EPA/AA/CTAB-89-01

Technical Report

Resistively Heated Methanol Dissociator for Engine Cold Start Assist - Interim Report II

by

Gregory K. Piotrowski

February 1989

NOTICE

U. S. Environmental Protection Agency
Office of Air and Radiation
Office of Mobile Sources
Emission Control Technology Division
Control Technology and Applications Branch
2565 Plymouth Road
Ann Arbor, Michigan 48105

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ANN ARBOR, MICHIGAN 48105

OFFICE OF
AIR AND RADIATION

APR 24 1989

MEMORANDUM

SUBJECT: Exemption From Peer and Administrative Review

FROM: Karl H. Hellman, Chief KH
Control Technology and Applications Branch

TO: Charles L. Gray, Jr., Director
Emission Control Technology Division

The attached report entitled, "Resistively Heated Methanol Dissociator for Engine Cold Start Assist - Interim Report II," (EPA/AA/CTAB/89-01) describes the evaluation of a methanol dissociation catalyst that provides a cold start assist for a light-duty methanol engine. Methanol was boiled in a steam-heated vessel, superheated and passed to a dissociator which made use of resistively heated porous silicon carbide technology. The catalyst used for the methanol dissociation reaction was a noble metal/rare earth formulation developed by Nissan Motor Corporation.

Since this report is concerned only with the presentation of data and its analysis and does not involve matters of policy or regulations, your concurrence is requested to waive administrative review according to the policy outlined in your directive of April 22, 1982.

Concurrence: Charles L. Gray, Jr. Date: 4-19-89
Charles L. Gray, Jr., Dir., ECTD

Nonconcurrence: _____ Date: _____
Charles L. Gray, Jr., Dir., ECTD

cc: E. Burger, ECTD

Table of Contents

I. Summary

A catalyst specifically formulated for the dissociation of methanol to hydrogen (H_2) and carbon monoxide (CO) was evaluated for the application of a cold start assist for a light-duty methanol-fueled engine. The dissociated methanol generating system consisted of a steam-heated methanol boiler, a gas superheater, and a catalyzed dissociation element. The dissociation element substrate was resistively heated and constructed primarily from fibrous silicon carbide.

The objective of this experimentation was to determine the ability of the catalyst to facilitate the dissociation of methanol, and to start and idle a 4-cylinder engine on the product gas from the dissociator.

H_2/CO product gas yield varied between 13 and 15 percent for a feed flowrate of 2500 grams of methanol per hour. Dissociator yield was not a function of superheater feed gas temperature, for feed gas temperatures into the dissociator between 400° and 700°F. Power to the dissociator was kept constant at 345 watts during this testing.

H_2, CO, non-dissociated methanol, and possibly other reactor products from the dissociator were piped to the exhaust gas recirculation port of the test engine. This product gas mixture served as the fuel supply during the engine start experiments; the stock methanol injectors on the test engine were disabled prior to this testing.

At an engine temperature of 73°F the product gas mixture easily started and idled the test engine. The combination of hot methanol vapor and H_2/CO may be too rich to enable extended idle, however; flowrates between 1800-2500 grams per hour of feed methanol are difficult to control with the test apparatus.

It is difficult to quantify emission control benefits from the use of dissociated methanol compared to M100 liquid fuel using the dissociation system described in this report. Only 13 to 15 percent of the feed flowrate of 2500 grams of methanol per hour was dissociated to H_2 and CO. Any emissions control benefit may be minimized by the presence of large amounts of unconverted liquid methanol in the H_2/CO fuel stream. Additional testing should be conducted with a fuel mixture much richer in dissociated product than M100 in order to more properly define the difference in emission levels between the two fuels at cold start.

No coking was observed on the walls of the ceramic substrate following this evaluation. Traces of coke were found at the interface between the silicon carbide substrate,

stainless steel wool gaskets, and the stainless steel electrical contacts. Hot spots caused by areas of high current density along this interface may have contributed to this localized coking.

II. Introduction

Light-duty M100 neat methanol-fueled engines are difficult to start and run in cold weather because of the high boiling point of methanol, methanol's high heat of vaporization (5.5 percent of the heat of combustion compared to less than 1 percent for gasoline), and the increased fuel flow needed for methanol (about double that of gasoline). Gasoline-fueled engines start with less difficulty under the same conditions partly because of the easily ignitable light ends of this fuel such as butanes, which are vaporized at relatively low temperatures.

Some state-of-the-art methanol engines require the addition of gasoline to the fuel to improve their startability.[1] Other methanol engines utilize separate cold start systems relying on gasoline or propane for cold start assist.[2,3] Finally, some researchers have suggested that stratified-charge combustion will produce reliable cold starts of a neat methanol-fueled engine at relatively low ambient conditions.[4]

Methanol may be catalytically decomposed to hydrogen and carbon monoxide gases. Hydrogens' higher flame speed and lower boiling point may make it an ideal cold start fuel.

Methanol dissociators using resistively heated ceramic and metal technology for substrates have been evaluated by EPA for their use in assisting the cold start of methanol-fueled engines.[5,6,7] The noble metal catalysts employed in these efforts were platinum and a platinum/palladium mixture. These catalysts, however, did not provide substantial yields of H_2 and CO at lower converter gas temperatures.

A significant problem noted during these earlier evaluations was the formation of soot in the superheater and dissociator sections.[6] Coke formation appeared to positively correlate with operating temperature in the superheater and dissociator. Temperatures in excess of 900°F invariably led to sooting of the superheater.

Other researchers working with methanol dissociation have noted this coking.[8,9] One solution to this problem is the use of a catalyst that promotes the dissociation reaction at lower temperatures (less than or equal to 570°F).

Representatives of Nissan Motor Company, Ltd., presented a summary of their experience with the "Methanol Reformed Gas Engine" to EPA on March 13, 1987.[10] One part of this briefing concerned the results of screening candidate methanol dissociation catalysts. Some of these catalyst formulations and their application processes have been patented.[11,12,13]

The catalysts referred to above utilize active components from the noble metal, rare earth and titanium families applied to granular or monolithic alumina substrates. A portion of the March 13, 1987 briefing to EPA concerned a confidential presentation of catalyst activity as a function of bed temperature for specific formulations of the catalyst materials above. This data indicated that several Nissan formulations could provide substantial dissociative activity at reactor temperatures below 600°F.

EPA sought permission from Nissan to use a specific dissociation catalyst formula [14] on a silicon carbide substrate similar to those tested in references 5 and 6. This permission was granted;[15] Engelhard Industries agreed to cooperate in this joint effort by catalyzing the silicon carbide substrate using the Nissan formulation. An agreement to provide Engelhard with access to the pertinent catalyst information was then reached between Nissan and Engelhard to facilitate this work.

III. Program Design

The testing was conducted in two separate phases:

1. Bench testing; and

2. Cold start and emissions testing at 73°F conditions.

The bench test phase consisted of determining catalyst yield at controlled steady-state feed methanol flowrate/temperature conditions. The cold start testing was conducted to determine whether a 4-cylinder, 1.8-liter engine could start and idle on the product gas from the dissociator with no supplemental liquid methanol fuel. If it proved possible to start and idle the test engine on the dissociator product alone, the engine would then be emission tested using alternately M100 liquid methanol from a conventional fuel injection system and product gas from the dissociator.

IV. Dissociator Operation

Methanol may be dissociated to hydrogen and carbon monoxide via the reaction:

$$CH_3OH_{(l)} \text{ ------ } 2H_{2(g)} + CO_{(g)}$$

The dissociator described below accomplished this reaction by a three-step process. First, methanol was vaporized in a boiler and the vapor stream flowed to a superheater. The vaporized methanol was then superheated and the hot gas passed to a catalyzed and heated dissociator. The hot methanol vapor was dissociated in this final stage and passed into the test engine intake manifold. A detailed description of each part of the process is given below.

A. Boiler Unit

The boiler was a 5-gallon capacity, type 316 stainless steel pressure vessel. The vessel was fitted with a steam heating coil, pressure relief valve, liquid temperature monitor, and pressure gauge. The boiler was filled with approximately three gallons of methanol prior to each test and sealed; no provision was made for adding fuel to the vessel following the commencement of a test.

Liquid temperature and pressure inside the boiler were maintained at approximately 190-195°F and 30 psig respectively during testing. Fuel feed rate was determined indirectly; the filled vessel was carefully weighed prior to and at the end of testing, and the test process timed.

B. Superheater

The superheater was constructed from a 3-foot-long section of 1-inch diameter 304 stainless steel pipe. This pipe section was heated by wrapping it with a ceramic bead insulated nichrome wire heater that utilized 120-volt alternating current. Power to the heater was controlled by a thyristor.

C. Catalytic Dissociator

The superheated methanol vapor passed through a porous silicon carbide substrate which had been coated with the catalyst to be evaluated. The substrate was resistively heated by passing direct current through it. This catalyzed heater acted as the methanol dissociator.

The substrate was shaped in the form of a hollow cylinder. Methanol vapor flowed radially through the porous heater walls; the dissociation reaction occurred as the vapor contacted the hot catalyzed walls. Element specifications are given in Appendix A.

V. Supporting Equipment

H_2 composition in the product gas mixture was determined by gas chromatography. A GOW-MAC Model 69-550 gas chromatograph was used, and its operation is detailed in Appendix B.

The test engine used for this experimentation was a Nissan CA18E, single-overhead camshaft, 1.8-liter displacement engine. Details and engine specifications are provided in Appendix C.

Emissions characterized as hydrocarbons were measured with a Beckman Model 400 flame ionization detector. A FID response factor of 76 percent was used.[16]

Exhaust formaldehyde was measured using a dinitrophenyl-hydrazine (DNPH) technique.[17] Exhaust carbonyls including formaldehyde are drawn through DNPH-coated cartridges forming hydrazone derivatives. These derivatives are separated from the remaining unreacted DNPH by high performance liquid chromatography (HPLC). A spectrophotometer in the chromatograph effluent stream drives an integrator which determines formaldehyde derivative concentration.

VI. Discussion

A. Bench Test Experiments

The bench test experiments were conducted to determine catalyst yield under specific inlet gas temperature conditions. Catalyst yield is defined as the percentage of feed methanol converted to H_2 and CO gases.

The methanol flowrate from the boiler during dissociator operation varied between 2400-2500 grams per hour; this was calculated to be close to the flowrate necessary to start and idle an engine of the same displacement as our test engine.[18] The temperature of the methanol vapor into the dissociator was an important parameter because it indicates the degree of superheating for a given methanol flowrate.

Methanol was heated in the boiler to 195°F and passed to the superheater. Current to the heating coils in the superheater was controlled to superheat the methanol vapor to various temperatures over the range 400°F to 700°F. Power to the dissociator was supplied by a Power Mate alternating current to direct current converter; this device allows a maximum power output of 1000 watts. The maximum power level attained with the dissociator was 345 watts; 15 amps current at 23 volts. Electrical resistance across the dissociator and its electrical leads was measured at 2.5 ohms.

Table 1 presents a summary of test conditions for the catalyst yield evaluation.

Table 1

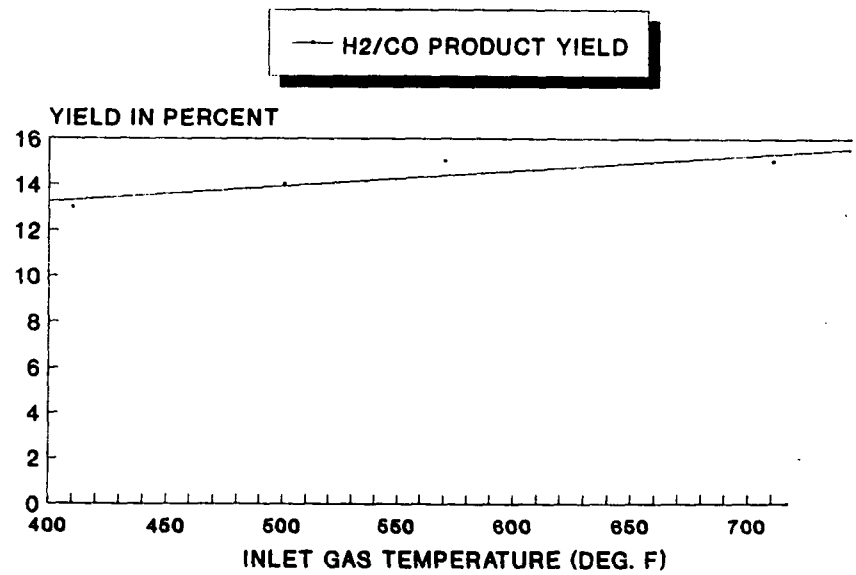
Test Conditions For Catalyst Yield Determination

Test cell temperature	73°F
Boiler liquid temperature	195°F
Boiler pressure	35 psig
Methanol flowrate from boiler	2400-2500 grams/hour
Gas temperature out of superheater	410-710°F
Gas temperature out of dissociator	316-365°F
Power to dissociator	345 watts

Tedlar sample bags were used to collect the product vapor from the dissociator; the collected vapor was then fed to the gas chromatograph by evacuating the sample bag to the chromatograph column. Unreacted methanol vapor was condensed in the sample bag and volumetrically measured to ensure its inclusion in the yield calculation.

A graph of superheated vapor temperature versus product yield is given below in Figure 1.

FIGURE 1
METHANOL DISSOCIATION CATALYST YIELD*
VERSUS GAS TEMPERATURE INTO DISSOCIATOR



*2500 G/HR METHANOL FEED FLOWRATE

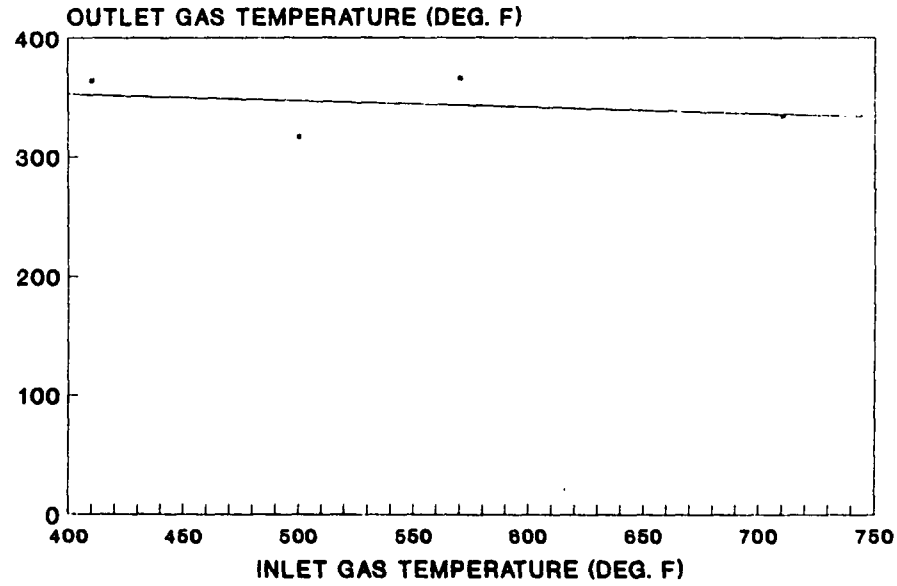
Product yield proved to be only slightly dependent on dissociator inlet gas temperature. A 300 degree increase in inlet gas temperature from 410°F to 710°F, increased the methanol conversion rate only 2 percent, from 13 to 15 percent.

The data in Figure 1 suggests that the yield may be limited by factors other than energy supplied by the superheater. Effective substrate surface area may be a problem here; the fibrous silicon carbide may not provide a surface area as effective for the catalytic activity required as alumina-coated monoliths or packed bed ceramic substrates, for example. Vapor flow inside the dissociator was not studied; flow through the catalyzed fiber walls may occur in such a manner as to make less than optimum use of the total catalyzed surface area. Flow conditions through the walls may allow certain sections of the wall to be exposed to higher volumetric flowrates of the hot vapor than other sections (uneven flow distribution through the substrate). The flow of vapor may also cause certain sections of individual substrate fibers to experience greater catalytic activity than other sections of the same fibers (geometry resulting in stagnant conditions on parts of individual fibers). Activity might also be limited by an insufficient amount of catalyst material coated on the substrate to carry the reaction to a greater degree of completion in the residence time of the gas in the dissociator.

Power to the resistively heated dissociator substrate was kept constant at 345 watts during the testing. High power levels for dissociator operation were considered desirable in order to provide sufficient energy for the endothermic dissociation to proceed to a high degree of completion.

Dissociator outlet gas temperature was also measured during sampling. A graph of gas temperature at the inlet versus gas temperature at the outlet of the dissociator is given in Figure 2.

FIGURE 2
GAS TEMPERATURE AT DISSOCIATOR
OUTLET VERSUS INLET GAS TEMPERATURE•



•2500 G/HR METHANOL FEED FLOWRATE

Outlet gas temperature from the dissociator did not positively correlate with increases in temperature of gas from the superheater. Instead outlet gas temperature remained relatively constant at approximately 350°F during testing.

Energy supplied by the resistively heated substrate may be a very important limiting factor for the dissociation reaction. Karpuk [19], in a private communication to EPA, calculated a power requirement of 2256 watts to dissociate 2000 grams per hour of methanol. Our calculations of this requirement show it to be 2230 watts, essentially the same. Significant heat transfer from the dissociator housing to the atmosphere may be occurring despite our efforts to insulate this housing. If the endothermic reaction is power limited, it may be necessary to reduce the feed flowrate of methanol to improve percent product yield at lower temperatures with the current dissociator system.

B. Cold Start Experiments

A cold start of the 73°F overnight-soaked engine was attempted using only the product gas from the dissociator as the fuel source. (Prior to testing the engine main fuel injectors were disconnected.) Test conditions are given in Table 2.

Table 2

Test Conditions For Cold Start Experiments

Test cell temperature	73°F
Boiler liquid temperature	190-195°F
Boiler pressure	20 psig
Methanol flowrate from boiler	2400 grams/hour
Gas temperature out of superheater	450°F
Gas temperature out of dissociator	335°F
Power to dissociator	345 watts

Approximately 12 feet of plastic tubing connected the dissociator to the EGR port. A valve to allow emissions sampling and a flame arrestor were also located in this line. These restrictions, however, did not combine to reduce fuel flow to the point that engine performance at idle was noticeably affected. Although the fuel entry passageway to the combustion chambers was not standard (via EGR chamber to intake runners) it proved sufficient to allow a start and idle at the conditions in Table 2.

Product gas from the dissociator was fed to the EGR port for 3 seconds prior to a crank attempt. The engine immediately started. The idle was rough, however, possibly signifying a fuel/air imbalance; spark from the ignition system was present during crank and run periods. Wetting of the plugs was noticed following rough idle periods that ended with engine stalls.

The engine may be operating in an improperly rich mode during an extended idle. Heating of the boiler, superheater, and dissociator cannot be regulated in a manner that would provide instantaneous changes in fuel flowrate to accommodate changes in fuel flow requirements. Dumping part of the fuel flow to the stack scrubber with a three-way bypass valve by hand was tried; the response was improved, yet this improvement was not sufficient to prevent engine laboring.

Two other factors combined to change the fuel mixture from those mentioned in reference 6. First, substantially more H_2/CO was produced at lower temperatures with the catalyst tested here than from other noble metal catalysts evaluated at similar feed methanol flowrates. Second, a practical, onboard methanol dissociator would not be provided with a blanket of nitrogen or other inert gas in the dissociator to prevent undesirable combustion reactions from occurring. Previously N_2 was added over the boiler to prevent these reactions and to act as a carrier gas to increase the quantity of methanol flow from the boiler. It was recently noticed that feed methanol flowrates similar to the rates in references 5 and 6 could be attained through changes in boiler operating temperature and pressure, rather than with the addition of N_2. These engine tests were conducted without the addition of N_2 to better simulate actual onboard conditions. The elimination of this additional diluent N_2 caused the fuel/air mixture to be somewhat richer than the mixture in references 5 and 6.

Emission results are presented in Table 3. Levels of emissions characterized as hydrocarbons and formaldehyde were measured in order to determine whether the choice of fuel systems influenced pollutant emission levels. The test cycle was a cold start followed by a 5-minute idle. HC and HCHO emissions are expressed in average rates of grams per minute and milligrams per minute, respectively. Oxides of nitrogen (NOx) and CO emissions were not measured with the M100 liquid fuel system due to problems with the analyzers.

Table 3

Emission Levels Over Cold Start and Idle (73°F)

Fuel System Configuration	HC (g/min)	HCHO (mg/min)	CO (g/min)	NOx (g/min)
Methanol injectors functioning	3.68	1.0	N/A	N/A
Dissociator fuel system	2.38	0.8	1.45	0.02

Emissions of HC were slightly lower with the dissociator system than from the injector-fed liquid fuel system. This difference may be due to improved starting performance caused by the methanol and H_2/CO fuels admitted to the engine in a hot gaseous state rather than as atomized liquid. HCHO emissions with the dissociator were relatively unchanged from liquid fuel system levels. NOx emissions with the dissociator were 0.02 grams per minute; engine coolant temperature however did not exceed 110°F during the test cycle. NOx and CO emissions with the liquid fuel system were not measured due to problems with the analyzers.

A trend toward lower HC and HCHO emissions with partial dissociation of the methanol fuel was observed. These decreases in emissions may not be definitive, however; the engine was tested only three times using the dissociator as the fuel supply system. Additional testing would have to be conducted in order to more properly define the difference in emission levels.

C. Examination of Substrate Following Testing

Following the cold start testing, the superheater and dissociator were disassembled to check for signs of coking and subsequent catalyst poisoning. This particular catalyst formulation was evaluated in order to determine its effectiveness during operation at lower temperatures less likely to promote the undesirable coking reaction.[20] Signs of coking would obviously be given serious consideration with regard to catalyst durability given the limited amount of testing conducted here.

The walls of the substrate were visibly free of any carbonaceous matter; no coking was observed on either the inner or outer walls of the hollow cylinder. Traces of coke were noticed at the interface between the nichrome flame-sprayed ceramic, the stainless steel wool gaskets, and the stainless steel electrical contacts.

Current density may be uneven across the flame-sprayed ceramic surface. Several rust/corrosion spots were noticed on the flame-sprayed surface; any unevenness in the physical characteristics of the interface could have caused areas of increased current density across the interface. Areas of higher current density would also be areas of higher temperature. Temperature was not measured at the ceramic-to-metal interface. It is possible that the interface temperature significantly exceeded the measured gas temperatures. The fiber substrates are very porous; it is possible therefore that some of the dissociated CO contacting the interface was brought to a high enough temperature to undergo decomposition to coke.[21]

Earlier in this report it was stated that electrical resistance across the dissociator, to include its electrical contact system, was measured at 2.5 ohms. Resistance over the substrate alone was measured at various points on the flame-sprayed ends of the hollow cylinder. These measured resistances varied between 2.0 and 10.5 ohms.

This variation in resistance may be caused by an uneven flame spray on the ends of the hollow cylindrical ceramic substrate. Flame-sprayed metal absorbs into the porous ceramic. The flame-spray process also must be carefully controlled to prevent cracking of the sprayed ceramic surface because of differences in thermal expansion coefficients between the ceramic and the metal. The ceramic-to-metal interface should be improved to reduce the possibility of hot spots developing at the bond surface that could promote undesirable side chemical reactions.

VII. Test Highlights

1. The catalyst evaluated converted 15 percent of a stream of 2400 grams per hour of methanol to H_2/CO gaseous fuel. Temperature of the feedstream into the dissociator reactor was 410-710°F during this testing.

2. The dissociation catalyst substrate was resistively heated; power was supplied to the dissociator at a rate of 345 watts during testing. Gas temperature out of the dissociator remained relatively constant, at approximately 350°F during testing. This temperature did not change as inlet gas temperature for a constant mass flowrate feedstream of 2400-2500 grams per hour varied between 410-710°F.

3. A 1.8-liter test engine was cold started and idled on the product gas stream from the dissociator alone. Extended idle periods were characterized by rough engine performance; plug wetting was noted after several stalls. The engine appeared to be operating in a very rich mode at idle with the dissociator. Methanol flowrates between 1800-2500 grams per hour are difficult to control with the tested dissociator apparatus, however.

4. Pollutant emissions from the test engine were measured over a cycle consisting of a cold start and a 5-minute no-load idle with the dissociator as the sole fuel source. Pollutants characterized as hydrocarbons and formaldehyde were measured at 2.38 grams per minute and 0.8 milligrams per minute, respectively. CO and NOx emissions over the same cycle were measured at 1.45 and 0.02 grams per minute, respectively.

5. No coking was observed on the walls of the ceramic substrate following this evaluation. Traces of coke were found at the interface between the silicon carbide substrate, stainless steel wool gaskets, and the stainless steel electrical contacts. Hot spots caused by areas of high current density along this interface may have contributed to this localized coking.

VIII. Acknowledgments

The silicon carbide substrate used in this experimentation was provided by Coloroll, plc., a United Kingdom corporation. The dissociation catalyst formulation evaluated here was developed by the Nissan Motor Company, Ltd. The catalysis of the silicon carbide substrate was done by Engelhard Industries. The test engine was also provided by Nissan Motor Company, LTD.

The author appreciates the efforts of James Martin, technician, Standards Development and Support Branch, Emission Control Technology Division, who greatly assisted the author with this project. Jim was also largely responsible for the setup of the engine used for this testing.

In addition, the author appreciates the efforts of Jennifer Criss and Marilyn Alff of the Control Technology and Applications Branch, ECTD, for typing, formating, and editing this report.

IX. References

1. "Development of Methanol Lean Burn System," Katoh, K. Y. Imamura, and T. Inoue, SAE Paper 860247, February 1986.

2. "Interim Report On Durability Testing of Low Cost Catalysts for Methanol-Fueled Vehicles," Wagner, R. and L. Landman, EPA/AA/CTAB/TA/84-4, August 1984.

3. "Using Methanol Fuels In Light-Duty Vehicles," Brown, D., F. Colden, E. Gons, R. Potter, SAE Paper 872071, November 1987.

4. "Unassisted Cold Starts to -29°C and Steady-State Tests of a Direct-Injection Stratified-Charge (DISC) Engine Operated On Neat Alcohols," Siewert, R. and E. Groff, SAE Paper 872066, November 1987.

5. "Evaluation of Coloroll Methanol Dissociator For Cold Start Assist Application," Piotrowski, G., EPA/AA/CTAB/87-08, December 1987.

6. "Resistively Heated Methanol Dissociator For Engine Cold Start Assist-Interim Report," Piotrowski, G., EPA/AA/CTAB/88-02, March, 1988.

7. "Resistively Heated Metal Monolith As A Cold Start Assist For A Methanol Engine - Interim Report," Piotrowski, G., EPA/AA/CTAB/88-11, December, 1988.

8. "Study of the Methanol Reformed Gas Engine," Hirota, T., Japan Society of Automotive Engineers Review, March 1981.

9. "Dissociated Methanol Citation: Final Report," Finegold, J., G. Glinsky, and G. Voecks, SERI/TR-235-2083, DE85000505, August 1984.

10. Briefing to C. Gray, Jr., U.S. EPA by Nissan Motor Company, March 1987.

11. "High Activity Catalyst For Reforming Of Methanol And Process Of Preparing Same," Masuda, K. to Nissan Motor Company, Ltd., United States Patent No. 4,499,205, dated February 12, 1985.

12. "Catalyst For Reforming Of Methanol And Process Of Preparing Same," Masuda, K. to Nissan Motor Company, Ltd., United States Patent No. 4,501,823, dated February 26, 1985.

13. "Catalyst For Reforming Of Methanol And Process Of Preparing Same," Eto, Y., to Nissan Motor Company, Ltd., United States Patent No. 4,511,673, dated April 16, 1985.

X. References (cont'd)

14. Letter from Hellman, K. H., U.S. EPA, to Kawajiri, H., Nissan Research and Development, Inc., February 16, 1988.

15. Letter from Kawajiri, H., Nissan Research and Development, Inc., to Hellman, K. H., U.S. EPA, April 4, 1988.

16. FID Methanol Response, Memo, Edward A. Barth, OAR/OMS/ECTD/TEB, Ann Arbor, MI, August 1987.

17. Formaldehyde Measurement In Vehicle Exhaust At MVEL, Memo, Gilkey, R. L., OAR/OMS/EOD, Ann Arbor, MI, 1981.

18. Dissociated Methanol Fuel Requirements to Start A Four-Cylinder Engine, Memo from Gregory K. Piotrowski, OAR/OMS/ECTD/CTAB, Ann Arbor, MI, 1986.

19. Private Communication, Karpuk, M. E., to U.S. EPA, 1987.

20. "Engine Cold Start With Dissociated Methanol," Greiner, L. and E. Likos, Proceedings of the Third International Symposium on Alcohol Fuels Technology, May 29-31, 1979.

21. "Dissociated Methanol Test Results," Finegold, J. G., and J. T. McKinnon, SERI/TP-235-1582, April 1982.

22. Fundamentals of Gas Analysis by Gas Chromatography, Thompson, B., Varian Associates, Inc., Palo Alto, CA, 1977.

23. Basic Gas Chromatography, McNair, H., Bonelli, E., Consolidated Printers, Berkeley, CA, 1968.

APPENDIX A

DISSOCIATOR ELEMENT SPECIFICATIONS

The dissociator substrate consists of a highly porous ceramic to which electric current is applied. The fluid to be heated is passed through the void spaces in the material. Heat transfer is encouraged by the very large surface area of the ceramic (the material contains greater than 80 percent void space).

Specification ranges for certain properties of the material used in the dissociator are given below. The exact specifications for the dissociator material are proprietary to the manufacturers of the elements, Coloroll, plc., Havenside, Boston, Lincolnshire, U.K.

Property	Range of Values
Power density	10-1600 W/cm^3
Normal range	10-300 W/cm^3
Power dissipation	0.01-0.75 W/cm^2
Heatup/response time	Milliseconds
Heat transfer surface/volume	400-750 cm^2/cm^3
Operating temperature	Up to 1000°C
Material density	0.1-0.5 gm/cm^3

APPENDIX B

HYDROGEN CONTENT DETERMINATION

Background

The basis for gas chromatographic separation is the distribution of a sample between two phases. One of these phases is a stationary bed, and the other is a gas which percolates through the stationary bed. An inert carrier gas carries the components to be separated through a column containing the stationary phase. The active component of the stationary phase selectively retards the sample components according to their distribution coefficients, until they form separate bands in the carrier gas. These component bands leave the column in the gas stream and are recorded as a function of time by a detector.

If the stationary phase is a solid, this particular gas chromatographic technique is referred to as gas-solid chromatography. Common packings used are silica gel, molecular sieve and charcoal. Gas-solid chromatography was used in this experimentation, and the details of the procedure are given below. More complete explanations of gas chromatographic technique are provided by Thompson and McNair.[22,23]

APPENDIX B

HYDROGEN CONTENT DETERMINATION (CONT'D)

Specifications:

Chromatograph model	GOW-MAC Model 69-550
Detector:	
Operating principle	Thermal conductivity type
Temperature control	Ambient to 300°C
Carrier gas	N_2
Detector elements	Four (4) rhenium tungsten elements
Noise	10-micro volts maximum
Drift	40-micro volts/hour maximum
Injection:	
Number of ports	Two
Control	Solid-state, variable-voltage phase control
Operating temperature	Ambient to 300°C
Column Oven:	
Temperature range	Ambient to 300°C
Control	Solid-state time apportioning
Column:	5' x 1/4" molecular sieve
Gas flow system:	Dual-column with dual-injection ports and exits
Thermal conductivity bridge control:	Continuous current adjust 50-300 mA. Bridge zero adjust. Attenuator for bridge output, 10 positions to 512.
Electrical:	
Power requirements	105-125 volts, 50/60 H_2
Circuit breaker	7 amps
Physical:	Two-section construction. Upper section houses column oven, detector and vaporizers. Lower section contains power supply, bridge control circuit and temperature controllers.

APPENDIX B

HYDROGEN CONTENT DETERMINATION (CONT'D)

Compressed Gas Auxiliaries:

Zero gas	N_2
Span gas	40 percent H_2/60 percent N_2

Output:

Stripchart recorder	Soltech model 3318

APPENDIX C

TEST ENGINE SPECIFICATIONS

Manufacturer	Nissan Motor CO., LTD.
Basic engine designator	CA18E
Displacement	1809 cc
Cylinder arrangement	4-cylinder, in-line
Valvetrain	Single-overhead camshaft
Combustion chamber	Semi-spherical, 2 spark plugs per cylinder
Bore x stroke	83 mm x 83.6 mm
Compression ratio	11.0
Compression pressure	17.0 kg/square cm (350 rpm, 80°C)
Fuel control system	Electronically controlled fuel injection
EGR	EGR not used
Valve clearance	0.30 mm HOT, intake and exhaust
Idle speed	700 rpm
Engine oil	Special formulation supplied by Nissan for methanol engine operation.
Fuel	M100 neat methanol
Engine cranking speed	240 rpm