

Technical Report

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

by

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March 1988

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Technical Reports do not necessarily represent final EPA decisions or positions. They are intended to present technical analysis of issues using data which are currently available. The purpose in the release of such reports is to facilitate the exchange of technical information and to inform the public of technical developments which may form the basis for a final EPA decision, position or regulatory action.

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

ANN ARBOR, MICHIGAN 48105

OFFICE OF  
AIR AND RADIATION

May 18, 1988

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," (EPA/AA/CTAB/88-02) describes a methanol dissociation system 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 product gas from this system was used to start and idle a test engine which had been cooled to 43°F.

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: 5-18-88  
Charles L. Gray, Jr., Dir., ECTD

Nonconcurrence: \_\_\_\_\_ Date: \_\_\_\_\_  
Charles L. Gray, Jr., Dir., ECTD

cc: E. Burger, ECTD

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## 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 steam-heated methanol boiler, a gas superheater, and a platinum-catalyzed dissociation element. The dissociation element substrate was resistively heated and constructed primarily from fibrous silicon carbide.

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

H<sub>2</sub>, 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 start experiments; the stock methanol injectors on the test engine were disabled prior to the start testing.

The engine was allowed to receive product gas for 5 seconds before cranking was attempted. At an engine temperature of 73°F the product gas mixture was sufficient to start and idle the engine. The engine was then cooled to 43°F; the product gas mixture was sufficient to start the engine on the second crank attempt and idle without laboring.

## 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.

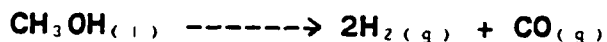
Some state-of-the-art methanol engines require the addition of gasoline to the fuel to improve their startability.[1] Other methanol engines utilize separate cold start systems relying on gasoline or propane for cold start assist.[2,3] Finally, some researchers have suggested that stratified-charge combustion 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 this project was to construct a methanol dissociator that could provide H<sub>2</sub> and CO fuels in quantities that could be used as a cold start assist for a methanol engine. This dissociator would utilize resistively heated ceramic technology to provide the energy necessary to bring the catalyst to operating temperature quickly. A methanol dissociator using this technology has been tested by EPA for its cold start assist potential.[5] Though that particular dissociator was unable to provide enough dissociated product gas to start a 4-cylinder engine, the resistively heated ceramic was able to quickly heat methanol vapor to temperatures necessary for the dissociation reaction to occur. EPA used this resistively heated ceramic together with equipment that would increase the flow of methanol vapor feed in order to improve the reactor's output and efficiency.

### III. Dissociator Operation

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



The dissociator described below accomplished this reaction by a three-step process (Figure 1). First, methanol was vaporized in a boiler and moved by an inert carrier gas to a superheater. The methanol/carrier gas mixture was then superheated to approximately 600°F and the superheated mixture passed to a catalyzed and heated dissociator. The hot methanol vapor was dissociated in this final stage and passed into an engine intake manifold. A detailed description of each part of the process is given below.

#### A. Boiler Unit

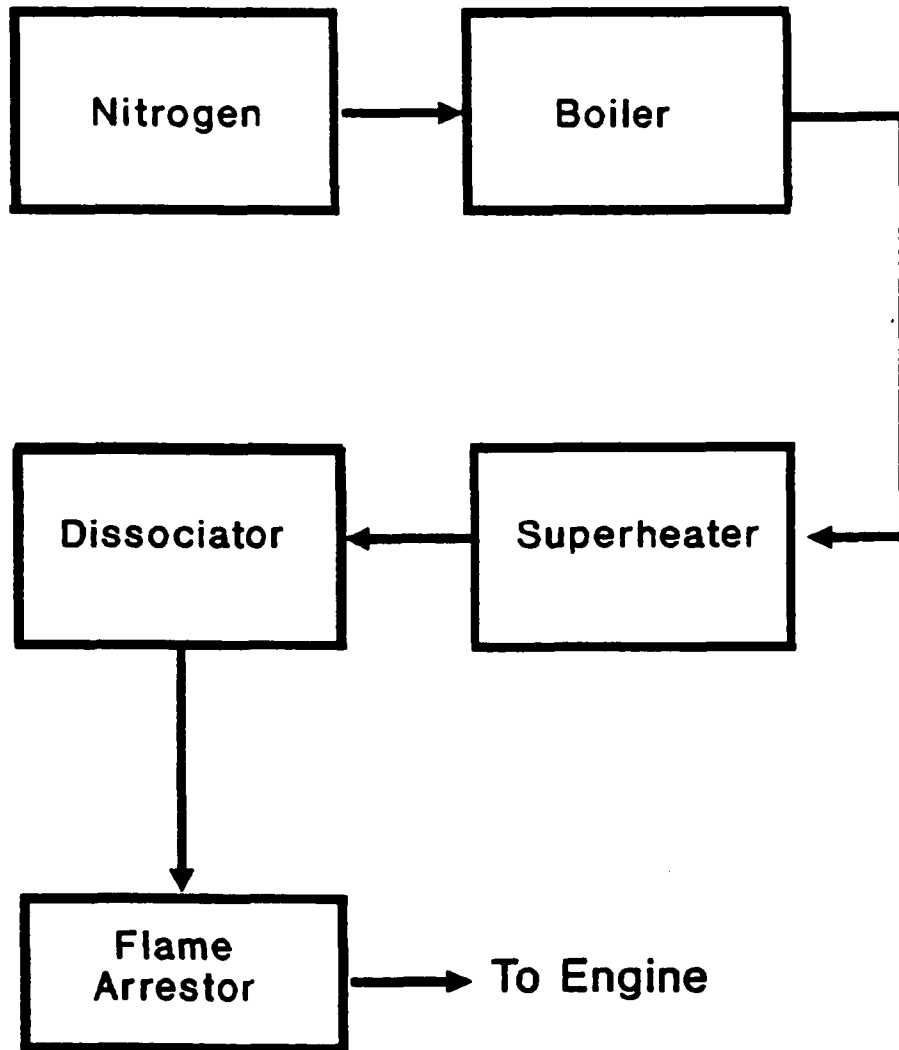
The boiler was a 5-gallon capacity, type 316 stainless steel pressure vessel. The vessel was fitted with a steam heating coil, pressure relief valve, liquid temperature monitor and pressure gauge. The boiler was filled with approximately three gallons of methanol prior to each test and sealed; no provision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

The flow of vaporized methanol was assisted by the passage of a pressurized carrier gas through the boiler. Nitrogen at 6 standard cubic feet per hour was added to the boiler during testing and the vessel was purged at the same flow rate for 10 minutes prior to the start of heating. This inert gas flow served three functions.

Figure 1

# Methanol Dissociation System



1. The  $N_2$  acted as a carrier gas to assist product flow throughout the system;
2. The inert  $N_2$  provided an atmosphere safe against rapid oxidation and fires in the dissociator; and
3. The absence of air in the dissociator hindered undesirable, competing chemical reactions such as complete oxidation of the methanol feed.

#### 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 hot methanol vapor and  $N_2$  carrier gas passed through a porous silicon carbide filter which had been coated with platinum. This filter was resistively heated by passing 120-volt alternating current through it. This catalyzed heater acted as the methanol dissociator.

The filter 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.

#### IV. 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 B.

Exhaust unburned fuel (UBF) emissions were measured with a Beckman Model 400 flame ionization detector. A FID response factor of 76 percent was used.[6]

Exhaust formaldehyde was measured using a dinitrophenylhydrazine (DNPH) technique.[7] 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.

## V. Program Design

The goal of this program was to start and idle a light-duty vehicle engine using the product gases from the methanol dissociator as a fuel supply. The program was conducted in two phases:

1. Construction of the dissociator and flow measurement; and
2. Engine testing of the dissociator.

The first phase of the program involved building the dissociator and measuring the methanol feed rate from the reservoir. We also attempted to determine product composition and thereby establish reactor efficiency. The second phase involved piping the product to a warmed engine and attempting a start. Immediately prior to the attempted start the methanol engine main injectors were disabled, in order to limit the fuel to the product gas supplied from the dissociator.

## VI. Discussion

### A. Boiler Flow Rate

The low flow rate provided by the boiler in the dissociator previously tested [5] may have substantially contributed to that dissociator's inability to start the test engine. The dissociated product flow rate to start an engine similar in displacement to our test engine has been calculated [8,9] as .3 to .6 grams per second or .45 grams per second. The product generated by the lower flow dissociator, [5] .013 grams per second  $H_2/CO$  and .053 grams per second non-dissociated methanol, was low when compared to these calculated requirements.

A steam-heated boiler was used in the system presented in this report to increase the feed rate to the dissociator. The temperature of the liquid in the boiler is a function of the pressure above the liquid charge in the boiler, the amount of fuel charge present, and the condition of the steam flowing through the heating coils. The flow of vaporized methanol out of the boiler is a function of boiler pressure, temperature, and the flow rate of carrier gas through the boiler. These variables were difficult to simultaneously control. Measurement of vaporized methanol flow rate was accomplished by weighing the boiler prior to testing, obtaining steady-state conditions and operating over a period of time, then reweighing the boiler after the cessation of testing. The difference in weight was divided by the time of operation to determine a rough flow rate.



At the conditions of 30 psig in the vapor dome above the liquid methanol, 195-200°F liquid temperature and 6 SCFH N<sub>2</sub> into the boiler, approximately 1900 grams per hour of methanol feed was delivered to the superheater. This was a significant improvement over the methanol feed rate of the lower flow dissociator mentioned previously, and within the guidelines of the rates necessary to ensure .3 to .6 grams per second of dissociated product gas to the engine.

A higher methanol flow rate could be obtained by increasing the flow of N<sub>2</sub> carrier gas to the boiler. Although this technique increases the amount of inert N<sub>2</sub> fed to the engine, a vaporized methanol flow rate in excess of 2500 grams per hour was made possible by increasing N<sub>2</sub> flow to 20 SCFH. The use of helium at 6 SCFH, rather than N<sub>2</sub>, also had the effect of raising the vaporized methanol flow rate over 2500 grams per hour. The use of these higher flow rates was not necessary, however, as a rate of 1900 grams per hour proved sufficient to start and idle the test engine.

#### B. Superheater Operation

The superheater was capable of heating the methanol vapor (1900 g/hr) and N<sub>2</sub> carrier gas (6 SCFH) stream to 600°F. Higher gas temperatures were made possible by lengthening the pipe and adding additional nichrome wire heaters (gas temperatures out of the superheater in excess of 1200°F were recorded).

A problem with coking of the methanol fuel was observed at elevated superheater temperatures. This coking led to plugging of the superheater and coating of the catalyst with coke. The coking, or decomposition of the methanol to elemental carbon, appeared to occur mainly on the inner wall surfaces of the superheater. Coking on the catalyst substrate surface also appeared to have occurred, although some of the carbon in the catalyst can may have flowed through from the superheater.

Coke formation appeared to positively correlate with operating temperature in the superheater and dissociator. Temperatures in excess of 900°F and a vaporized methanol/N<sub>2</sub> gas mixture invariably led to sooting of the superheater. However, some carbon formation was noted at a gas mixture temperature of 525°F and an outside wall temperature of the superheater of 700°F.

Other researchers working with methanol dissociation have noted this coking problem.[10,11] The optimum solution to this problem appears to be the use of a catalyst that promotes the dissociation reaction at very low temperatures (less than or equal to 570°F). For the present effort, we attempted to hold the gas mixture temperature below 600°F at all points in the system.

C. 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 1.

Table 1

Test Conditions For 73°F Cold Start Test

<u>Variable</u>	<u>Condition</u>
Engine temperature	73°F (overnight soak)
Boiler liquid temperature	192°F
Boiler pressure	30 psig
Methanol flow rate from boiler	1900 grams per hour
Gas temperature out of superheater	532°F
Gas temperature out of dissociator	300°F
Gas temperature into EGR port	149°F
N <sub>2</sub> carrier gas flow into boiler	6 SCFH

Product gas from the dissociator was fed to the EGR port for 5 seconds prior to a crank attempt. The engine started on the first 3-second crank attempt. It idled without laboring; at no time was there any indication of stalling. We allowed the engine to idle for 1 minute, then shut it off.

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 cylinders) it proved sufficient to allow a start and idle at the conditions in Table 1.

It was very difficult to calculate a dissociator yield for this experiment. The Tedlar sample bags used to determine H<sub>2</sub> content of the product gas also collected a substantial quantity of liquid which could not be passed through the gas chromatograph. The product that remained in the gas phase however was analyzed; the H<sub>2</sub> content of the gas was 7 percent. This indicates a yield of less than 10 percent. This experiment was repeated with essentially the same conditions as described in Table 1. A 6 percent H<sub>2</sub> concentration in the sample bag was obtained, and the engine started and idled with no observable difficulty.

The experiment was then repeated at a lower engine temperature. The test cell was chilled and the engine soaked to a temperature of 43°F. Lower temperatures were impractical because of the possibility of freezing water lines in the test cell. The higher flow rate of methanol was probably due to an improved quality of steam (less water) allowing for a more efficient heat transfer to the methanol. Attempts to control the boiler and superheater to the same operating conditions as in the previous experiment were made, but the quality of the steam in the lines is a function of demand on the building steam system on a particular day. The conditions for this test are given in Table 2.

Table 2

Test Conditions For 43°F Cold Start Test

<u>Variable</u>	<u>Condition</u>
Engine temperature	43°F
Boiler liquid temperature	193°F
Boiler pressure	30 psig
Methanol flow rate from boiler	2600 grams per hour
Gas temperature out of superheater	600°F
Gas temperature out of dissociator	300°F
Gas temperature into EGR port	139°F
N <sub>2</sub> carrier gas flow into boiler	6 SCFH

Product gas was fed from the dissociator to the EGR port for 10 seconds prior to the first crank attempt. The engine fired but did not start on the first 3-second crank. On the second crank attempt, the engine started and idled smoothly. We allowed the engine to idle for 30 seconds; it did not exhibit any tendency to stall. We then shut the engine off.

During this experiment a considerable quantity of liquid again accumulated in the sampling bag. The gaseous portion of the sample was tested by gas chromatograph, and a H<sub>2</sub> concentration of 12 percent was obtained. This indicates a dissociator efficiency yield of less than 15 percent.

D. Reactor Power Requirements

The gas temperatures in the superheater and dissociator were kept below 600°F during the cold start testing in order to prevent the coking mentioned previously. However, it is necessary to provide a significant amount of energy to the methanol at the catalyst surface in order to further the dissociation reaction.

Karpuk[12] in a private communication to EPA, calculated a power requirement of 2256 watts necessary to dissociate 2000 g/hr of methanol at 25°C. Our calculations of this requirement show it to be 2230 watts, essentially the same. Therefore,

increasing amounts of power were applied to a catalyzed filter while flowing 1900 g/hr vaporized methanol through it. The objective of this test was to determine how power level affected both gas temperature out of the dissociator and product yield.

Gas temperatures into and out of the dissociator at various power levels were recorded after the reaction had reached steady state. Voltage drop was measured across the dissociator while current was measured with an ammeter in series. H<sub>2</sub> concentration in the product gas stream was determined at higher power levels.

The power supply used for this experiment was a Power Mate AC to DC converter allowing a maximum DC output of 1000 watts. Resistance across the ceramic filter was measured at .65 ohms. Details from this experimentation are given in Table 3.

Table 3

Dissociator Power/Gas Temperature Characterization

<u>Volts</u>	<u>Amps</u>	<u>Watts</u>	<u>Gas Temperature Into Dissociator</u>	<u>Gas Temperature Out of Dissociator</u>
7	5	35	550°F	195°F
9	8	72	550°F	225°F
11	10	110	550°F	256°F
13	11	143	540°F	304°F
14	13	182	540°F	340°F
15	14	210	540°F	355°F
16	15	240	540°F	385°F
17	16	272	546°F	410°F
18	18	324	547°F	430°F
20	20	400	547°F	470°F
22	23	506	570°F	571°F
23	23	529	570°F	571°F

Total power dissipated was limited to 529 watts. Attempts were made, but failed to increase the current above 23 amps at 23 volts with this equipment. H<sub>2</sub> concentrations in the product gas of 6 and 10 percent were determined for power levels of 400 and 529 watts, respectively. Again, significant amounts of liquid collected in the sample bags; this indicates that the conversion rate of methanol was less than 10 percent even at the higher power level.

The 5KVA power supply that Coloroll provided to EPA was next utilized to increase the power to the dissociator. Gas temperature into the dissociator was also increased over previous levels in order to determine whether this would aid the dissociation reaction. The results of this experimentation are presented in Table 4.

Table 4

Dissociator Power/Gas Temperature Characterization

<u>Volts</u>	<u>Amps</u>	<u>Watts</u>	<u>Gas Temperature Into Dissociator</u>	<u>Gas Temperature Out of Dissociator</u>
5.73	5.0	28.7	733°F	138°F
7.35	7.0	51.5	814°F	150°F
10.26	10.8	110.8	832°F	265°F
13.30	14.8	196.8	823°F	363°F
15.36	17.8	273.4	783°F	401°F
19.04	22.9	436.0	755°F	428°F
22.40	27.3	611.5	755°F	440°F
<u>25.00</u>	<u>31.0</u>	<u>775*</u>	<u>751°F</u>	<u>460°F</u>
28.40	35.5	1008.2**	755°F	448°F

\* This power level maintained only 60 seconds.

\*\* This power level maintained less than 10 seconds; unit failed during this test.

The highest power levels attained here were not sustained; the information presented in Table 4 was obtained from several experiments. At gas temperatures out of the dissociator in excess of 450°F numerous leaks were experienced in the dissociator housing. Several methods of improving the seams were tried; the concentrated methanol vapor attacks most gasket materials at temperatures in excess of 450°F, however. Overheating of the electrical connections was also a problem: several measurement attempts at higher power were halted due to melted instrument connections.

Typically 5 to 10 minutes was necessary for the reaction to achieve steady-state status (constant gas temperature out of the dissociator) as the level of power applied changed in increments of 20 watts. This is due to heat loss through the insulated dissociator housing as well as from gas passing through the dissociator. At the last data point presented in Table 4, 1008 watts, only a 448°F gas temperature out of the dissociator was measured. The dissociator failed after operating for less than 10 seconds at this power level. The unit therefore never achieved steady-state operating conditions at this power level.

The dissociator failed shortly after the application of 1008 watts. The stainless steel wool gaskets and stainless steel contacts were unaffected; instead the nichrome flame-sprayed ceramic ends physically separated from the rest of the hollow ceramic cylinder. This indicates that failure was due to a difference in thermal expansion coefficients between the silicon carbide and the nichrome flame spray.

H<sub>2</sub> concentration in the product gas was measured at approximately 40 percent at a power input of 611 watts. Again, a substantial portion of liquid was present in the sample bag, making it difficult to calculate a H<sub>2</sub> yield. The higher gas temperature into the dissociator, because of greater superheating during this testing, may have substantially contributed to the higher H<sub>2</sub> bag concentrations. A thin film of carbon due to coking of the fuel was evident, however, on the surface of the catalyst when the unit was dismantled after testing.

A sample of the liquid which collected in the Tedlar bag at 611 watts was taken and analyzed for its distillation curve. The equipment used for this analysis was a Model TS-74645 AR-2 Automatic Distillation Apparatus (ADA III), made by the Precision Group, GCA Corporation. This analysis indicated that the liquid in the sample bag was 99 volume percent methanol and 1 percent water.

The data presented here suggests that the dissociation reaction may be more limited by the amount of energy supplied to the feed gas and catalyst surface than by the amount of catalyst present on the substrate. H<sub>2</sub> concentrations in the product gas increased slightly, from 6 to approximately 10 percent, as the product gas temperature increased from 300°F to 571°F respectively. According to an unpublished memorandum from Nissan,[13] a fresh Pt catalyst could have generated a H<sub>2</sub> concentration of approximately 30 percent in the 571°F product gas, a substantial increase over the level we experimentally obtained. Increasing the power output to 611 watts and the feed gas temperature to 755°F increased the H<sub>2</sub> concentration to 40 percent (cooling of the feed gas in the reactor from 755°F to 571°F would make available an additional 140 watts for the dissociation reaction). However, even at this increased power level a substantial amount of methanol condensed in the sample bag, indicating a much lower H<sub>2</sub> concentration, had the bag contents been entirely vaporized prior to chromatographic analysis.

Compounding the problem of an insufficient amount of energy necessary to completely dissociate 2000 grams per hour of feed gas is the energy loss from the dissociator due to heat transfer to its environment. Heat losses occur convectively to the air from the ceramic-wool insulation blanketing the dissociator housing and conductively to the metal fittings and polymer tubing which carry the product gas to the engine. These losses, though unquantified here, would lessen the amount of energy available to initiate the endothermic dissociation reaction.

The product yield, therefore, increases as the rate of energy supplied to the dissociator is increased, at conditions of approximately 600 watts and a 2000 grams per hour methanol feed rate to the dissociator. This indicates that at these conditions the rate of energy supplied to the dissociator limits the product yield.

E. Emission Levels

Levels of emissions characterized as unburned fuel (UBF) 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. UBF and formaldehyde emissions are expressed in average rates of g/min and mg/min respectively; this information is presented in Table 5. NOx and CO emissions were not measured due to problems with the analyzers. Each test was conducted following an overnight soak of the engine at 73°F.

UBF emissions for the dissociator fuel are reported as if they are all methanol. While this neglects the effect that the CO and H<sub>2</sub> have on the result, the nature of the exhaust emission measurement capability in the test cell at the time of the tests make this an appropriate approach.

UBF emissions increased slightly when the test engine was operated on fuel supplied from the dissociator. This increase in emissions, (.56 g/min), while noted, is not definitive; the engine was emissions-tested only once using the dissociator as the fuel supply system. Formaldehyde levels appear to vary considerably, from an average 1 mg/min using fuel injector-supplied methanol versus no detectable concentration when the dissociator supplied fuel. Again, however, only limited testing was conducted. Additional testing must be conducted to properly define the difference in emission levels.

Table 5

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

<u>Engine Fuel System Configuration</u>	<u>No. of Tests</u>	<u>UBF g/min</u>	<u>Formaldehyde mg/min</u>
Methanol injectors functioning	2	2.76	1.0
Dissociator fuel system	1	3.32	--

VII. Conclusions

1. The test engine started and idled at 43°F using dissociator product gas as the fuel, under the conditions described in Table 2. It is not possible to state to what extent the limited amount of H<sub>2</sub> produced under these conditions would assist a cold start at temperatures below 43°F.

2. Coking of the fuel and subsequent catalyst poisoning was a problem with the system at gas temperatures greater than 600°. Some coking was noticed, however, at lower gas temperatures into the dissociator.

3. At the conditions of 529 watts applied, gas temperature into the dissociator of 570°F and a methanol flow rate through the system of 1900 g/hr, a H<sub>2</sub> concentration of

10 percent in the product gas was noted. The ceramic element failed when 1000 watts were applied.

4. UBF emission rates from the test engine were measured over a 73°F cold start and 5-minute idle using two different fuel systems:

- a. Methanol from the engine fuel injectors; and
- b. Dissociator product gas with the engine fuel injectors disabled.

The emission levels measured were 2.76 g/min and 3.32 g/min, respectively. Formaldehyde emission levels over this cycle for these fuel systems were 1.0 mg/min and no detectable concentrations measured, respectively. Only a limited number of emission tests were conducted, however; two tests were conducted using the engine fuel injection system and one test was conducted using the dissociator product gas only as the fueling system.

#### VIII. Future Effort

A catalyst that will more favorably promote the dissociation reaction at temperatures below 500°F is currently being sought. A lower temperature reaction would have the dual advantages of requiring less activation energy and not promoting undesirable reactions such as the tendency to coke. A lower operating temperature would also make possible a more compact heat exchanger/dissociator design.

Some candidate catalyst configurations have been identified; permission is being sought to try these new catalysts on the resistively heated ceramic elements described here. The evaluation of these new catalysts will be the subject of a separate technical report.

#### IX. Acknowledgments

The methanol dissociator used in this experimentation was provided by Coloroll, plc., a United Kingdom corporation. The test engine was provided by Nissan Research and Development, Inc., Ann Arbor, MI.

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. The efforts of Michael Murphy, electrical engineer, also of SDSB, with several electrical problems that developed during setup and testing are also greatly appreciated.

In addition, the author appreciates the efforts of Jennifer Criss and Marilyn Alff of the Control Technology and Applications Branch, ECTD, who typed this manuscript, and J. Dillard Murrell, also of CTAB, who drew Figure 1.



X. 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. FID Methanol Response, Memo, Edward A. Barth, OAR/OMS/ECTD/TEB, Ann Arbor, MI, August 1987.
7. Formaldehyde Measurement In Vehicle Exhaust At MVEL, Memo, Gilkey, R. L., OAR/OMS/EOD, Ann Arbor, MI, 1981.
8. "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.
9. Dissociated Methanol Fuel Requirements to Start A Four-Cylinder Engine, Memo from Gregory K. Piotrowski, OAR/OMS/ECTD/CTAB, Ann Arbor, MI, 1986.
10. "Study of the Methanol Reformed Gas Engine," Hirota, T., Japan Society of Automotive Engineers Review, March 1981.
11. "Dissociated Methanol Citation: Final Report," Finegold, J., G. Glinsky, and G. Voecks, SERI/TR-235-2083, DE85000505, August 1984.
12. Private Communication, Karpuk, M. E., to U.S. EPA, 1987.
13. Briefing to C. Gray, Jr., by Nissan Motor Company, March 1987.
14. Fundamentals of Gas Analysis by Gas Chromatography, Thompson, B., Varian Associates, Inc., Palo Alto, CA, 1977.
15. 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.

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

## 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.[14,15]

## APPENDIX B (cont'd)

### Specifications:

<b>Chromatograph model</b>	<b>GOW-MAC Model 69-550</b>
<b><u>Detector:</u></b>	
Operating principle	Thermal conductivity type
Temperature control	Ambient to 300°C
Carrier gas	N <sub>2</sub>
Detector elements	Four (4) rhenium tungsten elements
Noise	10-micro volts maximum
Drift	40-micro volts/hour maximum
<b><u>Injection:</u></b>	
Number of ports	Two
Control	Solid-state, variable-voltage phase control
Operating temperature	Ambient to 300°C
<b><u>Column Oven:</u></b>	
Temperature range	Ambient to 300°C
Control	Solid state time apportioning
<b><u>Column:</u></b>	5' x 1/4" molecular sieve
<b><u>Gas flow system:</u></b>	Dual-column with dual-injection ports and exits
<b><u>Thermal conductivity bridge control:</u></b>	Continuous current adjust 50-300 mA. Bridge zero adjust. Attenuator for bridge output, 10 positions to 512.
<b><u>Electrical:</u></b>	
Power requirements	105-125 volts, 50/60 H <sub>2</sub>
Circuit breaker	7 amps
<b><u>Physical:</u></b>	Two-section construction. Upper section houses column oven, detector and vaporizers. Lower section contains power supply, bridge control circuit and temperature controllers.
<b><u>Compressed Gas Auxiliaries:</u></b>	
Zero gas	N <sub>2</sub>
Span gas	40 percent H <sub>2</sub> /60 percent N <sub>2</sub>
<b><u>Output:</u></b>	
Stripchart recorder	Soltech model 3318

## APPENDIX C

### TEST ENGINE SPECIFICATIONS

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