20°F. A detailed cost estimate of an under-the-car design capable of fitting the available space on all currently operational automobiles was conducted by Atomics International, and it was indicated that the cost to the user would range from \$35 for a factory installation to \$45 for retrofit units. It is presently estimated that the salt will require changing every 15,000 to 20,000 miles at a cost of \$10.

Aside from system design complexities and the need for adding another component to the already complicated emission control systems evolved to date, it is felt that the 90-percent lead removal capability from regular leaded gasoline predicted by Atomics International for their device is not adequate for the lead-sensitive catalysts presently predicted for use by the automobile industry. If one considers the use of low-lead gasoline (0.5 gm/gal), the Atomics International system might be compatible with catalyst maximum lead requirements. However, there have not been sufficient hardware tests

to establish reliable removal efficiencies, and durability tests on prototype systems are not available to assess the decrease in effectiveness versus mileage. Therefore, it is not felt that this system could be incorporated in 1975-76 model automobiles.

The removal of particulate lead compounds in the downstream portion of automobile exhaust systems can be accomplished by cyclone trap devices. However, such inertial separation schemes would only be applicable to exhaust systems in which catalytic reactors were either not present or were insensitive to lead compounds. Development and testing by both Du Pont and Ethyl indicate that 65 to 85 percent of the particulate lead compounds can be removed by this type of device.

**7. EFFECT OF LEAD
ADDITIVES ON OTHER
ENGINE PARTS**

SECTION 7

EFFECT OF LEAD ADDITIVES ON OTHER ENGINE PARTS

This section addresses the effects of lead, per se, on the basic engine components and systems. General factors related to engine durability are briefly discussed and detailed information is provided on certain components which are significantly affected by lead additives. In addition, fuel-associated maintenance costs are examined and their cost considerations identified. The effects with respect to emission levels and emission control devices are separately discussed elsewhere in this report.

7.1 ENGINE DURABILITY--GENERAL

The lead salts formed by the halogens added to leaded fuels for scavenging purposes would be expected to cause an increase in engine wear. As early as the 1940's, laboratory and proving ground tests were run with engines operating on leaded and unleaded fuels in order to determine this effect. Although the results from these tests showed slight but consistently greater wear with leaded fuel operation, it was concluded (Ref. 7-1) that "the increased wear, although clearly existent in practically all parts of the engine, was not considered to be of sufficient amount to be of practical importance."

A number of test programs have been run in more recent years which were also directed toward determining the effect on engine durability of leaded and unleaded fuel operation (Refs. 7-2 through 7-23). These investigations provided comparative data on varnish/sludge formation, piston ring gap increase and ring weight loss, cylinder bore wear, bearing wear, oil contamination, and rust. Although many conflicts were noted, the data generally confirmed a degradation in engine durability due to the effects of lead and its associated scavengers, as reported in the earlier tests.

Although these conditions which cause wear might be expected to affect the time until mechanical repair would be required, this effect was not quantified

in any of the data sources. As a result, these data are of little value for predicting the maintenance cost differential between operation with leaded or unleaded fuel. In retrospect, this is not surprising as evidenced by the extensive and costly controlled fleet test programs more recently instituted by American Oil (AMOCO), Du Pont, and the Ethyl Corporation in order to assess this effect.

7.2 FUEL-SENSITIVE COMPONENTS

From the results of the controlled fleet test program, exhaust systems and spark plugs were noted to be particularly cost sensitive to the effects on leaded operation. Since they have a major influence on the fuel-related maintenance costs, they are separately discussed in some detail. In addition, the valve recession with unleaded fuel is also covered since it too has cost implications.

7.2.1 Exhaust System

Reference 7-2 states that the cost to the motoring public is in excess of \$0.5 billion per year for muffler and exhaust pipe replacements. The high cost in this area is attributed to the corrosive nature of the exhaust products and the incapability of the materials used in exhaust systems to withstand this corrosive attack. Although the halogen acids present in the exhaust products with operation on leaded fuel contribute to this condition, there are little data which quantify this effect. Based on limited test conditions, it was reported (Ref. 7-3) that muffler life would be approximately doubled with operation on unleaded instead of leaded fuel. These limited data apparently have gained general acceptance and reference to this source is made in much of the literature which reflects this order of improvement in muffler life for unleaded fuel operation.

Although muffler life data for leaded fuel operation can be derived from the replacement numbers stated in the controlled fleet test programs, these data are not necessarily valid since the replacement interval could be quite sensitive to the test mileage cutoff time. An assessment of muffler life, therefore, was obtained based on data from Ref. 7-4. From these data, a muffler life

of 37,500 miles was indicated. Considering the life of the original equipment provided, this would result in a replacement of 1.67 mufflers for 100,000 miles of operation with leaded fuel.

The expected muffler life for unleaded operation would be even more sensitive to the test mileage cutoff time. Since the data in Ref. 7-4 are not applicable to this case, a statistical analysis was made of data provided by Ethyl for their fleet located in the Detroit area. Results of this analysis, presented in Fig. 7-1, show a median life of 77,500 miles. This would result in a replacement of 0.29 muffler for 100,000 miles of operation with unleaded fuel.

Exhaust system costs are a particularly difficult item to estimate because of the many, many differences in configuration and associated component costs.

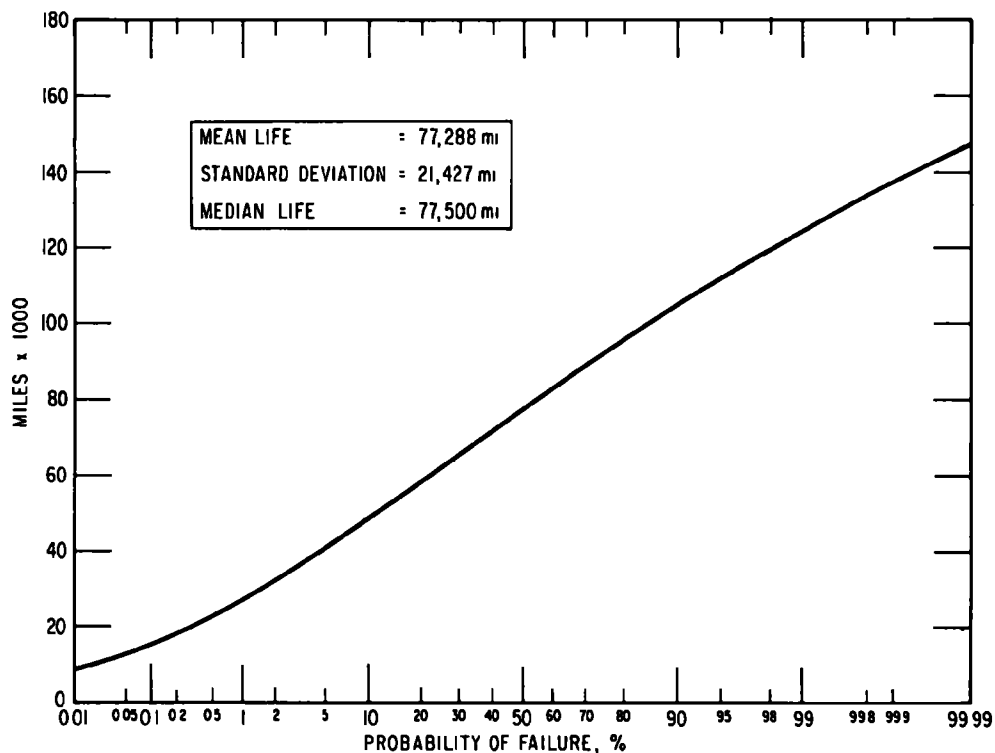


Fig. 7-1. Muffler Lifetime Probability (Operation on Unleaded Fuel)

This is further compounded by differences in replacement charges made by car dealers, garages, service stations, and specialty shops. Based on prices obtained from a number of sources, which included Chilton's Manual, specialty shops, and a large mail order/retail firm, the cost for a typical exhaust system replacement (muffler, pipes, fittings) is estimated to be \$45.

Based on the cost and number of replacements required for 100,000 miles of operation, then, the exhaust system expense would be 0.075 cent per mile for leaded fuel and 0.013 cent per mile for unleaded fuel.

7.2.2 Spark Plugs

7.2.2.1 Misfiring Mechanism

Spark plug misfiring is generally caused by one of three conditions: gap bridging, gap erosion or a reduction in shunt resistance (Ref. 7-5). The latter condition is particularly sensitive to leaded fuel operation where the lead oxides and lead chlorobromide deposits form on the internal ceramic and provide a conductive path from the center electrode to the spark plug base. In general, the conductivity of these deposits increases with temperature. The level of conductivity, however, is higher for deposits which are formed at the low temperature associated with low-power operation. Hence, under conditions of high acceleration, misfiring would be promoted since the generation of high temperatures is attained faster than the change in deposit composition. At sustained high-power operation, however, the initial deposit composition would change to a composition with lower conductivity and the conditions promoting misfiring would be alleviated.

The influence of lead and its accompanying chlorobromide scavengers on the gap bridging and gap erosion mechanism for spark plug misfiring is not as evident. Although heavy deposit accumulation on and around the electrodes with leaded fuel operation has been reported (Ref. 7-6), the composition of these deposits is not identified. A detailed understanding of both the mechanism for formation and the mechanical/chemical characteristics of these deposits is required to separate the effects due to lead additives on this

misfiring mechanism. It has been reported (Ref. 7-7) that lead additives have only a slight effect on the corrosion of nickel-alloy spark plug electrodes, and that the effects of sulphur contamination in a reducing atmosphere (rich mixture) are of much greater significance. Again, more data are required to quantify the effects of lead additives for this type of misfiring mechanism.

7.2.2.2 Life

Although a complete understanding of the misfiring mechanisms could provide a basis for establishing spark plug life for either leaded or unleaded fuel operation, it is doubtful that this information would be particularly meaningful except for establishing a car manufacturer's recommended-mile-change interval. Other driver-related factors such as driving characteristics, sensitivity to engine malperformance, and maintenance habits could well be overriding effects.

Again, for the same reason given for the determination of muffler life, spark plug life for leaded fuel operation was obtained from annual spark plug sales. From Ref. 7-4, spark plug life was determined to be approximately 13,000 miles per set. This figure was based on an assumed average annual vehicle mileage of 10,000 miles and 7.3 spark plugs per vehicle. If the set of spark plugs that was provided as original equipment is included, the spark plug life of 13,000 miles per set translates to a replacement of 6.7 spark plug sets for 100,000 miles of operation on leaded fuel.

For the unleaded fuel case the only data available for the determination of spark plug life are those reported by the controlled fleet test operations. Again, a statistical analysis was performed on data provided by Ethyl; the analysis considered the actual replacement mileage as well as the mileage of operation subsequent to replacement. The results of this analysis, presented in Fig. 7-2, show a median life of 20,350 miles for the Detroit fleet and 25,050 miles for the Baton Rouge fleet. The average of these values (22,700 miles) was used to establish a replacement of 3.4 spark plug sets for 100,000 miles of operation on unleaded fuel.

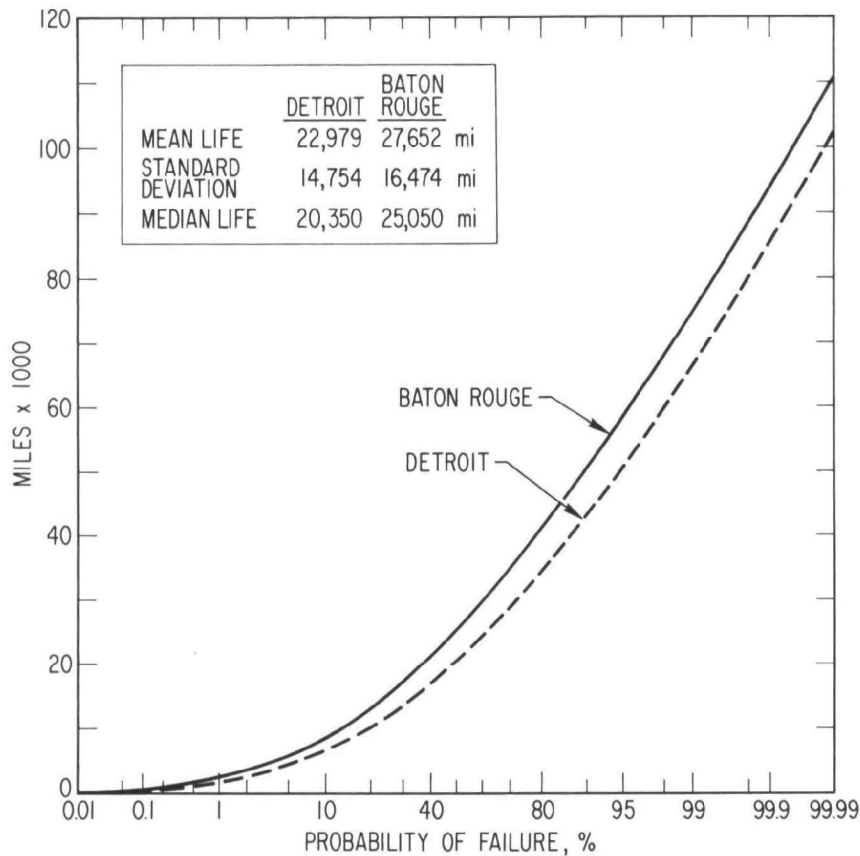


Fig. 7-2. Spark Plug Lifetime Probability
(Operation on Unleaded Fuel)

7.2.2.3 Cost

Spark plug replacement costs are also quite variable. Replacement cost per the Chilton Manual averages about \$17; for the do-it-yourself owner, the cost would be around \$5, assuming discount-priced spark plugs; and the service station charge would be somewhere between these values. A replacement cost of \$10 per set was somewhat arbitrarily assumed for this study.

With the replacement of 6.7 and 3.4 sets for 100,000 miles of operation as derived above, spark plug costs would be 0.067 cent per mile for leaded fuel and 0.034 cent per mile for unleaded fuel.

7.2.3 Exhaust Valve Recession

There is considerable evidence that exhaust valve seat wear increases with the removal of lead additives (Refs. 7-8 through 7-13). At operating conditions of sustained high speed and load, exhaust valve recession rates have been reported as high as a 0.010 inch per 1,000 miles (Refs. 7-10 and 7-12). Not all engine types, however, are similarly affected. Volkswagen, for example, anticipates no exhaust valve seat problems with use of unleaded fuels. It is also of interest to note that this wear mechanism was not apparent from the data obtained by the controlled fleet test programs for vehicles operating with unleaded fuel.

The mechanism for valve recession with operation on unleaded fuels is reported in Refs. 7-8, 7-9, 7-12, and 7-13; it is attributed to localized welding and subsequent pull-out of fragments with accompanying wear due to abrasion. This condition is apparently alleviated in leaded fuels by the lead chlorobromide deposits which act as high-temperature solid-film lubricants. Although a number of chemical and/or metallurgical approaches could be applied to reduce the valve wear condition apparent with the use of unleaded fuels, the change to induction-hardened exhaust valve seats, as recommended in Ref. 7-14, appears to be an immediate and reasonably low-cost solution to the problem.

7.3 MAINTENANCE

Fuel-related maintenance costs have been collected in three controlled fleet test programs for comparable vehicle groups operated on leaded and unleaded fuel. The results are of particular interest since, as it was concluded above, they represent the only source of data for the determination of such costs.

Unfortunately, the results obtained in the three programs are not in agreement. AMOCO (Ref. 7-15) reported an average fuel-related cost differential of 0.418 cent per mile in favor of unleaded fuel. The fuel-related maintenance costs reported by Du Pont (Ref. 7-13) resulted in a differential of 0.052 cent per mile in favor of unleaded fuel. Ethyl (Ref. 7-16) reported a

cost differential of 0.078 cent per mile, also in favor of unleaded fuel. In supplemental information provided by Ethyl, this differential was reduced to less than 0.016 cent per mile by elimination of some of the fuel-related maintenance items previously reported.

Since there is a significant difference between AMOCO results and those reported by Du Pont and Ethyl, an evaluation was made to establish the reason for the disparity. Unfortunately, the only data available from AMOCO were total fuel-related maintenance costs, and the number of spark plug and muffler changes. Further, these data were also compromised by a limited mileage accumulation which averaged less than 25,000 miles per vehicle. Nevertheless, it was found that the data were quite useful in the evaluation since spark plug and muffler expenditures represent a sizeable percentage of fuel-related maintenance costs.

Examination of AMOCO data showed that spark plug and muffler replacement costs represented approximately 40 percent of fuel-related maintenance costs for leaded fuels and approximately 31 percent for unleaded fuels. Expressed on a cents-per-mile basis, these percentages reflect a cost of 0.251 cent per mile for leaded fuels and 0.067 cent per mile for unleaded fuels. These numbers were derived on the basis of a spark plug replacement cost of \$10 per set and an exhaust system replacement cost of \$45 per replacement.

From examination of Du Pont data, spark plug and exhaust system replacement costs represented approximately 29 percent for leaded fuels and 14 percent for unleaded fuels. On a cents-per-mile basis, these percentages reflect a cost of 0.123 cent per mile for the leaded fuels and 0.052 cent per mile for the unleaded fuels.

From examination of Ethyl data, spark plug and exhaust system replacement costs represented approximately 38 percent for leaded fuels and 22 percent for unleaded fuels. These percentages reflect a cost of 0.134 cent per mile for leaded fuels and 0.062 cent per mile for unleaded fuels.

It should be noted that the Du Pont and Ethyl data were used to directly compute the percentages and costs given above. A check using the derived costs that were applied to the AMOCO spark plug and exhaust system replacements, however, showed an insignificant difference in results by the use of these derived costs.

On the basis of percentage of spark plug and exhaust system cost to the total fuel-related maintenance cost, the three data sources are in reasonable agreement. Further, on a cents-per-mile basis the costs reported for the unleaded fuel vehicles were in surprisingly close agreement. For the leaded fuel vehicles, however, AMOCO costs were approximately double that reported by Du Pont and Ethyl. These values are summarized in the table below:

Table 7-1. Spark Plug and Exhaust System Costs

| Source | Leaded Fuel | | Unleaded Fuel | |
|-------------------|-------------|--------|---------------|--------|
| | % of Total | ¢/Mile | % of Total | ¢/Mile |
| AMOCO | 40 | 0.251 | 31 | 0.067 |
| Du Pont Company | 29 | 0.123 | 14 | 0.052 |
| Ethyl Corporation | 38 | 0.134 | 22 | 0.062 |

To provide a basis for judging which costs were more reasonable, the previously derived exhaust system and spark plug life-and-cost data for the leaded case were used to arrive at a cost of 0.142 cent per mile for these replacements. Since this cost is in close agreement with the 0.123 and 0.134 cent per mile reported by Du Pont and Ethyl, it generally substantiates the reasonableness of their cost data. The very much higher costs reported by AMOCO apparently reflect a condition which for some reason is not typical.

If the fuel-related maintenance costs as reported by both Du Pont and Ethyl are accepted as valid, it is of interest to note that the difference in maintenance cost between the leaded and unleaded vehicles is almost exclusively

that associated with the difference in spark plug and exhaust system expense. For example, if spark plug and exhaust system costs are subtracted from the Du Pont data, the difference in fuel-related maintenance cost would be 0.019 cent per mile in favor of leaded fuel. Similarly for the Ethyl data, the differential would be 0.006 cent per mile, but in favor of the unleaded fuel.

On the assumption that spark plug and exhaust system replacement costs reflect the essential difference in fuel-related maintenance costs, the derived life-and-cost data for both the leaded and unleaded cases can be used to independently determine the difference in fuel-related maintenance costs. As given above, the cost would be 0.142 cent per mile for the leaded case; similarly for the unleaded case the cost would be 0.047 cent per mile. A differential fuel-related maintenance cost of 0.095 cent per mile is thus indicated in favor of unleaded fuel operation. This would amount to approximately \$81 over the lifetime of an average automobile.

REFERENCES

- 7-1. W.S. James, "Piston-Ring and Cylinder-Bore Wear," SAE Journal (August 1961), pp. 33-40.
- 7-2. R.A. Heath, "Muffler Corrosion--It's Cause and Control," SAE Transactions (1959), p. 553.
- 7-3. F.J. Cordera, et al., "TEL Scavengers in Fuel Affect Engine Performance and Durability," SAE Paper No. 877A (June 1964).
- 7-4. 1968/Automobile Facts/Figures Report, Automobile Manufacturers Association, Inc., Detroit (1968).
- 7-5. H.P. Julien and R.F. Neblett, "Spark Plug Misfiring--Mechanism Studies," SAE Preprint 123-T (October 1959).
- 7-6. Fuel Composition--Its Relationship to Emission Control on Future, Present, and Past Model Year Vehicle Systems, Ford Motor Company (7 March 1970).
- 7-7. C.M. Heinen (Chrysler Corporation), Letter to The Aerospace Corporation (14 September 1971).
- 7-8. W. Giles, "Valve Problems with Lead-Free Gasoline," SAE Paper No. 710368 (22 October 1970).
- 7-9. D. Godfrey and R.L. Courtney, "Investigation of the Mechanism of Exhaust Valve Seat Wear in Engines Run on Unleaded Gasoline," SAE Paper No. 710356 (January 1971).
- 7-10. H.W. Schwochert, "Performance of a Catalytic Converter on Non-leaded Gasoline," SAE Paper No. 690503 (May 1969).
- 7-11. Consequences of Removing Lead Antiknocks from Gasoline, A Status Report, No. AC-10, Ethyl Corporation, New York (August 1970).
- 7-12. A.E. Felt and R.V. Kerley, "Engines and Effects of Lead-Free Gasoline," SAE Paper No. 710367 (October 1970).
- 7-13. Effect of Lead Antiknocks on the Performance and Costs of Advanced Emission Control Systems, Du Pont de Nemours & Co., Wilmington, Delaware (15 July 1971).
- 7-14. W. Giles, "Induction Hardening Makes Exhaust Valve Seats Wear Less with Nonleaded Fuel," Presented at SAE International Mid-Year Meeting, Montreal, Canada (7-11 June 1971).

REFERENCES (cont.)

- 7-15. H.R. Taliaferro, L.T. Wright and R.C. Mallatt, "Gasoline for Reducing Automobile Pollution," An address before the American Association for the Advancement of Science Symposium, 137th Meeting, Chicago, Illinois (26 December 1970).
- 7-16. Car Maintenance Expense When Using Leaded and Nonleaded Gasoline, Ethyl Corporation, Detroit (2 July 1971).
- 7-17. A.J. Pahnke and J.F. Conte, "Effect of Combustion Chamber Deposits and Driving Conditions on Vehicle Exhaust Emissions," SAE Paper No. 690017 (January 1969).
- 7-18. L.G. Pless, "Some Effects of Experimental Vehicle Emission Control Systems on Engine Deposits and Wear," SAE Paper No. 710583 (June 1971).
- 7-19. L.G. Pless, "The Effects of Some Engine, Fuel and Oil Additive Factors on Engine Rusting in Short-Trip Service," SAE Paper No. 700457 (May 1970).
- 7-20. G.S. Musser, et al., "Effectiveness of Exhaust Gas Recirculation with Extended Use," SAE Paper No. 710013 (January 1971).
- 7-21. R.R. Allen (Universal Oil Products Company), Letter to The Aerospace Corporation (14 September 1971).
- 7-22. W.R. Epperly, "Future U.S. Emission Control Systems," Presented to the Environmental Protection Agency, Washington, D.C. (6 May 1971).
- 7-23. W.G. Agnew, "Gasoline Changes Affecting Emission Control," Presented to the Oil Companies, Office of Science and Technology, and HEW at the General Motors Technical Center (January-March 1970).

8. COST ANALYSIS

SECTION 8

COST ANALYSIS

The cost implications arising from the incorporation of emission control systems in cars to meet the 1975-76 emission standards encompass the areas of (1) initial investment costs, (2) maintenance-related costs, and (3) operating costs. In view of the fact that meeting the 1975-76 standards has not been adequately demonstrated by vehicle manufacturers and that no final selection of system components has been made, the cost estimates presented herein are limited to engineering estimates based on projections of current designs.

Initial investment cost, to the car purchaser, is the increase in initial purchase price occasioned by the installation of the emission control system hardware in the new car. Maintenance-related cost is that increase in maintenance cost directly attributable to the inclusion of the emission control system. Operating cost, similarly, is that increase in operating cost (i. e., fuel cost) directly related to changes in either the vehicle fuel economy resulting from the emission control system, or an increase in basic fuel cost per gallon as required by the nature of the emission control system.

The approach followed in this section is to select a baseline vehicle having performance and fuel economy characteristics typical of cars not employing sophisticated emission control systems; i. e., 1970 cars designed to operate within the constraints of the normal two-grade leaded gasoline supply system. Then, selected generic emission control systems (as previously defined in Section 4.3) are added to the baseline vehicle and typical fuel economy penalties associated with each generic class are assessed. The fuel penalty consists of the control device effects and any compression ratio limits occasioned in the case of generic classes of emission control

devices constrained to operation on unleaded gasoline. Finally, for each generic class overall costs to the consumer (initial, maintenance, and operating costs) are summed up based on an average vehicle operational lifetime.

8.1 CONTROL DEVICE/SYSTEM COST ANALYSIS

8.1.1 Control Device Costs

Specific control devices and their associated engine- or vehicle-related requirements were grouped in the general areas of (1) engine modifications, (2) emission control system components, and (3) exhaust system initial costs. The cost estimates presented are based on cost of materials used in the device, difficulty of manufacturing, comparisons with existing automotive components, and discussions with automotive vehicle and equipment manufacturers.

8.1.1.1 Engine Modifications

8.1.1.1.1 Carburetion

All auto manufacturers have stressed the need for improved carburetion (and/or fuel injection) for improved air-fuel ratio control in engines employing complex emission control systems. Informal estimates of hardware cost increases vary widely. For purposes of the present study, a differentiation was made between "lean" and "rich" systems. A nominal increase of \$13 was assessed for improved carburetion for "rich" systems. For the more difficult "lean" systems, which require better mixture preparation and distribution as well as air-fuel ratio control, this cost increase was selected to be \$25. Although fuel injection systems may be utilized on some car models, fuel injection system costs were not included as a variable since this system has not been identified as a requirement for any generic emission control system concept.

8.1.1.1.2 Ignition/Distributor/Control Systems

All automakers have stressed the need for some form of "unitized" ignition system for longer life and better control of ignition spark to prevent

degradation of emission levels. Some have also expressed the opinion that a new engine control system may be required to provide more precise control of the variables and coordinate spark timing and carburetion. For purposes of the present study, it was assumed that all advanced emission control system concepts would incorporate features of this' general type, and an estimated cost penalty of \$37 was assessed all generic system classes.

8.1.1.1.3 Long-Life Exhaust Systems

Exhaust system components become part of or are replaced by emission control system components in nearly all advanced emission control system concepts. Also, exhaust gas temperature levels are generally increased (severely, in some cases) to provide more optimum operating conditions for certain control system components (e.g., catalytic converters) or because of the operation of certain components [e.g., rich thermal reactor (RTR)]. Because of the postulated requirement for 50,000 maintenance-free miles of operation, and the interaction between control system components and normal exhaust system components, a long-life exhaust system (e.g., stainless steel) was assumed to be included in every generic class of emission control system. An initial cost of \$60 was estimated for this system, and a cost credit of \$28 allowed because of the deletion of the normal exhaust system, resulting in a net additive cost penalty of \$32 for every generic class.

8.1.1.1.4 Exhaust Valves and Seats

As discussed in Section 7, the use of lead-free gasoline, for most cars, will result in the requirement for valves and/or valve seat modifications to prevent valve recession effects. Any generic class of emission control systems operating on unleaded gasoline was assessed at \$3-per-car cost penalty for such modifications.

8.1.1.2 Emission Control System Components

8.1.1.2.1 Exhaust Gas Recirculation (EGR) Systems

A wide variety of EGR system designs exists, as was shown in Section 4.2.2. Similarly, there is a rather wide variation in available cost estimates for

EGR systems, per se (see Table 8-1). For purposes of the present study, a representative value of \$25 was assessed all systems incorporating EGR.

Table 8-1. EGR System Cost Data

| Source | Materials Cost (dollars) | Manufactured Cost (dollars) | Cost to Consumer (on new car) (dollars) | Maintenance Costs (dollars) | Description |
|---|--------------------------|-----------------------------|---|-----------------------------|--|
| Chrysler Corporation | | | 30.00 | | 1973-74 system (Ref. 8-1) |
| Du Pont (EGR System) | 2.96 | 3.70 | 7.40 | 8.28 | Cooled gas, above-throttle injection (Ref. 8-2) |
| Du Pont (In-line filter) | 0.35 | 0.44 | 0.88 | | |
| Esso Research & Engineering | | ~10.00 | | | Cooled gas, above-throttle injection (Ref. 8-3) |
| Universal Oil Products | | | 25.00 | | (Ref. 8-4) |
| Research Triangle Institute (1970) | | | 25.00 | 8.00/year | (Ref. 8-5) |
| Research Triangle Institute (1971) - EGR system | | | 20.00 | | Fixed-orifice system (Ref. 8-6, unpublished draft) |

8.1.1.2.2 Catalytic Converters

Considering the state of development for catalytic converters, there is an understandable lack of cost data and a reluctance on the part of the catalyst manufacturers and the automobile companies to estimate what the cost will be. However, some speculative costs have been obtained from available reports and by visits to certain sources as shown in the following table:

Consumer Cost per Car, Dollars

| <u>Source</u> | <u>HC/CO</u> | <u>NO_x</u> | <u>Dual-Bed</u> | <u>Tricomponent</u> | <u>Reference</u> |
|---------------|--------------|-----------------------|-----------------|---------------------|------------------|
| UOP | 150 | | | 120 | 8-4 |
| Engelhard | 50 | 50 | | | 8-7 |
| Esso | | | 84 | | 8-8 |
| RTI | 75 | 75 | 92 | | 8-6 |
| SR1 | 130 (avg) | | | | 8-9 |

Since there was a great deal of disagreement on catalyst converter costs and a general lack of cost data, an independent estimate was made. This estimate considered: (1) catalyst cost, (2) converter material cost, (3) manufacturing labor, overhead, and profit, (4) installation costs, and (5) sales profits. The resulting values are:

| <u>Converter Type</u> | <u>Original Equipment Cost to Consumer, Dollars</u> |
|---------------------------|---|
| HC/CO Catalytic Converter | |
| Base or Noble Metal | 98/car |
| Dual-Bed Converter | |
| Base or Noble Metal | 129/car |
| Tricomponent Converter | |
| Noble Metal | 98/car |

It is interesting to note that base metal and noble metal catalyst costs per vehicle are about the same even though the cost per pound is much greater for the noble metal catalyst. The reason of course is that a smaller amount of noble metal catalyst is required. With the cost of the base metal and noble metal catalyst equalized, the remaining cost for metal fabrication, profit, installation, etc., also tends to equalize such that cost to the consumer is about the same for the two types of catalytic converter.

8. 1. 1. 2. 3 Thermal Reactors

Du Pont (Ref. 8-2) estimated that the cost of their RTR is approximately \$48 (two times the estimated manufacturing cost of approximately \$24).

Ethyl (Ref. 8-13) estimated the cost of their lean thermal reactor (LTR) to be approximately \$100 (including an upgraded exhaust pipe).

Again, because of these substantial variances and general lack of cost data from the automakers, an independent estimate was made. This estimate considered volumetric and materials differences between the LTR and RTR approaches and included considerations of materials cost, manufacturing

labor and profit, installation costs, sales profits, and credit for standard exhaust manifolds. The resulting values are:

| <u>Reactor Type</u> | <u>Original Equipment Cost to Consumer, Dollars</u> |
|-------------------------|---|
| RTR | 125/car |
| LTR | 110/car |

In a similar manner, the cost of a "low-grade" thermal reactor, rich or lean, was estimated to be \$70 per car. Such "low-grade" reactors would be smaller in volume, have less insulation, might not have a core liner, etc., and would approach an oversize standard exhaust manifold in configuration.

8.1.1.2.4 Air-Injection Pump

A nominal cost of \$29 was assessed each configuration incorporating an air pump. Additional costs for plumbing, etc., were assumed to be accounted for either in the thermal reactor or catalytic converter cost estimates.

8.1.1.2.5 Overtemperature Protection System

As mentioned in Section 4, RTR and/or catalytic converter systems may require overtemperature protection systems. Their need is not established at the present time, as automakers are searching for catalysts with higher temperature capabilities to avoid the system complexity introduced by the addition of such a protection system, the exact details of which are ill-defined at the present time.

Informal cost estimates for such systems range from \$25 for the simpler to approximately \$100 for the more complex type. For purposes of the present study, a cost penalty of \$50 was assessed any generic concept incorporating either a catalytic converter or an RTR.

8.1.1.3 Discussion of Device Costs

The foregoing engine modification and emission control system component cost penalties, as noted, are based on consideration of a variety of

assumptions and evaluation techniques. Every effort has been made to ensure that cost levels are "comparable," both as to variation in devices within a given component class (e. g. , within thermal reactors) and from component class to component class (e. g. , from thermal reactors to catalytic converters).

In this manner, although the cost values used herein may not exactly coincide with those eventually forthcoming from the automakers, the relative cost levels between the various generic classes of overall emission control system concepts made up of these components are meaningful on a comparative basis.

Informal cost estimates seen to date generally support the component cost assessment levels made herein.

8. 1. 2 Emission Control System Initial Hardware Costs

As previously noted in Section 4, meaningful complete emission control system concepts fall into discrete generic classes. All of the various experimental emission control system concepts evaluated by industry to date can be reasonably identified within this generic system of classification.

As a primary purpose of the cost analysis effort was to provide a measure of the cost differences between the various conceptual approaches, all generic classes were assessed component or hardware cost penalties on a common basis by use of the component costs described above (Section 8. 1. 1).

Table 8-2 summarizes the initial hardware costs for the generic classes considered in the cost analysis. Identified are the discrete components (and their costs) of each generic class and a summation of the initial total hardware cost to the consumer, as installed in a new car.

It should be noted that systems incorporating both a thermal reactor and catalytic converter have been selected to use a "low-grade" thermal

**Table 8-2. Installed Hardware Cost Summary
(Cost to Consumer in New Car)**

| Generic Concept Cost Item | Thermal Reactor Systems ^a | | Combination Systems ^b | | |
|--|--------------------------------------|------------|---------------------------------------|--|--|
| | LTR + EGR | RTR + EGR | Low-Grade LTR + EGR + HC/CO C.C | Low-Grade RTR + EGR + HC/CO C.C. | Low-Grade RTR + EGR + Dual C. C. |
| Initial Costs (dollars) | | | | | |
| Engine Modifications | | | | | |
| Carburetion | 25 | 13 | 25 | 13 | 13 |
| Ignition/Distributor | 37 | 37 | 37 | 37 | 37 |
| L.L. Exhaust System | 60 | 60 | 60 | 60 | 60 |
| Valves, Seats | - | - | 3 | 3 | 3 |
| Emission Control Components | | | | | |
| EGR | 25 | 25 | 25 | 25 | 25 |
| Thermal Reactor | 110 | 125 | 70 | 70 | 70 |
| Catalytic Converter (C. C) | - | - | 98 | 98 | 129 |
| Air-injection Pump | - | 29 | 29 | 29 | 29 |
| Overtmp. Protection System | - | 50 | 50 | 50 | 50 |
| Exhaust System Credit | -28 | -28 | -28 | -28 | -28 |
| Total Installed Hardware Cost (dollars) | 229 | 311 | 369 | 357 | 388 |
| ^a Use Leaded Gasoline | | | | | |
| ^b Catalytic Converter + EGR are the same except for \$70 decrease due to omission of Low-grade Thermal Reactor. | | | | | |

reactor, since the primary purpose of the reactor is to warm up the catalytic converter. Therefore, it is felt that the full-size thermal reactor is unwarranted in this case.

Catalytic-converter-only systems were not treated as a separate item because of their poor cold start characteristics to date. However, with regard to their costs, they would be identical to the RTR + EGR + HC/CO catalytic converter and RTR + EGR + dual catalytic converter concepts of Table 8-2, except for the deletion of the RTR cost (\$70). Similarly, their SFC- versus NO_x-level characteristics are considered the same as their thermal reactor plus catalytic converter counterparts and, therefore, the overall consumer costs hereinafter developed are equally applicable to

them, except for the \$70 cost differential. In addition, the tricomponent catalytic converter concept has not been treated since it requires a precision in air-fuel ratio control not yet demonstrated. As the required air-fuel ratio control system has not been identified, it has not been possible to provide a reasonable cost estimate for this function.

Similarly, the RTR plus NO_x Catalytic Converter plus RTR concept of American Motors was not costed as American Motors regards it as a laboratory experiment only and not a viable contender for 1975-76 systems.

As shown in the table, initial installed hardware costs range from \$229 to \$388. Thermal reactor systems are lowest in cost, and the dual-bed catalytic converter system is the most expensive, as would be expected.

8.2 OVERALL COSTS TO THE CONSUMER

To the foregoing initial hardware costs must be added the various maintenance and operating costs, as pertinent to each generic emission control system class, in order to determine the total or overall cost to the new car buyer. The various cost determinations and assumptions in this regard are delineated in the following sections.

8.2.1 Maintenance Costs

Several maintenance cost areas affected by the emission control system concept and/or the use of leaded or unleaded gasoline were identified. These are spark plug life, maintenance of the overtemperature protection system, catalytic converter system replacement, and exhaust system replacement. An average lifetime mileage of 85,000 miles and an average automobile age of 8.4 years are used in the analysis. These values are based on the statistics of the percentage of cars still registered as a function of the car age (Ref. 8-11) and on the average miles per years as a function of the age of the car (Ref. 8-12).

As treated in Section 7, it was determined that spark plugs operated with unleaded gasoline have an average longer lifetime than when operated with

leaded gasoline. Although the exact lifetime levels in each case are not a priori determinable when installed in the various emission control system concepts (particularly with improved ignitor systems), representative values of 13,000 miles for leaded gasoline and 20,000 miles for unleaded gasoline were selected to illustrate typical maintenance cost differences for spark plug changes in the two cases.

Each spark plug change was estimated to cost \$10 (representing a combination of installations at a garage and home replacement). For the 85,000-mile baseline car life used herein, this resulted in a cost savings of \$23 for cars using unleaded gasoline.

The next area of maintenance cost considered is in regard to the over-temperature protection system. As noted previously, if needed and incorporated, this system is a critical part of the overall emission control system. A nominal cost value of \$5 per year has been assessed for inspection only of this system. No cost for actual repair has been included. Again, based on the average 8.4-year lifetime used herein for the baseline car, this results in a total inspection cost of \$42 for the concepts incorporating overtemperature protection systems.

The goal of the automakers is to develop a catalytic converter unit capable of meeting a 50,000-mile maintenance and/or replacement-free requirement. Demonstration of this capability at 1975-76 emission levels has not been made to date. However, for purposes of the present cost assessment, it is assumed that this requirement will be met for HC/CO catalysts. Both 25,000- and 50,000-mile replacement intervals are considered for illustrative purposes for NO_x catalytic devices since to date the demonstrated life is quite low.

The exact method of catalytic converter replacement or refurbishment is a matter of current debate. Potential users of converters incorporating pelletized catalyst beds project the eventual possibility of being able to

withdraw used catalyst pellets from the converter (by vacuum means, etc.) and insert new or fresh pellets. Potential users of monolithic catalyst beds similarly envision converter designs which enable simple cartridge-type replacement of the monolithic bed. If these replacement/refurbishment techniques become a reality, they might reduce converter replacement costs.

In both cases, these are mere projections at the moment, with demonstrated capability lacking. Therefore, for purposes of the present cost analysis it has been assumed that the total catalytic converter unit will be replaced. Discrete costs for replacement were estimated based on original manufactured cost, wholesaler's costs, dealer installation cost, and nominal profits. These values are:

| <u>Converter Type</u> | <u>Replacement Cost, Dollars</u> |
|------------------------------|----------------------------------|
| HC/CO Catalytic Converter | 123/car |
| Dual-Bed Catalytic Converter | 156/car |

As mentioned in Section 8.1.1.1.3 above, a long-life exhaust system was a basic part of each generic class of emission control system considered. It was assumed that this system would last the life of the car. As the consumer has been penalized for this added cost, the exhaust system replacement costs normally anticipated in the baseline car case must be subtracted from the overall costs to the consumer to maintain the relative cost effect of the car equipped with the new emission control system.

As discussed in Section 7, a representative average value of \$45 per exhaust system replacement and an average life of approximately 37,500 miles are assumed. This results in a total cost credit of \$60 for each emission control system concept for an average car lifetime of 85,000 miles.

8.2.2 Operating Costs

Operating costs, as utilized herein, are restricted to fuel economy cost penalties.

8.2.2.1 Fuel Economy Cost Penalty

Fuel economy cost penalty is defined as the cost of fuel for the car over its lifetime when equipped with the emission control system being evaluated minus the car lifetime fuel cost of an average 1970 car. This definition gives the increase in fuel costs due to the emission control system. When added to the emission control system initial hardware and maintenance costs, the total cost of the emission control system is obtained.

8.2.2.1.1 1970 Car

The characteristics of the 1970 car are:

Weighted average compression ratio: 9.37:1 (Refs. 8-13 and 8-14)

Miles/gallon: 13.5 (Ref. 8-14)

Lifetime mileage: 85,000 miles (as noted in Section 8.2.1.)

Weighted average price of fuel (leaded) for 1970 car: 37.40 ¢/gal
(based on regular at 35.69 ¢/gal (Ref. 8-14), premium at
39.69 ¢/gal, price spread from Ref. 8-15, and regular
gasoline sales 57.4 percent of total gasoline sales;
from Ref. 8-14)

Lifetime fuel cost for the 1970 car from the above: \$2355

To account for the fact that some 1970 cars are designed to use regular gasoline and some premium, a weighted average compression ratio has been used for the baseline 1970 car. Similarly, since some drivers of cars designed to use regular buy premium, an average price of gasoline based on the percentage of sales of each grade has been selected as the baseline gasoline cost per gallon.

8.2.2.1.2 Fuel Economy Effects of Emission Control Devices--General

As discussed in Section 4, the fuel economy of a car equipped with an emission control system depends primarily on the method of reducing NO_x emissions, the NO_x emission level achieved (see Fig. 4-34), and whether or not the emission control system can tolerate lead in the engine exhaust (catalytic systems are lead intolerant). HC/CO emission reduction devices have only secondary effects on fuel economy, excluding unleaded gasoline effects, since engine air-fuel ratio is set by the NO_x emission reduction device for low NO_x emission levels. These secondary effects are due to increased engine exhaust backpressure, and to power for a secondary air pump (in some cases), and are much the same for most systems. For the reasons discussed in Section 6, lead scrubbers in the engine exhaust will not be considered and all systems incorporating catalytic devices are assumed to use unleaded gasoline. Fuel economy effects considered, therefore, consist of those due to NO_x emission reduction devices and the use of unleaded gasoline for systems containing catalytic devices. These are considered separately and then combined to obtain an overall fuel cost penalty for several basic classes of systems which encompass the major types of systems proposed for 1976 cars.

8.2.2.1.3 NO_x Emission Reduction System Effects on Fuel Economy

As discussed in Section 4, NO_x emission reduction systems fall into two broad categories: (1) those depending only on the use of a combination of engine air-fuel ratio change and EGR, and (2) those utilizing NO_x catalysts in conjunction with a smaller change in engine air-fuel ratio and a lower EGR rate than in the first category.

Typical engine fuel economy changes with the addition of emission control systems are shown in Fig. 8-1 which was developed from information in Section 4. For the two categories shown, the fuel penalties differ. All engines are assumed to have the same compression ratio so there are no unleaded gasoline effects reflected in the values. The curve for EGR plus air-fuel ratio change applies to thermal reactor systems and those

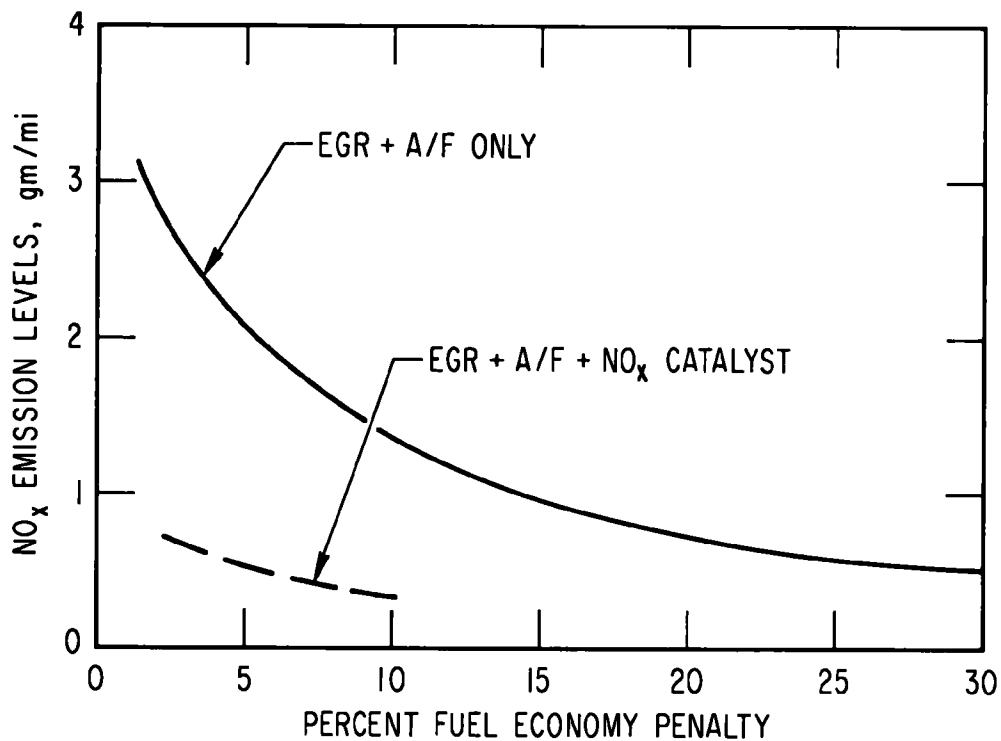


Figure 8-1. Fuel Economy Penalty due to NO_x Emission Reduction

incorporating HC/CO catalysts, without an NO_x catalyst in the system. The NO_x catalyst curve applies regardless of the method of HC/CO emission reduction used.

It is evident from the figure that, excluding the cost effects of their use of unleaded fuel, NO_x catalyst systems are attractive from a fuel economy standpoint. It is also evident from the figure that decreasing the required NO_x emission level for any type of system reduces fuel economy. This is due to the necessity of increasing the EGR rate and/or decreasing the air-fuel ratio as the NO_x emission level is reduced.

8.2.2.1.4 Fuel Economy Cost Effects of Using Unleaded Gasoline

Engine efficiency improves as compression ratio increases. In general, as the compression ratio increases, however, the gasoline octane number must also increase. The addition of lead to the fuel has proven to be the cheapest way of providing high octane number fuels. Engines with emission control systems which cannot tolerate lead in the fuel (e. g., catalytic systems) must, therefore, either operate at lower compression ratios with poorer efficiency than engines equipped with emission control systems which are lead tolerant, or use more expensive fuel than is required for the engines equipped with lead-tolerant emission control systems. A compromise between compression ratio reduction and higher cost fuel for the engines equipped with lead-intolerant emission control systems is of course another alternative. As will be shown later, the latter is the minimum cost approach for engines equipped with lead-intolerant emission control devices.

The determination of a cost optimum compression ratio-fuel octane number combination is, of course, dependent upon the assumptions made in the analysis, particularly those for fuel price and the percent of "knock-free" satisfaction. As a result, it can be expected that different investigators would arrive at different optimums, depending upon their particular selection of the input variables. Reference 8-16 has determined such a cost optimum compression ratio-fuel octane number combination. Unfortunately, the analysis was based on providing a gasoline with which 98 percent of all cars would be knock-free when tested by the Coordinating Research Council method (based on technical or "trace-knock" satisfaction). This is a much higher percentage of knock-free cars than has been typical of pre-1971 cars (Ref. 8-17 indicates 80-percent knock-free, based on technical satisfaction, is more typical of cars with leaded fuel; this is equivalent to approximately 95-percent customer satisfaction). The analysis of Ref. 8-16 has therefore been recalculated with the only changes being that 80 percent of all cars are considered knock-free (based on

technical satisfaction) and a slightly different variation of gasoline cost with octane number is used. The increase in average price of unleaded (clear) gasoline used, versus octane number, exclusive of distribution costs, is shown in Fig. 8-2.

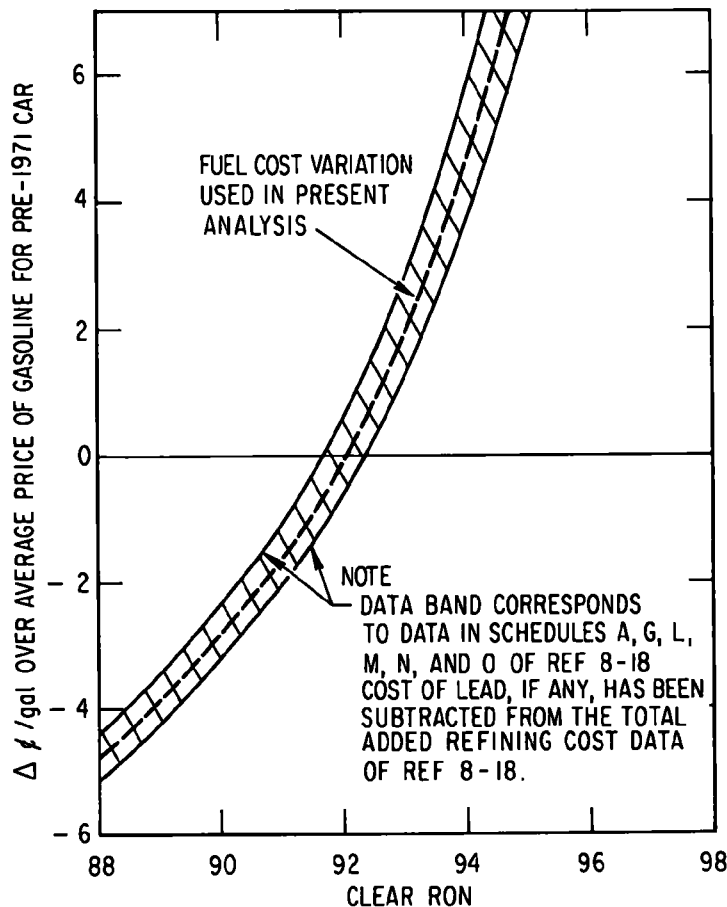


Figure 8-2. Cost of Unleaded Gasoline (Exclusive of Distribution Costs)

As noted on the figure, the data band corresponds to a wide range of clear-pool RON's. This band was determined from specific data points in Ref. 8-18 (Schedules A, G, L, M, N, and O) pertinent to total added refining costs calculated for a variety of postulated lead removal schedules. However, in cases where lead was still in use in a given schedule, the cost of the lead was subtracted to reflect only the clear-pool added refining

costs. It should be noted that there are three data points (from Ref. 8-18) in the region of most interest that have zero lead in the total pool:

| <u>Schedule</u> | <u>Year</u> | <u>Clear-Pool RON</u> | <u>Total Added Refining Cost, ¢/gal</u> |
|-----------------|-------------|---------------------------|---|
| L | 1980 | 93.5 | 0.34 |
| L | 1976 | 94.4 | 0.60 |
| M | 1980 | 94.2 | 0.43 |

Also, Schedule N, having very low lead content in the total pool for year 1980, indicates an added refining cost of 0.10 ¢/gal at a clear-pool RON of 92.6.

To the foregoing added refining cost of unleaded gasoline (Fig. 8-2) was added 0.26 cent per gallon to reflect the cost of a third pump and associated storage tanks for the distribution of unleaded gasoline (Ref. 8-18). It should be noted that this value does not incorporate any costs associated with segregated pipeline and distribution systems to ensure against contamination by leaded products, i.e., only "normal" precautions were contemplated. If the trace-lead-level content is required to be substantially lower than that obtainable by normal precautions, such pipeline and distribution costs would increase, perhaps substantially. The exact trace lead level at which this change in requirements exists is presently unknown to any degree of certainty.

The computed optimum RON for unleaded fuel (based on the foregoing assumptions) is between 94 and 95 (the solution is characteristically rather shallow in slope in the optimum region). A 93 RON gasoline, however, was selected for the fuel cost penalty assessment to be consistent with concurrent studies (EPA-funded) to determine unleaded gasoline investment and manufacturing costs (Ref. 8-18). The choice of 93 RON gasoline, rather than the optimum RON gasoline determined herein,

increases the fuel cost penalty only slightly, and reduces the refinery capital investment required.

The 93 RON chosen is, of course, different from the 91 RON with which the U. S. automobile manufacturers have indicated their cars will be capable of operating, at least in the immediate future. However, several automobile manufacturers in informal discussions have indicated that they do not consider 91 RON optimum and may very well increase their RON requirement with time. Their choice of 91 RON was apparently heavily influenced by their desire to specify a fuel which could be more easily made available during the sudden transition to the use of unleaded gasoline. The long-term case is believed more appropriate for the purposes of this analysis and, hence, 93 RON has been chosen.

Both single- and three-grade (three different ON unleaded fuels sold) unleaded gasoline cases have been analyzed since it is anticipated that, at the initial introduction of unleaded gasoline, a single grade will be offered because of need to retain service station pumps to sell leaded gasolines for older cars. However, as the older cars disappear from the road the leaded fuel pumps could gradually be converted to dispense additional grades of unleaded gasoline.

A multigrade unleaded gasoline system is advantageous to the consumer. The reason is that different engines of the same design do not all have the same octane number requirements because of manufacturing tolerances and variations in operating conditions. With a single-grade system, the fuel octane number must be selected to satisfy the cars with the highest requirement, and all cars must use this expensive fuel. With a multigrade system, those cars capable of using a cheaper fuel of lower octane number may do so, lowering the average price of gasoline; or conversely, if the average price of gasoline is held constant, the compression ratio and fuel economy may be increased as the number of grades is increased.

The results of the analysis are shown in Table 8-3. The fuel cost shown is that for 93 RON from Fig. 8-2 (0.20 cent per gallon) plus 0.26-cent-per-gallon distribution cost, as noted above. Again, there have been varying

Table 8-3. Cost Effects of Use of Unleaded Gasoline

| Item | 1-Grade | 3-Grade |
|---|-------------------|-------------------|
| Calculated Optimum RON | 94 ⁺ | 94 ⁺ |
| Pool RON Used in Analysis | 93 | 93 |
| Compression Ratio (93 RON) | 8.35:1 | 8.95:1 |
| Percent Change in Fuel Economy due to Compression Ratio Change from 1970 Car ^a | -5.4 | -2 |
| Fuel Price-- Δ ¢/gal over Average Fuel Price for 1970 Car | 0.46 ^b | 0.46 ^b |
| Fuel Cost Penalty due to Price/Gallon of Unleaded Fuel, 85,000 Miles. ^c No SFC Loss | \$30.00 | \$30.00 |
| Unleaded Gasoline Fuel Cost Penalty over 85,000 Miles ^c (Compression Ratio plus Δ ¢/gal Effects) | \$160.00 | \$80.00 |
| ^a Constant car performance (acceleration, power) | | |
| ^b Equivalent to 2.16 ¢/gal above leaded regular grade gasoline | | |
| ^c Approximate, varies with NO _x emission level, these values assume no NO _x SFC related cost | | |

estimates from different sources as to the eventual increased cost of unleaded gasoline. Although there may be differences of opinion regarding manufacturing cost increase, distribution cost effects, etc., the overall (circa 1980) cost increase of 0.46 cent per gallon used in this study for calculation purposes should be sufficiently representative to illustrate unleaded gasoline cost effects.

Traditionally, refiners, distributors, and service stations have made larger profits from the manufacture and sale of premium grade leaded gasoline than from regular grade leaded gasoline. Premium grade has accounted for approximately 42.6 percent of gasoline sales, but with the

introduction of unleaded gasoline, the sales of premium grade will decrease. When only unleaded gasoline is available, to make the same average profit per gallon the cost of unleaded gasoline should be the present weighted-average price of leaded gasoline plus the increased cost of manufacturing unleaded gasoline (over that of the weighted-average leaded gasoline) plus any associated increase in distribution costs for unleaded gasoline. This is the 0.46-cent-per-gallon figure derived above. However, since the price of leaded regular grade gasoline is less than the weighted-average sales price for leaded gasoline, this 0.46 cent per gallon is equivalent to a 2.16 cents per gallon increase above the price of leaded regular grade gasoline.

It was assumed that the three-grade system would have the same clear-pool RON (93) as the single-grade system and that the overall manufacturing plus distribution cost effects (0.46 cent per gallon over conventional leaded gasoline weighted-average price) would be the same. Although the incremental manufacturing costs for the three-grade system might be slightly different (even at the same 93 RON pool) from the 0.20 cent per gallon of the single-grade case, it is not felt that this difference would be large enough to significantly alter the results (e.g., 0.1-cent-per-gallon gasoline cost increase is equivalent to less than \$8 over 85,000 miles of operation.)

As can be seen from Table 8-3, the fuel cost penalty associated with the higher cost per gallon of unleaded fuel is not large (approximately \$30). The major fuel cost penalty with the use of unleaded gasoline (over leaded gasoline) is due to the lowering of engine efficiency associated with reduced compression ratio required by the lower octane number of the unleaded gasoline. For the single-grade system, there is an additional \$130 fuel cost penalty due to the necessity of reducing compression ratio to 8.35:1 (from 9.37:1 for the leaded fuel case; 80-percent knock-free technical satisfaction) with its attendant loss in fuel economy of 5.4 percent. In this case, then, the total fuel cost penalty attributable to the use of unleaded gasoline is \$160.

The most significant effect of the three-grade 93 overall RON system is the ability to increase compression ratio (to 8.95:1 at 80 percent knock-free technical satisfaction). This compression ratio-octane number satisfaction relationship was determined (as was the single-grade case) in a manner similar to that developed in Ref. 8-16 (constant car performance, acceleration, power).

As shown in Table 8-3, the increase in compression ratio made possible by the three-grade system reduces the fuel economy penalty loss to \$50 (for a 2-percent fuel economy loss compared to the leaded fuel reference case) and gives a total fuel economy penalty (compression ratio effect plus increased price-per-gallon effect) of \$80. This represents a savings of \$80 over the single-grade 93 RON case shown in the table. Although not shown, a two-grade unleaded system (at the same overall 93 RON) would be expected to provide similar (but not identical) cost savings over the single-grade system.

8.2.2.1.5 Fuel Economy Cost Penalty Results

As discussed in Section 4, the change in engine fuel economy (excluding unleaded gasoline) due to the addition of an emission control system, is a function of the NO_x emission level and whether or not an NO_x catalyst is used. Figure 8-1 gives these relationships. They have been combined with the previously described compression ratio and higher costs of unleaded gasoline effects to obtain the total fuel cost penalty for emission control systems as a function of NO_x emission level shown in Fig. 8-3. The following observations may be made from the figure:

1. The fuel cost penalty is sizable at the lower NO_x emission levels, regardless of the type of emission control system, because of the necessity of using low air-fuel ratios and/or high EGR rates.
2. Emission control systems incorporating NO_x catalysts have more potential for lower fuel costs than other systems, particularly at low NO_x emission levels, because of their ability to use higher air-fuel ratios and less EGR. It should

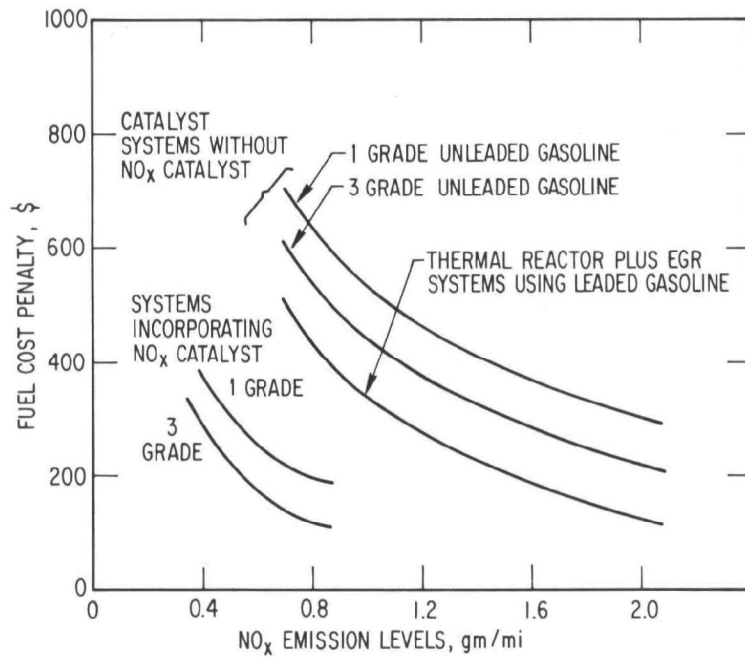


Fig. 8-3. Fuel Cost Penalty

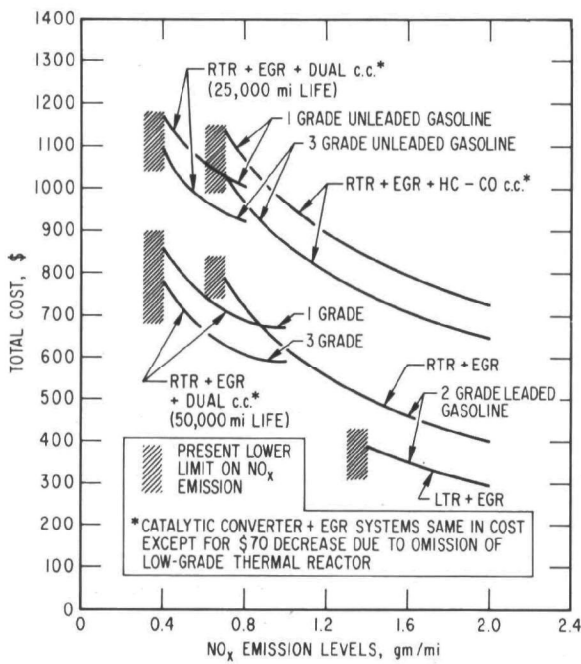


Fig. 8-4. Increased Consumer Costs Over Lifetime of Car

be noted, however, that no one has yet demonstrated reasonable life with a high-performance NO_x catalyst.

3. If a durable NO_x catalyst does not become available, emission control systems which do not incorporate HC/CO catalysts are superior from a fuel cost standpoint because of their ability to use leaded gasoline and a higher compression ratio engine.
4. For emission control systems which incorporate catalytic converters and must use unleaded gasoline, multigrade gasoline systems offer significant fuel cost advantages over single-grade systems.

8.2.3 Excluded Costs

No costs have been included for:

1. Research and development activities
2. Compliance emission testing after car purchase
3. Production emission testing

The required tests are undefined at present, and research and development costs are not yet all accrued and the rate of their amortization unknown.

8.2.4 Cost Analyses Results

The overall sum of the emission control system initial hardware cost, maintenance cost, and operating cost is shown in Fig. 8-4 for the selected generic systems as a function of the NO_x emission level. The cost is displayed as a function of the NO_x emission level, since the various systems are not all capable of the same NO_x emission reduction and the operating costs (fuel costs) are highly dependent on the NO_x emission reduction. Also shown on the chart are the presently demonstrated lower limits on NO_x emissions for the various systems as discussed in Section 4.

A breakout of the fuel costs from the total cost at selected NO_x emission levels is shown in Fig. 8-5. The emission levels selected correspond to those values which represent the presently demonstrated lower limit NO_x emission level for one or more systems.

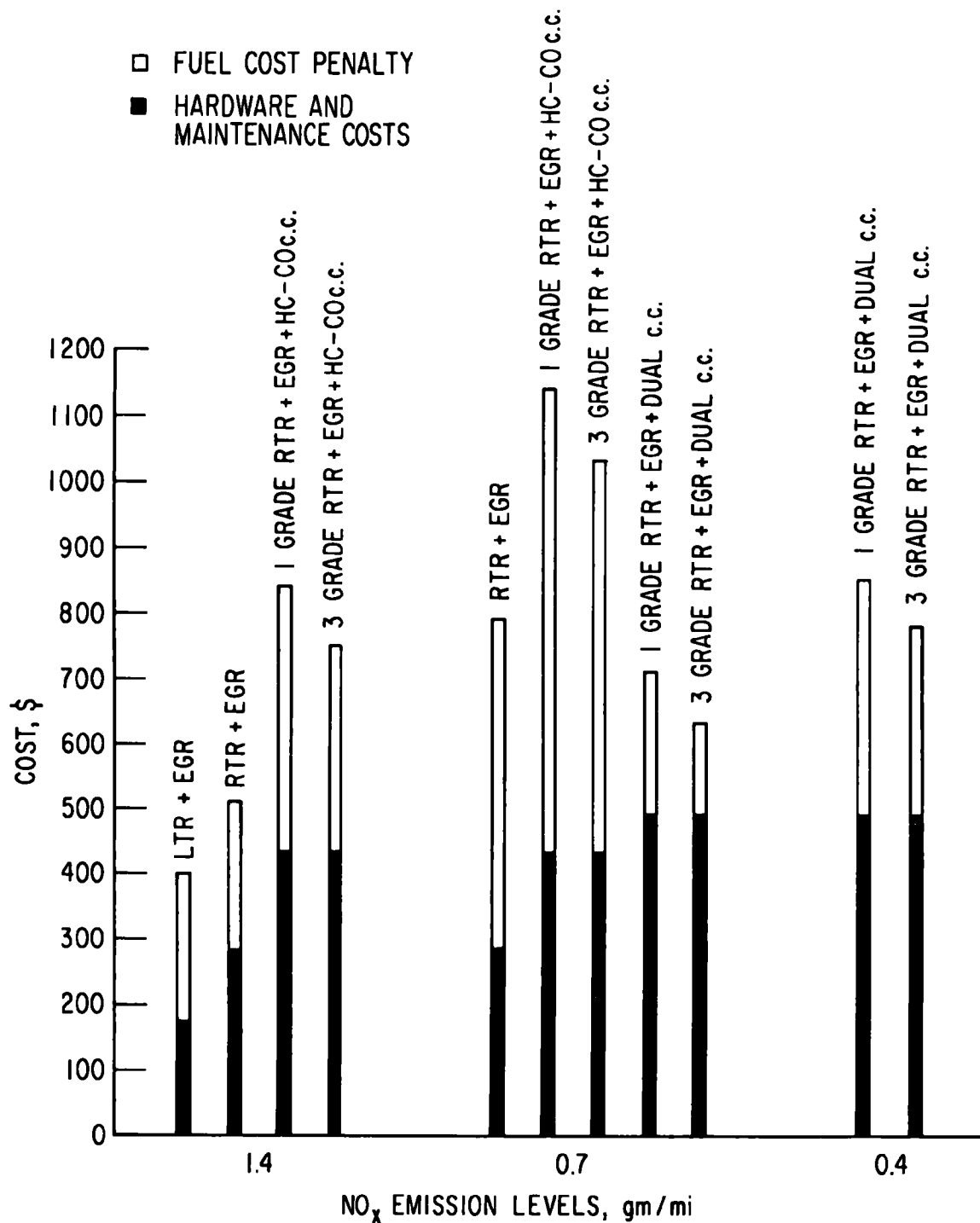


Fig. 8-5. Breakdown of Increased Consumer Costs over Lifetime of Car

The following cost observations and conclusions are based on the engineering cost estimates made herein:

1. All systems have high overall costs. The cost increases rapidly as NO_x emission level decreases. If the cost of an emission control system over the car lifetime were \$1000, the national annual cost with all cars on the road using this system would be of the order of \$10 billion.
2. Systems incorporating an NO_x catalyst are the only systems with the potential to meet the Federal standard of 0.4 gm/mi by 1976. In addition, at low emission levels they are the minimum cost systems provided that a 50,000-mile catalyst life can be achieved. The total cost of ownership in this case is approximately \$860. However, severe problems in developing a durable NO_x catalyst have been encountered, and such a catalyst may not be available by 1976. If only a 25,000-mile lifetime NO_x catalyst is available, the total cost of ownership is increased by approximately \$300.
3. The increased cost of unleaded gas is 0.46 cent per gallon compared to the average leaded gas cost. This amounts to about a \$30 increase over the life of the car. If the lowering of the average compression ratio -- and the associated fuel economy penalty -- is attributed to lead removal, another \$130 can be added to the cost of unleaded gasoline.
4. If the durability problems of the NO_x catalyst system cannot be resolved and its use is precluded, the RTR system, which can tolerate leaded gasoline, would be lowest in cost. Therefore, there is no cost advantage in unleaded gasoline unless a durable NO_x catalyst can be developed.
5. The lead-tolerant LTR system is attractive from a cost standpoint, but its NO_x emission levels are high.
6. In general, the lead-intolerant systems (catalyst plus thermal reactor systems) have higher initial hardware costs than those systems tolerating lead in the gasoline. This is because the catalyst plus thermal reactor systems include most of the parts of the straight thermal reactor systems as well as the catalyst. The thermal reactor in these systems is needed to provide fast warmup of the catalyst bed. If a fast warmup catalyst (of equivalent cost) is developed, the initial cost for the catalyst system is reduced by only \$70, because of the omission of the low-grade thermal reactor.

7. Lead-intolerant systems (catalyst systems) have higher maintenance costs than those systems tolerating lead because the cost of replacement of the catalyst bed is greater than the cost savings on spark plugs with unleaded gasoline. Muffler cost savings discussed earlier were precluded by the use of a long-life exhaust system on all 1976 systems.
8. A system incorporating a NO_x catalyst has the lowest fuel cost because it has the lowest SFC which more than offsets the higher cost effects of unleaded gasoline.
9. A lead-intolerant HC/CO catalyst system without a NO_x catalyst has higher fuel costs than a lead-tolerant thermal reactor system. This is due primarily to the cost effects of unleaded gasoline and compression ratio, as both systems have about the same SFC for a given NO_x level.

Of course, as more definitive data become available on emission control system technology (e. g., emission levels, durability, costs), the foregoing conclusions may be subject to appropriate modification.

REFERENCES

- 8-1. Personal discussion with representatives of the Chrysler Corporation (29 June 1971).
- 8-2. Effect of Lead Antiknocks on the Performance and Costs of Advanced Emission Control Systems, Du Pont de Nemours & Co., Wilmington, Delaware (15 July 1971).
- 8-3. Personal discussion with a representative of the Esso Research and Engineering Company (6 July 1971).
- 8-4. R.R. Allen and C.G. Gerhold; "Catalytic Converters for New and Current (Used) Vehicles," Paper presented at the Fifth Technical Meeting, West Coast Section of the Air Pollution Control Association, San Francisco, California (8-9 October 1970).
- 8-5. "Chapter 3: Mobile Sources," The Economics of Clean Air, Report of the Administrator of the Environmental Protection Agency to the Congress of the United States, Senate Document No. 92-6 (March 1971).
- 8-6. Personal discussion with a representative of the Research Triangle Institute (unpublished data)(6 August 1971).
- 8-7. Personal discussion with representatives of Engelhard Industries, Inc., (July 1971).
- 8-8. L.S. Bernstein, A.K.S. Raman and E.E. Wigg, "The Control of Automotive Emissions with Dual Bed Catalyst Systems," Presented to the 1971 Central States Section of the Combustion Institute (23 March 1971).
- 8-9. R.S. Yolles, H. Wise and L.P. Berriman, "Study of Catalytic Control of Exhaust Emissions for Otto Cycle Engines," Stanford Research Institute, Final Report, SRI Project PSU-8028 (April 1970).
- 8-10. The Ethyl Lean Reactor System, Ethyl Corporation Research Laboratories, Detroit (1 July 1971).
- 8-11. Automotive News--1971 Almanac, 35th Review and Reference Edition, Slocum Publishing Co., Detroit (26 April 1971).
- 8-12. Relationships of Passenger Car Age and Other Factors to Miles Driven, U.S. Department of Transportation, Bureau of Public Roads, Washington, D.C.

REFERENCES (cont.)

- 8-13. Consequences of Removing Lead Antiknocks from Gasoline, A Status Report, No. AC-10, Ethyl Corporation, Detroit (August 1970).
- 8-14. "Passenger Cars: Oil, Automotive Trends," 1971 National Petroleum News Factbook Issue.
- 8-15. Personal discussion with representatives of Du Pont de Nemours & Co., regarding their winter and summer gasoline surveys (October 1971).
- 8-16. E.S. Corner and A.R. Cunningham, "Value of High Octane Number Unleaded Gasolines in the United States," Presented before the Division of Water, Air, and Waste Chemistry, American Chemical Society, Los Angeles, California (28 March-2 April 1971).
- 8-17. W.E. Morris, et al., "1971 Cars and the 'New' Gasolines," SAE Paper No. 710624 (June 1971).
- 8-18. Economic Analysis of Proposed Schedules for Removal of Lead Additives from Gasoline, Bonner & Moore Associates, Inc., Houston, Texas (25 June 1971).

APPENDICES

A. VISITS AND CONTACTS

APPENDIX A

VISITS AND CONTACTS

A.1 ORGANIZATIONS VISITED

American Motors Corporation
American Oil Company
Atomics International
Bayerische Motoren Werke (BMW), Germany
Bonner & Moore Associates
California Air Resources Board
Chrysler Corporation
Degussa, Germany
E.I. Du Pont de Nemours & Company
Engelhard Minerals & Chemicals Corporation
Esso Research & Engineering Company
Ethyl Corporation
Ford Motor Company
General Motors Corporation
Kali-Chemie, Germany
Mobil Oil Company, Research Laboratories
NASA/Lewis Research Center
NSU-Audi, Germany
Research Triangle Institute
Universal Oil Products
Volkswagen (VW), Germany

A.2 ORGANIZATIONS CONTACTED

(Response by Phone or Letter)

Cooper Union
Daihatsu Kogyo Company, Japan
Dow Chemical Company
W.R. Grace Company
Houston Chemical Company
Illinois Institute of Technology, Research Institute (IITRI)
Monsanto Company
Nissan Motor Company, Japan
Toyo Kogyo, Japan
University of California at Los Angeles

**B. POSSIBLE CATALYST
POISONING MECHANISMS**

APPENDIX B

POSSIBLE CATALYST POISONING MECHANISMS

Degradation of the performance of catalytic converters employed as pollution control devices on automobiles run on leaded and unleaded gasoline is observed to occur much more rapidly with leaded gasoline. Degradation may occur either by loss of catalytic activity, or physical attrition, or both. The lead component of gasoline thus clearly constitutes a catalyst "poison" which acts through a variety of chemical and mechanical toxicity mechanisms that are not mutually exclusive.

B.1 SUMMARY OF CATALYST POISONING MECHANISMS

Among the possible chemical poisoning mechanisms are:

1. Chemisorption of toxic species at active surface sites, thereby rendering the catalyst inactive
2. Chemical conversion of the catalyst to an inactive, nonvolatile compound
3. Chemical conversion of the active component of the catalyst to a volatile compound, thereby reducing the quantity of catalyst
4. Reaction of toxic species with the catalyst support, resulting in a decrease in the structural stability of the catalyst and subsequent decline in surface area or mechanical attrition

Among the possible mechanical poisoning mechanisms are:

1. Deposition of a coating on the catalyst surface, rendering the latter inaccessible to reacting species
2. Deposition of poison at the mouths of catalyst pores, thereby also reducing the availability of much of the catalyst surface

B.2 CHEMICAL AND MECHANICAL POISONING MECHANISMS

B.2.1 Chemical Poisoning Mechanisms

Substances which are capable of forming much stronger bonds with the catalyst surface than the bonds normally formed by reactants and products

are termed chemisorptive poisons. A poison, because of its high bonding energy, resides on a catalyst surface for times very much longer than the necessarily brief residence times characteristic of reactants. Criteria for predicting the toxicity of various compounds toward metallic catalysts have been developed by Maxted (Ref. B-1). Although much of Maxted's work was done with catalysts suspended in liquids, the conclusions may be applicable to gaseous media as well, and should also be applicable to metal oxide catalysts. Two of Maxted's categories of catalyst poisons are relevant to the leaded gasoline problem:

1. Poisons containing nonmetallic elements of groups Va and VIa of the Periodic Table, notably sulfur and phosphorus
2. Poisons containing toxic metal ions

Nonmetals, such as sulfur or phosphorus, tend to be poisons in compounds because of their lower oxidation states, whereas lead is a chemisorptive poison for metallic catalysts in essentially any oxidation state. Because the mode of bonding metal ions to a metal surface differs from that of nonmetals, the toxicity criteria for metal ions are different. Maxted notes that a toxic metal ion must have a particular electronic structure (at least five d electrons) and lead meets this criterion. G.C. Bond (Ref. B-2) suggests a theoretical explanation of Maxted's observations.

The toxic species present in automobile exhausts could react chemically with the catalyst to form a layer consisting of a new compound or compounds that do not display catalytic activity. Possible reactions are presented in Ref. B-3.

Roth (Ref. B-4) has reported that a copper catalyst volatilized when exposed to a stream of chlorobenzene at high temperatures. This was interpreted as occurring by conversion of the copper to copper chloride, which was sufficiently volatile to leave the remaining catalyst material. Since the vapor pressure of most transition metal halides is exceptionally small at automotive catalyst operating temperatures, it is difficult to understand how the halides of these metals could volatilize into streams of higher pressure. Nevertheless, the complexity of exhaust gases from the combustion of leaded gasoline is such

that volatilization of a portion of the catalyst is possible, regardless of the nature of the mechanism.

The catalyst poison may chemically attack not only the active catalyst material, but the support as well, resulting in structural degradation of the catalyst and in subsequent loss of catalyst by attrition. Lead has also been observed to attack preferentially along the grain boundaries of a Monel NO_x catalyst, thereby causing agglomeration (Ref. B-5).

B.2.2 Mechanical Poisoning Mechanisms

The deposition of a catalytically nonreactive layer of material on the catalyst surface is another possible poisoning mechanism for automotive pollution control catalysts. This coating need not be chemically bonded to the catalyst surface.

X-ray diffraction analysis confirms the presence of lead sulfate, lead oxysulfate, and lead oxyhalides on the surface of spent catalysts (Refs. B-4, B-6, and B-7). Hofer, et al., also report the presence of lead halides (Ref. B-6). All these authors agree that lead sulfate is the principal lead compound. Yarrington and Bambrick found pyromorphite $[3\text{Pb}_3(\text{VO}_4)_2 \cdot \text{PbCl}_2]$ (Ref. B-7). The presence of the compound $3\text{Pb}_3(\text{PO}_4)_2 \cdot \text{PbCl}_2$ has been reported (Ref. B-8).

Deposition of lead compounds may occur preferentially at catalyst pore mouths, which will destroy catalytic activity by making the internal surface of the catalyst unavailable. The rate at which catalyst activity declines is an indication of whether poisoning is by blockage of pore mouths or by uniform deposition over the entire catalyst surface (Ref. B-9). Yarrington and Bambrick conclude that poisoning occurred by uniform deposition over the active surface for the catalysts which they tested (Ref. B-7).

The complex composition and huge variety of exhaust gas constituents and the wide range and number of engine operating parameters, together with the many types and configurations of catalytic materials, make it very difficult

to arrive at generalizations regarding the most likely mechanisms .
Nevertheless, a review of these mechanisms has indicated that lead would have a deleterious effect on catalysts . Experimental data with prototype catalysts, run with actual automotive exhausts under realistic operating conditions, are therefore most meaningful in assessing the effects of lead .

REFERENCES

- B-1. E.G. Maxted, in Advances in Catalysis III, W.C. Frankenberg, V.I. Komarewsky, and E.K. Rideal, editors, Academic Press, New York (1956).
- B-2. G.C. Bond, Catalysis by Metals, Academic Press, New York (1962).
- B-3. W.H. Page II, U.S. Patent 3,072,458, Universal Oil Products Company (8 January 1963).
- B-4. J.F. Roth, Paper presented at the 161st Meeting of the American Chemical Society, Los Angeles, California (April 1971).
- B-5. Esso Research and Engineering Company (private communication).
- B-6. L.J.E. Hofer, J.F. Schultz and J.J. Feenan, Bureau of Mines Report No. RI 6243 (1963).
- B-7. R.M. Yarrington and W.E. Bambrick, (to be published).
- B-8. D. Bienstock, et al., Bureau of Mines Report No. RI 6323 (1963).
- B-9. A. Wheeler, in Advances in Catalysis III; W.C. Frankenberg, V.I. Komarewsky, and E.K. Rideal, editors, Academic Press, New York (1951).

**C. LEAD TRAP DEVICES
FOR AUTOMOTIVE
VEHICLES**

APPENDIX C

LEAD TRAP DEVICES FOR AUTOMOTIVE VEHICLES OPERATING ON LEADED GAS

C.1 INTRODUCTION

Devices that would allow the use of leaded gasoline with catalytic converters are under development. These devices would have to remove lead from the engine exhaust upstream of the catalyst. Techniques for collecting lead from exhaust emissions of automobiles operating on leaded fuel fall into two basic categories. The first technique removes lead in the gaseous, as well as particulate, form at exhaust manifold temperatures so that the exhaust is held sufficiently hot for further catalytic treatment to control NO_x , HC and CO emissions. The second technique requires that exhaust gases be cool enough for a sufficient amount of lead to be in particulate form for collection. Thus, in order to utilize the second technique prior to catalytic treatment, additional equipment will be required to first condense the lead into particulate form for collection upon exiting the exhaust manifold and then to reheat the exhaust gas for efficient catalytic reaction. In addition to the extra complexity and cost for such a device, the limited available space in present automobile designs would appear to make this technique impracticable for use with catalytic reactors. However, such systems are considered appropriate for removal of lead from exhaust emissions subsequent to catalytic treatment, or in a system where catalytic converters either are not present or are insensitive to lead compounds. The various lead removal techniques will be identified and discussed under the two classifications described above, namely, (1) combined lead compound vapors and particles, and (2) lead compound particles only.

A literature search and telephone contact with knowledgeable industry representatives for past and current activities directed toward devices for collecting lead from automobile exhaust emissions revealed that the extent of such work seems to have been primarily limited to Atomics International, Cooper Union,

Dow Chemical, Du Pont, Ethyl, Houston Chemical Company, and Illinois Institute of Technology (IIT) Research Institute. These seven organizations have been responsible for a total of eight devices in various stages of development. With the exception of Atomics International, all techniques required that lead be in a particulate form for collection and removal. The Atomics International approach has been the subject of considerable development that has included laboratory, as well as automobile road and engine dynamometer testing, whereas four of the seven particulate-only collection techniques proposed by Cooper Union, Dow Chemical, and IIT Research Institute have not progressed beyond exploratory testing in the laboratory. The cyclone-type traps proposed by Du Pont and Ethyl for collecting lead and other particulates have apparently undergone a fair amount of design and testing effort. Additional details of each system are summarized in the following paragraphs.

C.2 TECHNIQUE FOR REMOVING COMBINATIONS OF LEAD COMPOUND VAPORS AND PARTICLES FROM EXHAUST EMISSIONS

As indicated in the foregoing discussion, Atomics International has developed the only approach for removing lead in the vapor as well as particulate form. A description of the early development work is presented in Refs. C-1 and C-2. For purposes of the present discussion, pertinent information relative to the concept, current design approach, efficiency, costs, and compatibility with catalytic reactors is summarized.

C.2.1 Atomics International Molten Carbonate Process

This approach is based on the fact that lead halides and sulfur dioxide, which are mildly acidic, can be expected to react chemically with a basic alkali carbonate. Thus, a molten carbonate salt was evolved to scrub gaseous, liquid, or solid lead compounds from automobile exhausts. The carbonate, the choice of which resulted primarily from melting point and cost considerations, consists of roughly equal parts by weight of lithium, sodium, and potassium carbonate, and melts at a temperature of 750°F. The lead and

sulfur compounds react with the carbonate and are removed from the exhaust stream within the scrubber.

Laboratory tests and road tests of a breadboard device installed in an automobile suggested that a muffler replacement device could potentially remove a large portion of the lead from the exhaust. An under-the-hood molten carbonate device was designed, fabricated, and installed on an automobile for road tests. A schematic of this device is illustrated in Fig. C-1. The gas from the exhaust manifold is brought into the device through the inlet and maintains the salt in a molten state. The flow of hot gas is accelerated through the venturi tube, across the venturi throat, out the venturi recovery tube, and into a wetted-mesh reaction zone. The venturi action provides the pumping power to lift the molten salt up through the salt intake tube and aspirate it into the gas stream. As the

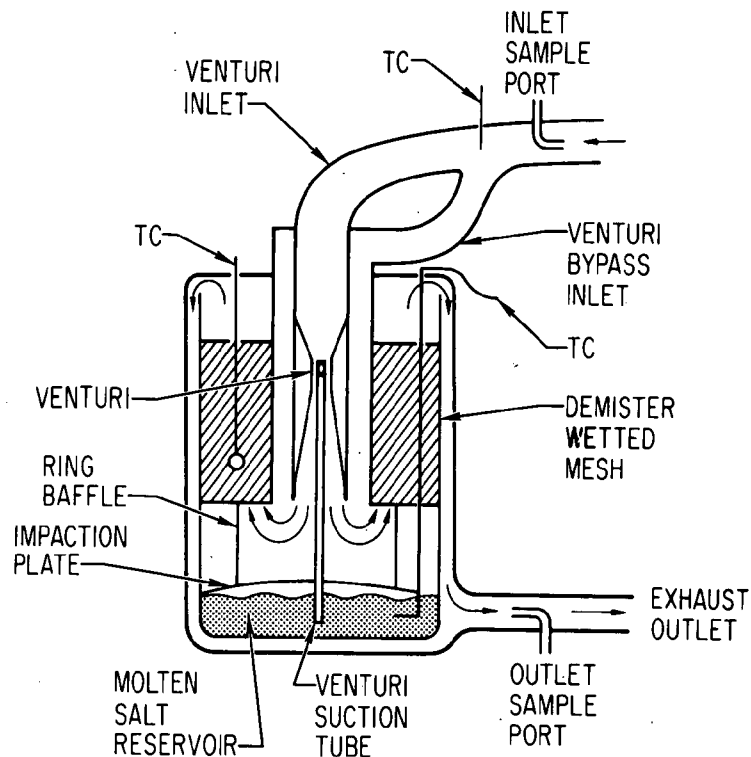


Fig. C-1. Schematic of an Engine-Compartment-Mounted Molten Salt Scrubber (from Ref. C-2)

gas stream passes through the wetted mesh, removal of particulates is accomplished by absorption on the mesh. After the gases pass through the reaction zone, they pass over a baffle into the demisting zone where final removal of the entrained salt is accomplished. The absorbed particles are carried with the demisted melt into the melt pool where the heavier particles of lead and corrosion products form a slurry at the bottom of the molten salt pool. From the demister zone, the exhaust gases flow through the outlet port with a maximum reduction in temperature of 10-20°F. To reduce corrosion, an air-cooled bypass line is provided at the device inlet to permit temperature control of exhaust gases passing the molten salt pool; this prevents the melt from exceeding temperatures of 1200°F. The exhaust passed through the bypass line is combined with gas flowing through the venturi in the wetted-mesh reaction zone.

A fabricated under-the-hood molten carbonate device is shown with a catalytic reactor in Fig. C-2, and installed in an automobile engine compartment in Fig. C-3. Eight thousand miles of random over-the-road operation, and subsequent California 7-mode cycling tests (Ref. C-3) on an engine dynamometer for an additional 7500 equivalent miles, indicated that this device could be expected to remove over 90 percent of the lead, essentially all the sulfur oxides, and in excess of 80 percent of all particulates over the entire operating range of an automobile, in addition to attenuating engine noise as well as standard mufflers. It was also observed that backpressures in the exhaust system did not exceed those experienced in standard mufflers.

The device contains 10-12 pounds of carbonate and requires an engine compartment space of 10 inches in diameter and 14 inches in height. When servicing is required, the salt is removed from the device and fresh carbonate is added through a fill tube. The salt must be changed periodically to maintain the melting point of the mixture and to remove accumulated waste particles from the system. Oxidation of sulfite to sulfate in the carbonate melt results in an increase of about 25°F in the melting temperature in about 10,000 miles of operation. Lead and other metals form a sludge at the bottom of the salt.

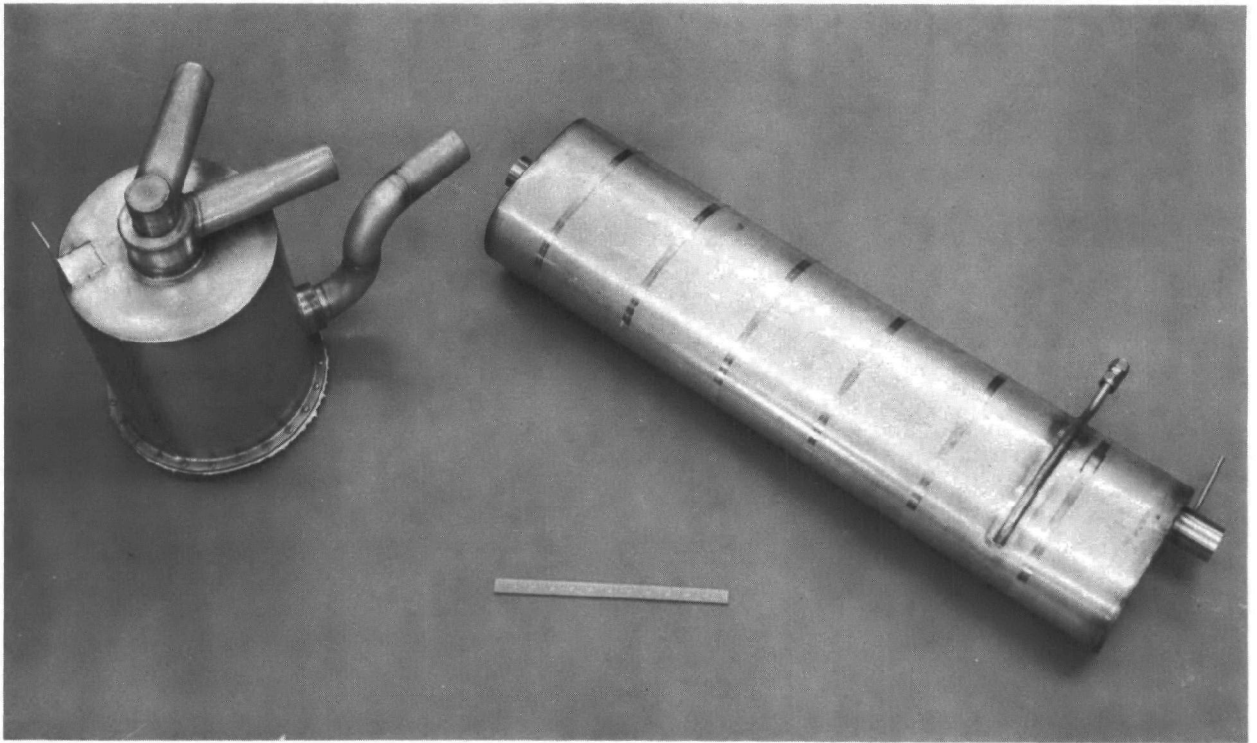


Fig. C-2. Fabricated Engine-Compartment-Mounted Molten-Salt Scrubber (Courtesy of Atomics International)

It is presently estimated by Atomics International that the salt will require changing every 15,000 to 20,000 miles at a cost of \$10. By extrapolating the deepest corrosion penetrations linearly, Atomics International predicts that the life of a device fabricated from aluminized steel will be a minimum of 50,000 miles.

Atomics International has recognized that the under-the-hood prototype device cannot be accommodated in all automobile engine compartments, and is therefore, currently in the process of developing an under-the-car device which may be capable of retrofit onto all currently operational automobiles. A conceptual design of such an under-the-car device is shown in Fig. C-4. The Pricing and Estimating Division of Atomics International has estimated that the production cost of this device will be \$19.58 per unit based on one million units per year. At typical markup and profits plus installation, the cost to

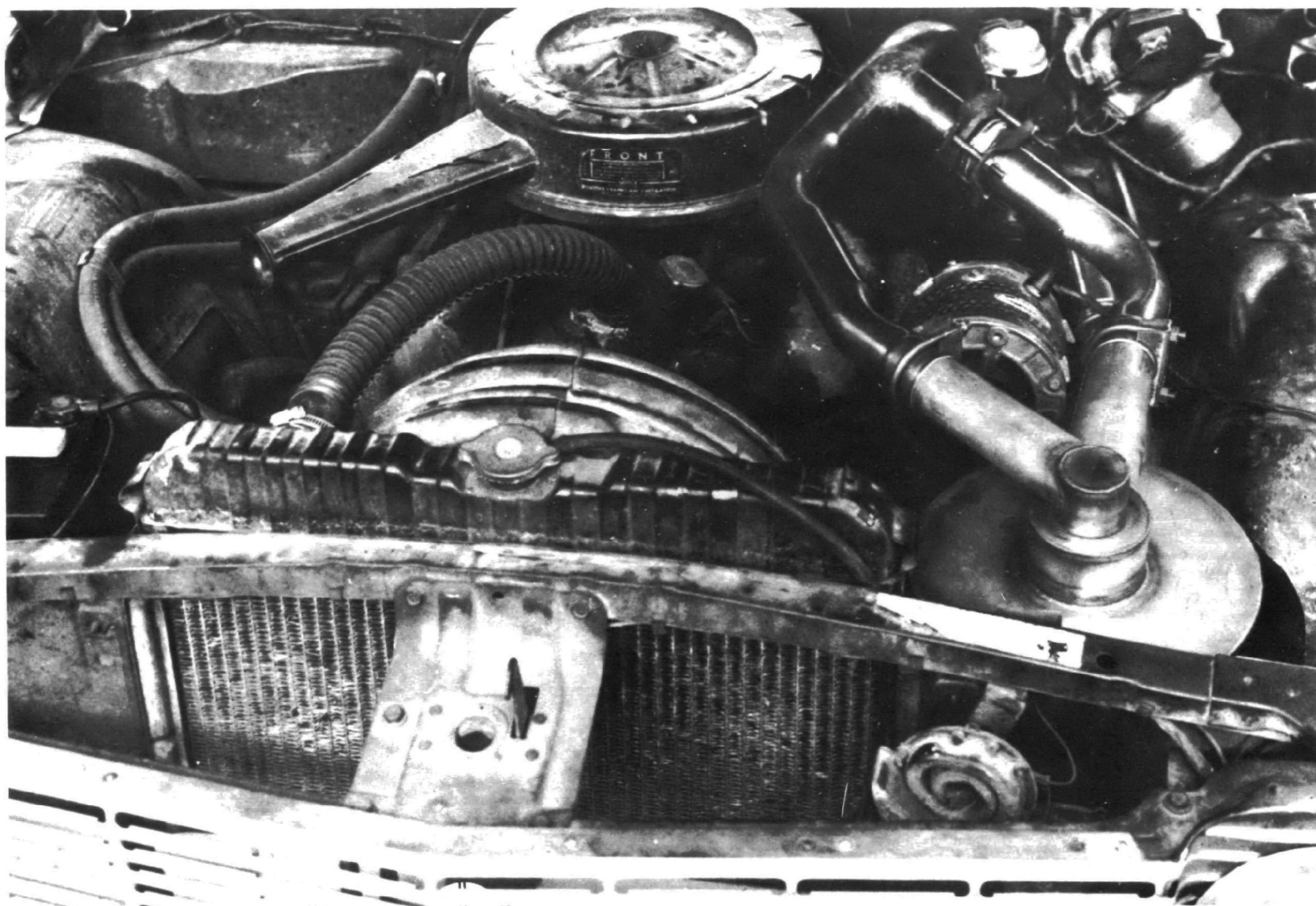


Fig. C-3. Installation of Engine-Compartment-Mounted Molten-Salt Scrubber
(Courtesy of Atomics International)

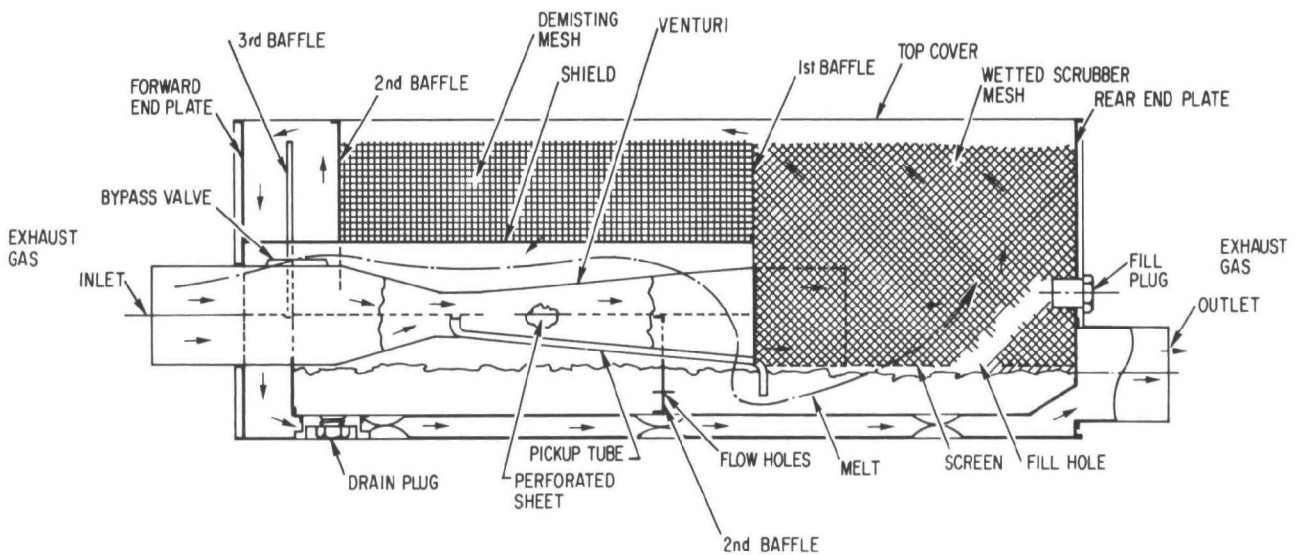


Fig. C-4. Under-the-Car Lead Trap--Conceptual Design (from Ref. C-2)

the user is reported to range from \$35 for a factory-installed device to \$45 for retrofit units.

The molten carbonate lead trap device will not be compatible for leaded fuel operation in conjunction with a catalytic reactor unless the lead is removed in sufficient quantities and durability of removal capability is sufficiently long. The lead trap should not provide any significant delay in attaining efficient operating temperatures for the catalytic reactor. During the 7-mode cycling tests (Ref. C-3), the lead trap achieves operating temperatures of 1000°F in slightly over 2 minutes, with temperature drops across the device never exceeding 20°F. As previously mentioned, the molten carbonate process removes practically all SO₂ from the exhaust gases and thus permits consideration of catalytic reactors which are susceptible to SO₂ poisoning. Finally, the lead trap device has not exhibited backpressures in excess of those found in conventional exhaust systems and attenuates the engine noise as well as standard mufflers.

C.3 TECHNIQUES FOR REMOVING LEAD COMPOUND PARTICLES ONLY FROM EXHAUST EMISSIONS

This section summarizes the seven known trap devices that have been suggested for collecting lead particles from automobile exhaust emissions. With the exception of the IIT Research Institute's thermal packed bed and Cooper Union's molten salt device, each system includes inertial separation with varying degrees and types of coagulation and/or agglomeration of the particles to facilitate separation. With the exception of the Du Pont and Ethyl devices, the techniques suggested have not progressed beyond limited exploratory testing in the laboratory.

Dow Chemical (Ref. C-4) and Ethyl (Ref. C-5) appear to be in general agreement that lead in the automobile exhaust system remains in a partially vaporized state above 650°F. To ensure temperatures below this value in the exhaust system for speeds up to 60 mph, it would be necessary to locate lead particulate collection devices near the end of the tailpipe. Du Pont (Ref. C-6) indicates that to achieve maximum effectiveness in collecting lead particles from auto emissions by inertial separation, the exhaust gases should be cooled below 550°F.

C.3.1 Du Pont Cyclone Trap System

A relatively simple exhaust particulate trapping device which replaces the normal exhaust system has been devised by Du Pont. It consists of a dual fluted pipe to cool the exhaust, and a cyclone trap to separate and collect the solid particles (Ref. C-6). The combination of the fluted pipe and the dual system increases the surface area and cools the exhaust gas below 550°F under normal driving conditions. (This temperature limitation is considered necessary in order to achieve maximum effectiveness for inertial separating devices such as cyclones.) After being cooled in the fluted pipe, the gases flow into a mesh-lined cyclone trap box. The exhaust gas first passes through wire mesh to agglomerate the particles and then through a cyclone to separate the particles from the gas. The cyclone boxes have sufficient capacity to store all the separated lead salts for the expected life of the car.

A 64,000-mile test of this device on a 1966 car resulted in a 70-percent reduction by weight in lead particulate emissions compared with an equivalent vehicle with a conventional exhaust system.

The simple cyclone device was further developed to provide additional cooling and agglomeration by wire mesh-lined pipes and a mesh-filled box placed ahead of the two cyclone traps. Lead particulate exhaust emissions from two cars equipped with the advanced trap system operating for an equivalent 70,000 miles was compared with those from two similar cars with conventional exhaust systems over the same operating range. The reported results indicated that the improved trap system reduced lead particulate emissions by 80 to 85 percent.

C.3.2 Ethyl Corporation Particulate Traps

Ethyl reports exploration of a wide variety of trapping devices and concludes that for a simple, low-cost, muffler-type device, the principal of inertial separation is the most promising approach (Refs. C-5, C-7, C-8, and C-9). Ethyl has also discovered that the greatest hindrance in the use of inertial trapping systems is the high temperatures (ranging from 1000°F to 1500°F) of the gas exhausting from the manifold. Since Ethyl considers lead halides to be partially vaporized above 650°F, it has been necessary to design and test several heat exchangers to obtain one that is capable of giving temperature drops of up to 900°F.

Advancement of the inertial separation principle has led to the development of a unit (Fig. C-5) composed of two inertial elements referred to as anchored vortex tubes. Particulates separated at the walls are rejected at high energy through slots near the base of the closed-end tube. This unit is currently undergoing tests and has been subjected to 24,000 miles of operation to date, resulting in a 65-percent reduction in exhausted lead. On the basis of present test mileage, the capacity of this device is considered to permit a life of at least 50,000 miles. Costs are estimated to be in the range of standard-type mufflers.

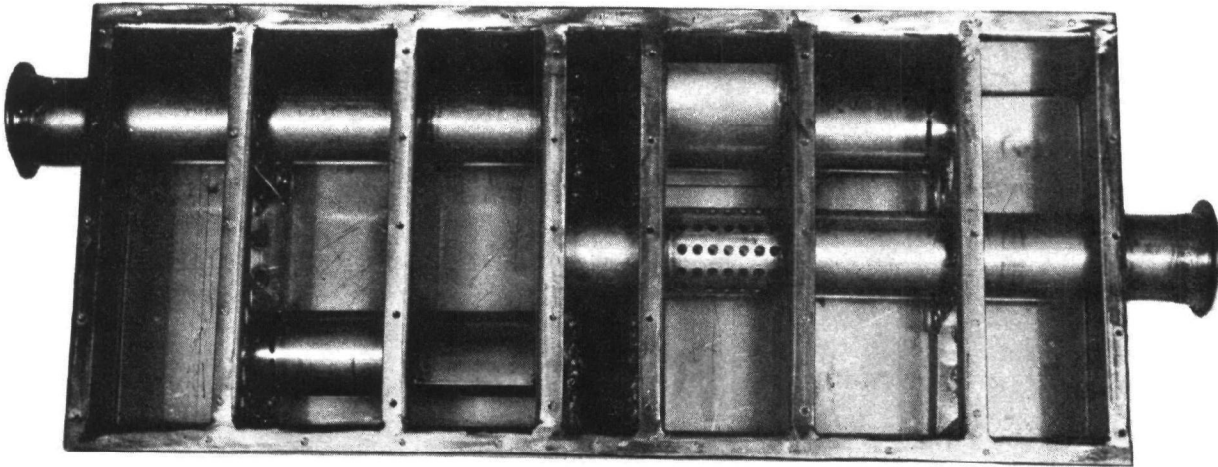


Fig. C-5. Experimental Dual-Anchored Vortex Trap (from Ref. C-9)

Ethyl believes that more complex devices which add an interceptor ahead of an inertial device are more promising than the plain inertial device. The interceptor is a chamber of loosely packed or loosely woven material on which particles can impinge and grow, and then migrate on through to be collected by the inertial device. Although preliminary testing of this approach is reported to have given reductions in exhausted lead in the 70 to 90 percent range, Ethyl considers that further development work is necessary to make such devices simple and practical.

C.3.3 Dow Chemical Molten Salt Particulate Trap

In a limited effort by Dow Chemical, the approach selected for design of a trapping device was to wet the exhaust particles with a suitable liquid medium which increases the mass of the particles and facilitates inertial separation (Ref. C-4). Prototypes were constructed and subjected to a restricted number of laboratory tests. Sufficient data have not been obtained to evaluate this system at this time.

C.3.4 Cooper Union Molten Salt Approach

Cooper Union also conducted an exploratory study on the removal of lead particulates from automobile exhausts by means of molten salt (Ref. C-10). The approach was based on the assumption that lead particles, once captured and wetted by molten salts, would be prevented from being re-entrained into the gas stream because of the relatively high surface tension of molten salts. Exhaust gases from an idling 1964, 6-cylinder Falcon were passed through a molten salt kettle and the resulting lead content was compared with that of the untreated gas. Limited data from these tests showed a reduction of lead particulate emissions which varied from 32 to 72 percent.

C.3.5 ITT Research Institute Devices

ITT Research Institute has conducted research efforts to establish the feasibility of developing two collection devices for the removal of particulate matter from internal combustion engine exhausts (Ref. C-11). The first approach considered thermal precipitation which makes use of the phenomenon of particle migration and deposition in a temperature gradient. The second approach was the fluidized bed, which makes use of the phenomenon of high-velocity gradients.

C.3.5.1 Thermal Packed Bed Device

The thermal deposition approach is based on the fact that particles move from hot-gas streams to cold surfaces under the influence of thermal force. A particle in the thermal gradient can be expected to be hotter on one side than the other. On the average, gas molecules striking the hot side will rebound at a higher temperature and, hence, at a higher velocity than those striking the cold side. This imbalance creates a force on the particle directed toward the colder end of the temperature gradient.

On the basis of this principle, an experimental laboratory setup of a packed bed made up of high-heat capacity material was subjected to aerosols approximating lead basic constituents found in automobile exhausts. The collection efficiency of the thermal packed bed device was determined by simultaneous

sampling of the gas both upstream and downstream of the bed. Initial tests were conducted using a packed bed of 8-mm glass helices at a gas-packing temperature difference of 1112°F . The collection efficiency of this device was found to be 86 percent.

Experimental results from tests indicated that the most important variable affecting the collection efficiency of the thermal packed bed device is the gas-packing temperature difference. It was found essential to maintain temperature differentials in excess of 390°F to operate the device with a high efficiency. Thus, it becomes necessary for the device to be located downstream of the manifold, where most of the lead is in particulate form and where the exhaust temperature difference will be sufficient to ensure high collection efficiency. Since the bed will heat with time on the passage of hot exhaust gases, a technique is required to permit operation of the device while maintaining a large gas-packing temperature differential at all times. One method proposed for accomplishing this result is shown schematically in Fig. C-6. Two packed beds would be used intermittently to clean the gas. As the exhaust gas flows through one bed, the other is cooled by a flow of relatively cold outside air. When the temperature sensor indicates that one bed is becoming too warm for efficient operation, the butterfly valve changes to channel the flow to an alternate bed. Another approach to cool the bed internally was also suggested in order to require only one packed bed.

Again, insufficient effort has been directed towards developing the thermal packed bed device to permit prototype designs for automobile installation and estimates of frequency of replacing packing material, maintenance, and life of device as well as costs.

C.3.5.2 Sonic Fluidized Bed Device

The second technique studied by IIT Research Institute to control particle emissions from auto exhausts was the fluidized bed. The mechanism of aerosol removal in fluidized beds is related to the high-velocity gradients in a gas flow around the particles in the bed. The gas particles do not follow the flow

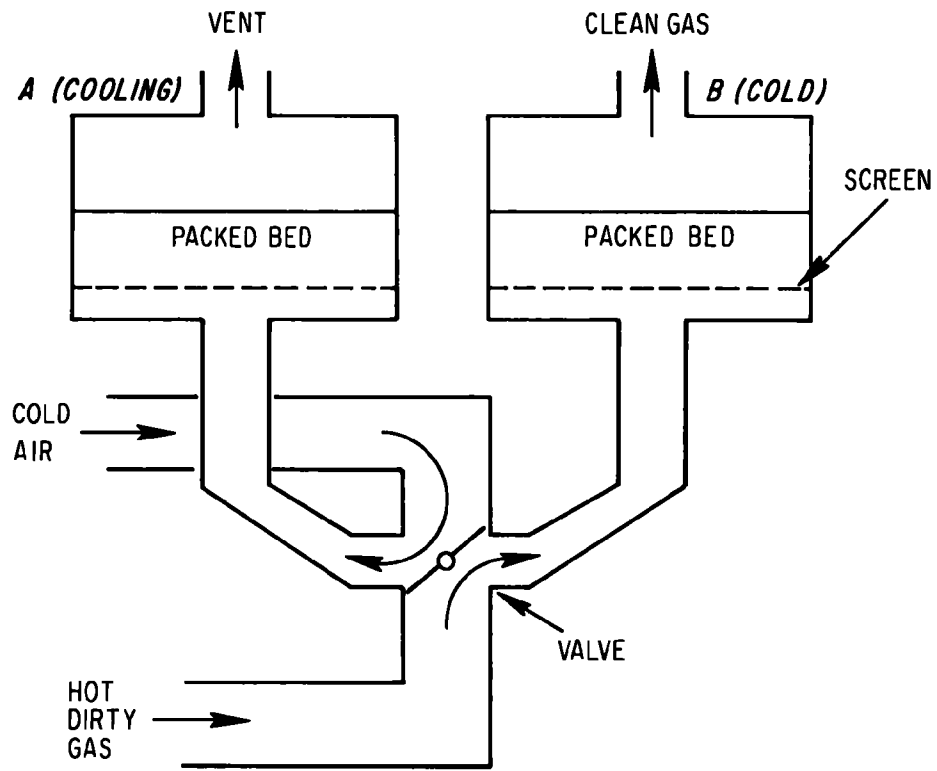


Fig. C-6. Packed Beds for Collection of Submicron Particles by Thermal Precipitation (from Ref. C-11)

stream lines because of their inertia and impact on the fluidized bed particles adhering to them. The velocity gradients between the bed and aerosol particles can be enhanced by superimposing a sound field.

Collection efficiency of the fluidized bed was found to increase sharply with power input to the sound driver units when standing waves were used. In these tests, 210-500-micron glass beads were used as the fluidized material and efficiencies of up to 90 percent were obtained with the generation of standing sound waves for inputs of 125 watts to each of four loudspeaker sound driver units. Since natural sound levels in an auto exhaust are not sufficient, an auxiliary acoustic unit would be needed to generate an additional 200 watts of acoustic energy.

IIT Research Institute envisions that such a device designed for installation in automotive systems would occupy about 2.5 cubic feet of space and weigh approximately 45 pounds. The sonic generator would probably be an air-driven siren supplied by a belt-driven air compressor. The cost for such a device was estimated to be somewhat less than \$100 at the retail level. Maintenance is considered to be minimal and the material for refilling the fluidized bed would cost approximately \$2.50. Although this particular approach has not progressed beyond the conceptual stage, the dissipation of acoustic energy from such a device installed in an automobile could result in significant design problems.

C.3.6 Houston Chemical Company Particulate Trap

In a news release (Ref. C-12), PPG Industries' Houston Chemical Company disclosed the development of a new particulate trap that it claimed would remove 99 percent of all particulate matter from automobile exhausts and might protect catalytic reactors from lead poisoning. This system is expected to replace the normal exhaust system of an automobile, to be only slightly more expensive, and to have a life expectancy of at least 50,000 miles.

Preliminary discussions, subsequent to this news release, indicate that the system consists of a fiberglass filter system designed to be used after a cyclone separator. The system will operate only at exhaust temperatures below 700°F to avoid decomposition of the fiberglass. Also, it is necessary to control the exhaust to low temperatures (approximately 500°F) to ensure that the lead particulates have condensed from the vapor phase. As such, this system would only be compatible with a lead-sensitive catalyst that could function at low temperatures. However, such catalysts have not been identified to date. Mileage accumulation to 10,000 miles indicates removal capability of 99 percent (of particulates above 0.3 micron) and a backpressure increase equivalent to the standard muffler, according to the Houston Chemical Company.

REFERENCES

- C-1. Development of the Molten Carbonate Process to Remove Lead and Other Particulates from Spark Ignition Engine Exhausts, Report No. AI-70-47, Atomics International, Canoga Park, California (8 July 1970) (HEW Contract No. CPA 70-3).
- C-2. L.F. Grantham and S.S. Yosin, "Removal of Lead Gases with Molten Alkali Metal Carbonates," Paper presented at the American Chemical Society Symposium on Current Approaches to Automotive Emission Control, Los Angeles, California (28 March - 2 April 1971).
- C-3. "Standards for Exhaust Emissions, Fuel Evaporative Emissions, and Smoke Emissions Applicable to 1970 and Later Vehicles and Engines," Federal Register, Vol. 33, No. 108, Part II (4 June 1968).
- C-4. J.B. Moran, et al., Development of Particulate Emission Control Techniques for Spark Ignition Engines, Report No. EHS70-101, Dow Chemical Company, Midland, Michigan (July 1971)(EPA Contract No. EHS 70-101).
- C-5. H.D. Coffee, Jr., et al., "Clean Air Car," Ethyl Corporation, Detroit (Unpublished report)(24 July 1970).
- C-6. K. Habibi, et al., "Characterization and Control of Gaseous and Particulate Exhaust Emissions from Vehicles," Paper presented to the Air Pollution Control Association, San Francisco, California (October 1970).
- C-7. D.A. Hirschler and F.J. Marsee, Meeting Future Automobile Emission Standards, Report No. AM-70-5, Ethyl Corporation, Detroit (April 1971).
- C-8. G.L. TerHaar, et al., "Composition, Size and Control of Automotive Exhaust Particulates," Paper presented to the Air Pollution Control Association, Atlantic City, New Jersey (June 1971).
- C-9. Consequences of Removing Lead Antiknocks from Gasoline, A Status Report, No. AC-10, Ethyl Corporation, Detroit (August 1970).
- C-10. Shang-I Cheng, et al., "Removal of Lead from Automobile Exhausts by Molten Salts," Environmental Science and Technology, Vol. 5, No. 1 (January 1971).

REFERENCES (cont.)

- C-11. S. K. Sood and Richard Karuhn, Development of Particulate Emissions Control Techniques for Spark Ignition Engines, Report No. C6186-5, Illinois Institute of Technology Research Institute (February 1971) (EPA Contract No. CPA-22-69-134).
- C-12. Chemical Engineering News (20 September 1971).