EPA/AA/CTAB/88-11

Technical Report

Resistively Heated Metal Monolith As A Cold Start Assist For a Methanol Engine - Interim Report

by

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December 1988

NOTICE

U. S. Environmental Protection Agency
Office of Air and Radiation
Office of Mobile Sources
Emission Control Technology Division
Control Technology and Applications Branch
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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ANN ARBOR, MICHIGAN 48105

OFFICE OF
AIR AND RADIATION

DEC 19 1988

MEMORANDUM

SUBJECT: Exemption From Peer and Administrative Review

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

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

The attached report entitled "Resistively Heated Metal Monolith As A Cold Start Assist For a Methanol Engine - Interim Report," (EPA/AA/CTAB/88-11) describes the evaluation of this technology with regard to its ability to provide a cold start assist for a light-duty methanol engine. The primary focus of this work was the determination of the ability of this technology to act as a methanol dissociator capable of supplying gaseous H_2/CO fuels to an engine during cold start.

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 Gray Jr. Date: 12-14-88
Charles L. Gray, Jr., Dir., ECTD

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

cc: E. Burger, ECTD

Table of Contents

I. Summary

A methanol dissociation system was constructed to provide a cold start assist for a methanol-fueled light-duty engine. The system consisted of a fuel delivery unit, fuel injector, and a palladium-catalyzed dissociation element. The dissociation element substrate was resistively heated and constructed primarily from metal foil.

The objective of this experimentation was to start and idle a 4-cylinder engine on the product gas from this methanol dissociator.

Three different configurations of the resistively heated metal monolith were evaluated. The first consisted of a catalyzed, heated bed followed by a catalyzed unheated bed. The product stream from this dual-bed configuration was liquid, rather than gaseous, under the conditions given in Section V, Discussion, of this report. We tested a resistively heated, but uncatalyzed single-bed configuration; though the product was vaporized rather than dissociated methanol, the test engine started and idled without hesitation with no other fuel source than the single injector-fed fuel vaporizer. Finally, a two-stage system utilizing the single-bed unit as a vaporizer and the dual-bed unit as a methanol dissociator was constructed and evaluated. Product gas from this configuration was used to start and idle the test engine in the same manner as the single-bed unit. The product gas temperature out of the dissociator was very low, approximately 130°F. This suggests that the engine started on vaporized methanol, rather than H_2 and CO gases.

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.

The goal of the project was to construct and test a methanol dissociation system that could provide H_2 and CO gaseous fuels in quantities that could be used as a cold start assist for a methanol-fueled engine. This dissociator would utilize resistively heated metal foil technology to provide the energy necessary to bring the catalyst to operating temperatures quickly.

Methanol dissociation systems using resistively heated ceramic technology have been evaluated by EPA to determine their cold start assist potential.[5,6] Reference 6 refers to a dissociation unit which was able to cold start and idle a 4-cylinder, 1.8-liter light-duty engine which had been soaked to 43°F. We hoped to improve H_2/CO yield, dissociator durability and heat transfer to the methanol fuel beyond what was experienced in that effort through the use of the resistively heated metal foil.

III. Discussion of Technology

The subject technology is a metal foil which may be washcoated, catalyzed and resistively heated. The rolled metal foil is encased in a metal housing; the housing is electrically insulated from the electrified foil. Two metal contacts protrude from the sides of the housing. Electrical contact to a direct current power source, a 12-volt automobile battery, is made to these contacts.

Two resistively heated monoliths were tested in this effort. The first was a dual-bed configuration consisting of an unheated metal monolith catalyst and a smaller resistively heated metal monolith catalyst. The second unit was an uncatalyzed, resistively heated monolith similar in size to the smaller heated bed in the dual-bed configuration. The exteriors of both housings were insulated with ceramic fiber insulation to improve heat retention. Details are provided in Appendix A.

The resistively heated monoliths were provided by Camet, a manufacturer and sales agent for W. R. Grace Company. Details relating to catalyzing the foil, packaging, and resistive heating of the catalysts are considered proprietary to Camet and Grace.

IV. Program Design

Three different configurations, a single-bed, a dual-bed, and a combination of these two systems were evaluated for their ability to provide a cold start assist. The dual-bed catalyzed

system had the potential to act as a methanol dissociator, using resistive heating to first vaporize the feed methanol and then to supply the necessary energy for the endothermic dissociation reaction. The single-bed, uncatalyzed monolith was evaluated to determine the ability of the heated substrate to transfer energy to the feed methanol in the absence of the larger catalyzed-but-unheated monolith located downstream. The combination system used the single-bed unit as a vaporizer and the dual-bed as the dissociation element.

Figure 1 contains a diagram of the system we constructed to support the various configurations mentioned above. Methanol is pumped to the catalyst or vaporizer from a 2-gallon plastic fuel tank by an electric roller-type fuel pump. The fuel passes through stainless steel tubing fitted with a flowmeter. The flowmeter is connected to an electrically actuated clock. Given the proper electrical signal, the clock and flowmeter operate simultaneously to determine fuel flow over the desired time period.

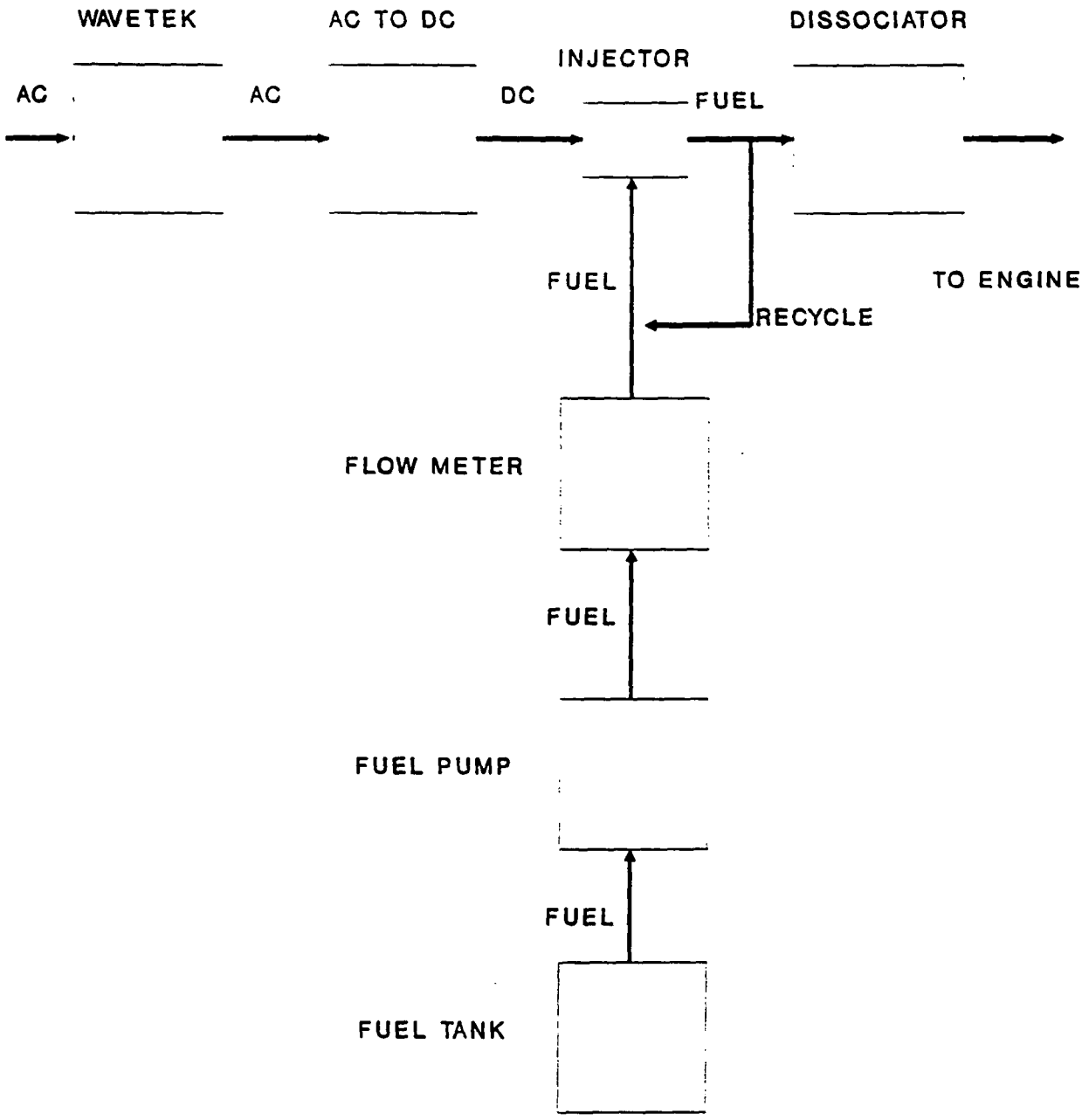
A fuel injector was installed in the catalyst housing approximately 3 inches from the face of the smaller, resistively heated metal monolith. When testing the dual-bed unit alone, the methanol spray impacted on the resistively heated catalyst first before passing through to the larger, catalyzed but unheated monolith. To prevent metering fuel which did not pass through the injector, a recycle was provided around the injector and the pump.

Fuel flow to the dissociator was controlled by changing the pulse width of the non-continuous flow injector. Line alternating current (AC) operated a Wavetek Model 193 wave/frequency generator. The equipment was used to generate pulsed square wave signals of various widths that controlled the quantity of fuel injected. An AC to direct current (dc) device was then used to change the pulse to a dc signal before it passed to the fuel injector.

Thermocouples were installed to measure liquid fuel temperature as well as gas temperatures midbed in the monolith and immediately after the dissociator. N_2 gas was used to replace the air in the dissociator just prior to heating. N_2 was added for two reasons: 1) to encourage the dissociation of methanol, and 2) to provide a safety factor upon the initial heating.

The test procedure consisted of supplying the fuel to the resistively heated elements at various flowrates and determining whether a vaporized fuel was produced. Provision was made for sampling the dissociator gas product stream and analyzing it with a gas chromatograph to determine its H_2 content, if a gaseous product was generated from a catalyzed unit.

FIGURE 1
METHANOL DISSOCIATION SYSTEM



The production and analysis of the hot product gas would be followed by its introduction into a light-duty vehicle engine for cold start testing.

V. Discussion of Test Results

A. Evaluation of Dual-Stage Unit

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

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

This reaction is endothermic; assume that the reaction occurs at atmospheric pressure and 500°F.[7] This situation requires the input of energy to:

1. Preheat the methanol at 148°F;
2. Vaporize the methanol at 148°F, 1 atmosphere pressure;
3. Superheat the vapor to 500°F; and
4. Decompose the vapor to H_2 and CO gases.

The dissociated product flowrate to start an engine similar in displacement to our test engine has been calculated [8,9] as 0.3 to 0.6 grams per second. Karpuk [10] in a private communication to EPA, calculated a power requirement of 2,256 watts necessary to dissociate 2,000 g/hr of methanol at 25°C. Our calculations of this requirement shows it to be 2,230 watts, essentially the same. We hoped that the resistively heated monolith would generate power at a rate in excess of these requirements and transfer energy to the fuel efficiently to ensure at least partial dissociation in the brief timeframe of interest.

The dual-stage unit was tested with the fuel injector mounted in front of the resistively heated element. The spray would then impact the heated element before passing through to the catalyzed, unheated catalyst. Some results and conditions of testing in this configuration are given in Table 1.

N_2 gas at 2 psig was admitted into the catalyst vessel for 1-minute prior to operation to assist the dissociation reaction. The gas flow was shut off prior to catalyst heating however, and remained off during the test.

The heating scheme involved preheating the catalyst for 10 seconds prior to fuel on and heating for 30 seconds following fuel on. We measured current in the electrical leads to the catalyst at approximately 300 amps at the beginning of heating; current dropped in straight line fashion over the 30-second heating period to approximately 220 amps at the conclusion of heating. We charged the battery power source to 12 volts prior to each test.

Table 1

Dual-Bed Configuration Evaluation

Variable	Specification or Result
N_2 flowrate	2 psig over catalyst prior to test, off during test
Battery voltage	11.5-12.5 volts
Voltage across monolith during heating	9-volts
Current to monolith	290 amps at start of heating, 210-230 amps at finish
Heating scheme	Heat on for 10 seconds prior to fuel on; heat on for 30 seconds after fuel on
Fuel to injector	Flow rates 35-140 cc over a period of 30-33 seconds
Gas Temperatures:	
Fuel into dissociator (liquid)	70-72°F
Mid-bed gas temperatures	Approximately 300°F at fuel on; approximately 190°F at 10 seconds after fuel on; approximately 150°F at end of heating
Gas out of dissociator	75°F at end of test

Fuel flow to the injector was varied from a high rate of 140 cc for a 30-second period (approximately 3.7 grams per second) to 35cc over 30 seconds (approximately 0.9 grams per second). Even the lowest flowrate tried here should have provided a sufficient flow of fuel to start and idle the test engine. Liquid temperature of the fuel was 70-72°F during this testing.

Midbed gas temperatures varied considerably over the duration of the test. Typically, this temperature would rise to approximately 300°F after 10 seconds of heating with no fuel injected. At 10 seconds after beginning the injection of fuel (20 seconds into the test) temperatures had fallen linearly to approximately 190°F. At the end of heating, or 40 seconds into the test, midbed gas temperatures had fallen to 150°F. These temperatures were consistently noted regardless of fuel flowrate into the dissociator.

Gas temperatures out of the dissociator remained almost constant, at 70-72°F, during this testing. This temperature did not change when fuel flowrate into the dissociator was varied. The dissociator product line was made of clear plastic tubing; the product after 40 seconds of heating remained liquid. Not enough gas was generated to enable bag sampling to determine if any methanol dissociation to H_2/CO had occurred.

It is difficult to determine why the desired reactions did not occur and why the dissociator product stream appeared to be liquid. Much more about the heat transfer characteristics of the material contained in the housing would have to be known from the manufacturer. Methanol vaporized in the resistively heated section of the housing may be condensing in the non-heated monolith.

It was clear that the particular configuration was incapable in its present form to efficiently transfer the necessary energy in a 40-second timeframe to dissociate methanol at the required flowrate.

B. Evaluation of Single-Stage Unit

The dual-stage dissociator did not produce a gaseous product stream under the conditions given in Table 1. We next evaluated a single-stage configuration to determine if a single heated monolith would transfer heat to the fuel more efficiently.

Some results and conditions of testing in this configuration are given in Table 2.

Table 2

Single-Bed Configuration Evaluation

Variable	Specification or Result
N_2 flowrate	No N_2 gas used
Battery voltage	12 volts
Voltage across monolith during heating	9 volts
Current to monolith	315 amps at start of heating, 210-230 amps at finish
Heating scheme	Heat on for 10 seconds prior to fuel on; heat on for 30 seconds after fuel on
Fuel to injector	23-27 cc over a period of 30-32 seconds
Gas Temperatures:	
Fuel into dissociator	70-72°F
Midbed gas temperature	Approximately 390°F at fuel on; approximately 250°F at 10 seconds after fuel on; approximately 145°F at end of heating
Gas out of dissociator	138-145°F at end of test

N_2 gas was not used during testing in order to better simulate actual cold start conditions. The battery used to electrify the substrate was fully charged to 12 volts; during testing, voltage drop across the substrate was measured at 9 volts. At the start of heating a current of 315 amps was measured in the heating circuit; 40 seconds into the test, at finish, the current had dropped linearly to 210-230 amps. The same heating scheme that was used in the dual-bed evaluation was also used here (heat 10 seconds, fuel on, heat 30 seconds). Fuel flow was measured at 23-27 cc over a period of 30 seconds, or 0.66 grams per second.

Midbed gas temperature rose to 390°F after 10 seconds of heating. This was a considerable improvement from the 300°F temperature noted during the dual-bed evaluation. Near the end of each test, midbed gas temperatures dropped to 145°F. This temperature is consistent with a flow of vaporized but not superheated methanol vapor.

Gas temperature out of the substrate was approximately 145°F after 30 seconds of heating. This temperature is consistent with a flow of vaporized methanol. This was again an improvement over the 72°F temperature experienced with the dual-stage unit.

We then piped the product gas from the resistively heated monolith to a 4-cylinder light-duty engine and attempted a cold start at 70°F. A complete description of the test engine is given in Appendix B.

Approximately 4 feet of plastic tubing connected the vaporizer 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 cylinders), it proved sufficient to allow a start and idle at the conditions in Table 2.

The engine started and idled without hesitation. Crank time to start was 1-1/2 seconds. This experiment was successfully repeated several times. Cranking was attempted after 30 seconds of heating time had elapsed (the final 20 seconds of that period involved sending fuel to the heated monolith). The four engine fuel injectors were electronically disabled during this testing; fuel entered the engine only from the single-injector/heater system.

We tried repeating this cold start experiment with this same hardware but without heating the monolith. Gas temperature out of the catalyst housing did not exceed 72°F under the conditions in Table 2, and the engine did not start. Disassembling the catalyst housing after this test, we discovered it filled with liquid methanol.

The resistive heating had the effect of vaporizing the incoming methanol stream. The vaporized methanol, under the conditions in Table 2, was sufficient to start and idle the test engine in spite of the less than optimum fuel intake system.

C. Evaluation of Single/Dual-Stage Configuration

The dual-bed configuration was not successful under the conditions in Table 1, probably because the methanol vaporized in the first, heated stage, had condensed on the metal foil in the second, unheated stage. The time period of interest here was 40 seconds; during that time current dropped significantly, from 290 to 220 amps, due to discharge of the battery. It may have been difficult to transfer sufficient energy effectively from the heated to the unheated monolith in the timeframe of interest to permit the desired reaction to occur. The single-bed configuration heated and vaporized the methanol feed stream. The energy transferred here in the time of interest was sufficient to start and idle the test engine on methanol fuel alone. Midbed gas temperature recorded with this configuration 10 seconds after the introduction of methanol, 250°F, was still too low to permit methanol dissociation with the noble metal catalyst we used in the dual-bed configuration.

We next combined the single and dual-bed monoliths in an attempt to increase the product gas temperature. The single-bed monolith was placed first in this new configuration; the injector sprayed on this heated monolith. The single-bed, non-catalyzed unit would therefore act as a vaporizer ahead of the dual-stage unit. The catalyzed dual-stage unit would then be the dissociator, receiving a vaporized product gas from the single-bed unit.

Two uncertainties still remained with this approach, however. Though we measured midbed gas temperature, we were unable to measure the metal substrate temperature during resistive heating. This measurement would give a good indication of the actual boundary layer temperature during heating. We were also unable to generate enough product gas during the timeframe of interest to permit sampling by gas chromatograph, given our current bag sampling methods.

Details of the conditions of this testing are given in Table 3.

We constructed two separate circuits for this vaporizer/dissociator configuration; each resistively heated element was powered by a 12-volt battery. We preheated the vaporizer and dissociator simultaneously for 10 seconds prior to fuel on. The fuel was then allowed to flow through the heated system for an additional 10 seconds (total heating time

Table 3

Single/Dual-Stage Configuration Evaluation

Variable	Specification or Result
No flowrate	No N_2 gas used
Battery voltage	12 volts
Voltage across monoliths	9 volts
Current to monoliths	300 amps at start of heating, 230 amps at finish
Heating scheme	Heat for 10 seconds prior to fuel on; heat for 30 seconds after fuel on
Fuel to injector	25 cc over a period of 30 seconds
Key on	Key on after 20 seconds of heating (fuel on for 10 seconds prior to start)
Gas Temperatures:	
Fuel into single-bed unit (liquid)	70-72°F
Midbed gas temperature (dual-stage unit)	Approximately 400°F at fuel on 136°F at 10 seconds after fuel on
Gas out of dissociator	130°F at end of test

20 seconds). The product gas was piped to the engine through the EGR port as mentioned in the discussion of the single-bed unit evaluation. A cold start was then attempted; the engine started immediately, without hesitation. Repetition of this test without resistive heating gave the same result as in the single-bed evaluation; the engine refused to start after repeated cranking.

At a voltage drop across a heated substrate at 9 volts and a current of 300 amps, power at 2700 watts is generated. Assuming that heat transfer from the heated substrate to the methanol fuel occurred at maximum efficiency, the power requirement of roughly 2500 watts for dissociation would appear to have been exceeded with the single-dual bed configuration. Gas temperatures out of the dissociation reactor suggest however, that dissociation did not occur (product gas temperatures in excess of 400°F were not recorded).[7] At 230 amps, power output falls to approximately 2000 watts. Obviously, dissociation becomes much more difficult at a lower power output assuming heat transfer to the methanol is not improved.

Heat transfer to the surroundings and the catalyzed, nonresistively heated element in the dissociator may account for significant heat losses in the 30-second timeframe of interest. The engine started and idled without hesitation when the monoliths were resistively heated, however; the cold start assist may have been provided by vaporized methanol.

Several ways to assist the dissociation reaction with this technology are now mentioned. First, a platinum/palladium mixture may not be an optimum catalyst with which to coat the resistively heated substrate. An optimized low temperature dissociation catalyst could be on technique to minimize the reactor power requirement. Second, the metal foil bed may not be of sufficient size to provide the amount of energy required over the short time period of interest. A larger heated monolith may provide additional reaction surface area. The rectangular brick may not be the optimum shape for this application; the fuel injector may distribute the fuel very unevenly across the surface area, causing puddling and hot spots to occur. A cylindrically shaped unit may be a better geometry. Though we insulated the vaporizer and dissociator housings with ceramic fiber insulation, a considerable amount of heat transfer (therefore energy loss) may be occurring with the surrounding air. This condition was also probably aggravated by the location of the dissociator approximately 3 feet from the engine EGR port. Finally, a very large amount of energy may have to have been transferred from the hot vapor to the catalyzed, unheated monolith in the dual-stage dissociator to bring this bed to catalytically active temperature. An improvement on the dual-bed configuration may be the use of two single-bed resistively heated monoliths. The first would be used to vaporize the incoming methanol feed stream. The second bed, located downstream, would be catalyzed and would serve as a resistively heated dissociator support.

VII Future Effort

Our immediate plans for future efforts with this technology in the methanol dissociator cold start assist application concern:

1. Additional energy provided to the fuel ahead of the dissociation reaction; and

2. The use of a more appropriate methanol dissociation catalyst.

We are procuring a Bosch flame glowplug capable of burning fuel at a volumetric rate of 290 cc/minute. This hardware will be mounted ahead of the catalyst to superheat the vaporized methanol.

We are evaluating a noble metal/rare earth methanol dissociation catalyst formulated by Nissan Motor Corporation. This catalyst may provide a significant yield at lower temperatures; if the initial evaluation of this catalyst is successful, we will try to have the resistively heated metal monolith substrate coated with this formulation.

W. R. Grace has agreed to provide EPA with a base metal formulation for use as a methanol vehicle catalyst. This catalyst will have been applied to a resistively heated substrate. We will test this formulation as a potential dissociation catalyst when it is received.

We are also requesting Camet to supply EPA with a platinum-catalyzed single-bed unit for use as a dissociator. This unit will eliminate the catalyzed, but unheated bed in the dual-bed configuration that may have been causing the vaporized methanol to condense or cool to a lower, inactive temperature. This unit will be tested together with the single-bed uncatalyzed vaporizer.

VIII. Acknowledgments

The catalyst used in this test program was supplied by Camet, located in Hiram, OH. Camet is a manufacturer and sales agent for W. R. Grace and Company. The test engine was supplied by the Nissan Motor Corporation.

The authors appreciates the efforts of James Martin of ECTD who served as the primary technician and greatly assisted in this work.

In addition, the author appreciates the efforts of Jennifer Criss and Marilyn Alff of the Control Technology and Applications Branch, ECTD, whose cooperation and able assistance during the preparation of this report, tables, and figures was greatly appreciated.

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APPENDIX A

RESISTIVELY HEATED METAL MONOLITH DISSOCIATOR SPECIFICATIONS AND POWER REQUIREMENTS

Construction	Dual-bed element composed of two metal monolith catalysts, a smaller resistively heatable one and a larger one with no provisions for resistive heating
Catalyst material/loadings	Platinum/palladium; proprietary
Shape	Rectangular
Overall outer dimensions (excluding mounting flanges)	10-3/4" x 4-1/4" x 2-3/4"
Length: flange to flange	14-3/4"
Heated brick dimensions	3" x 4-1/4" x 2-3/4" (approx)
Unheated brick dimensions	4" x 4-1/4" x 2-3/4" (approx)
Power supply	12-volt automotive battery
Current delivered to dissociator	300-230 amps at 10-11 volts
Heatup time to 600°F with no gas flow through the converter	Less than 20 seconds from 70°F

APPENDIX B

TEST ENGINE SPECIFICATIONS

Manufacturer	Nissan Motor Company, 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