

Technical Report

Evaluation of Coloroll Methanol Dissociator
For Cold Start Assist Application

by

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

ANN ARBOR, MICHIGAN 48105

OFFICE OF
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December 22, 1987

MEMORANDUM

SUBJECT: Exemption From Peer and Administrative Review

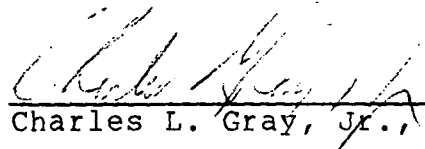
FROM: Karl H. Hellman, Chief KH
Control Technology and Applications Branch

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

The attached report entitled, "Evaluation of Coloroll Methanol Dissociator For Cold Start Assist Application," (EPA-AA-CTAB-87-08) describes the evaluation of a methanol dissociator supplied by Coloroll, plc., with regard to its ability to start and idle a light-duty engine. Dissociator product gas was piped to a warm engine and a start attempted. This dissociator was unable to start and idle the test engine due to its low product flowrate.

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.

Approved:


Charles L. Gray, Jr., Dir., ECTD

Date:

3-10-88

Table of Contents

	<u>Page Number</u>
I. Summary	1
II. Introduction	1
III. Dissociator Operation	2
A. Boiler Unit and Feedback Tank	2
B. Superheater	4
C. Catalytic Dissociator	4
D. Ancillary Dissociator Components	4
IV. Supporting Equipment	5
V. Program Design	5
VI. Discussion of Test Results	5
VII. Conclusions	8
VIII. Acknowledgments	8
IX. References	10
APPENDIX A - Hydrogen Content Determination	A-1
APPENDIX B - Test Engine Specifications	A-2

I. Summary

A low flow methanol dissociator was procured from Coloroll, plc., U.K., for use as a cold start assist for a methanol engine. This dissociator made use of resistively heated ceramic and carbon fiber filters in the boiler, superheater, and catalytic dissociator elements.

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

H₂ and CO product gas mixture from the dissociator was piped to the exhaust gas recirculation ports of the test engine. This product gas mixture served as the fuel supply during the start experiments; the main methanol injectors on the test engine were disabled prior to the start testing. Prior to attempting this start, the engine was operated at idle for 30 minutes to ensure a warmed engine, and thus very favorable starting conditions.

The engine was allowed to receive product gas for various periods, of 15 seconds to 4 minutes in duration, before cranking was attempted. The engine received product gas continuously during each cranking period. On each attempt, the engine failed to start. The most probable cause of this failure to start was the low flowrate of product gas generated, approximately .013 grams per second. An air/fuel ratio during the attempted start was calculated; this calculated value exceeded 40, too lean to have allowed a cold start.

II. Introduction

Light-duty M100 neat methanol-fueled engines are difficult to start and run in cold weather because of the single boiling point characteristic of this fuel. 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 may be vaporized before the cylinder at relatively low temperatures.

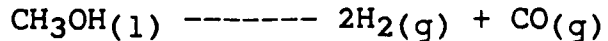
Some state-of-the-art methanol engines require the addition of gasoline to the fuel to improve their startability.[1] Other methanol engines utilize separate cold start systems relying on gasoline or propane for cold start assist.[2,3] Finally, some researchers have suggested that a combination of mechanical approaches may 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 fuel for cold start.

The goal of this project was to evaluate a methanol dissociator supplied by Coloroll, plc, for use as a cold start assist to a methanol engine. Ideally, the dissociator should have provided enough fuel to start and idle a 2.0-liter, 4-cylinder methanol engine. The design of the program and a discussion of the results obtained is given below.

III. Dissociator Operation

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



The Coloroll-supplied dissociator accomplishes this reaction by a three-step process. First, methanol is vaporized in a boiler and moved by an inert carrier gas to a superheater. The methanol/carrier gas mixture is then superheated to approximately 500°C and the superheated mixture is passed to a catalyzed and heated dissociator. The hot methanol vapor is dissociated in this final stage and passes out of a product tube and into an engine manifold. A detailed description of each part of the process is given below.

A. Boiler Unit and Feedback Tank

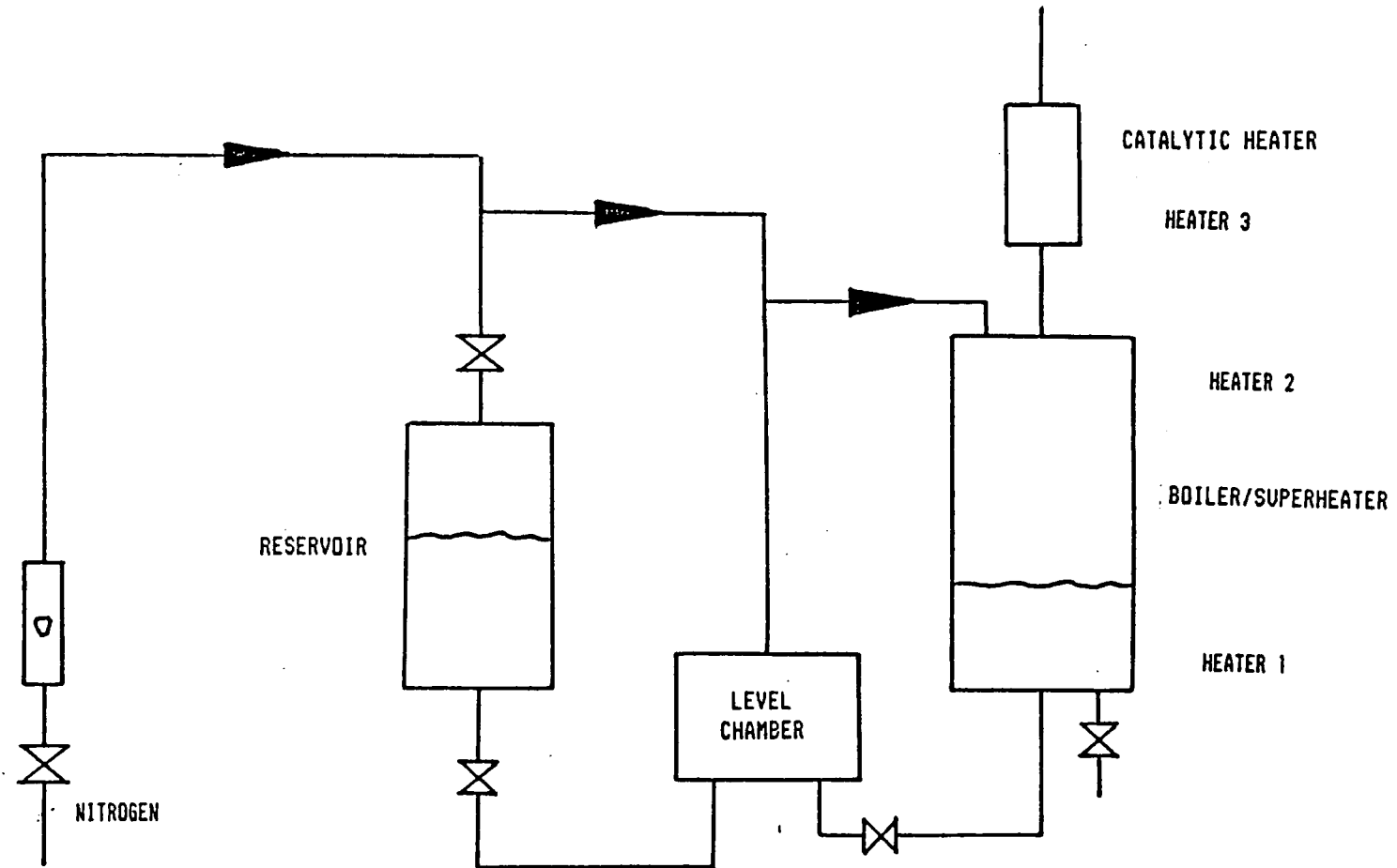
The methanol feed is provided from a sealed glass pipe section fitted with stainless steel end plates. The capacity of this fuel reservoir is approximately 3 liters. A connection to the top of the tank is made to a bottle of compressed nitrogen gas. The inert gas serves three functions.

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

A schematic drawing indicating the locations of ties to the N_2 gas supply made to equalize pressure over the entire system is provided as Figure 1. The bottom of the reservoir contains a drain and a feed line to the level control tank.

A level control tank was installed between the fuel reservoir and the boiler. This tank controls the level of methanol in the boiler. A level switch ballcock in the tank switches off power to all electrically heated elements if fuel level in the controller falls below a certain level. An outlet in the bottom of the controller feeds the boiler.

Figure 1
Schematic Drawing of Coloroll Methanol Dissociator



The boiler used for the evaporative stage is a ceramic element with a resistance of approximately 40 ohms. This element was powered by 220-volt alternating current, and is isolated electrically from the rest of the dissociator by a base plate constructed from "Tufnol" brand insulation. The amount of current supplied to the boiler element determines the vaporization rate of the liquid methanol. A drain is also fitted to the boiler to facilitate maintenance of the unit.

B. Superheater

The superheater is an electrically heated carbon element with a resistance of approximately one ohm. This element is powered from a 12-volt tapping of a transformer. A perforated metal plate surrounds this element, and this surround absorbs radiation from the heating element and transfers it to the gases passing through it. The outlet temperature of the superheater is measured by a thermocouple in the tube above the cover plate.

The vessel housing the boiler and superheater consists of two glass tube sections held together by end and middle flanges. Gaskets throughout form gas-tight seals. Tie rods from the base plate to the top plate hold the unit firmly in place. A "Perspex" tube surrounds the glass tube for extra safety.

C. Catalytic Dissociator

The hot methanol vapor and N₂ carrier gas pass upward through a further porous element heater which has been coated with platinum. This catalyzed heater acts as a dissociator. Gas flows radially through the porous heater walls and out of the unit through a 1-inch nominal bore tube. A thermocouple in the gas stream measures temperature out of the dissociator.

D. Ancillary Dissociator Components

Several ancillary components were also installed in order to make the dissociator safer to operate. First, a safety device consisting of a rotameter and an electrical control unit was installed between the compressed N₂ source and the dissociator. This device shuts off electrical power to the dissociator unless a specified minimum flowrate of N₂ was exceeded, approximately 5.0 standard liters per minute. A pressure relief valve constructed of stainless steel and having an opening pressure of 35 psig was installed in the product tube out of the dissociator, to prevent an unsafe buildup of pressure in the unit. A flame arrestor constructed of stainless steel and filled with stainless steel wool, was also installed after the product tube. Finally, a 7.5 kilovolt-amp isolation transformer of 240-volt input/output capacity was purchased and installed between the 220-volt AC supply (line, line, neutral and ground) and the dissociator, which was wired for 240-volt AC Mains Electricity (line, neutral and ground).

Power to each of the porous element heaters was controlled by a remote control box, which may be operated up to 20 feet away from the dissociator. This remote panel contained three potentiometers which were adjusted to limit the current to each element.

IV. Supporting Equipment

The flow of methanol feed to the boiler was determined by an indirect method, which involved a procedure for weighing the fuel supply before and after dissociator operations and accounting for hang-up in the level controller, reservoir and boiler. H₂ composition in the product gas, however, was determined by gas chromatography. A GOW-MAC Model 69-550 gas chromatograph was used, and its operation is detailed in Appendix A.

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.

V. Program Design

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

1. Installation, checkout and flow measurement; and
2. Engine testing of the dissociator.

The first phase of the program involved setting up the dissociator and measuring the methanol feed rate from the reservoir. Product composition was also determined, and reactor efficiency thereby established. 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 that supplied by the dissociator product.

VI. Discussion of Test Results

Initial testing involved the determination of feed methanol flowrate from the reservoir and H₂ composition of the product gas. From these measurements the dissociator capacity and efficiency could be determined.

During this initial testing, the boiler element was exposed to a current of 2.55 amps over a voltage of 220 volts for 561 watts applied. The superheater element experienced a current of 55 amps over a voltage of 12 volts (limited by a transformer) for a power output of 660 watts. Gas temperature out of the superheater was in the range of 500-515°C during

sampling. The dissociator operated at 57 amps over 12 volts for a power output of 680 watts. Product gas temperature out of the dissociator was measured at 490°C during sampling.

Methanol feed rate was measured indirectly by a careful sequence of controlled weighings of the fuel introduced into the reservoir. These weighings accounted for methanol hangup in the reservoir, flow level controller and boiler. A flowrate of 160-170 grams per hour of vaporized methanol from the boiler was determined by this process.

H₂ content of the product gas was measured at 9.5 volume percent. Inert N₂ carrier gas flowed into the dissociator at a rate of 6 liters/minute. The dissociated product yield calculated from these conditions was 29 percent, equating to a dissociation of roughly .013 grams per second of feed methanol. Dissociated product yield is defined here as grams of methanol dissociated to H₂ and CO per minute over grams of methanol per minute into the dissociator.

The next phase of this program involved piping the product gas into a warm engine and attempting a start and idle. The engine described in Appendix B was utilized. Product gas was piped into the intake manifold runners via ports for exhaust gas recirculation. The engine was warmed for 30 minutes prior to beginning the start test. The engine fuel injectors were disabled prior to the test, allowing a fuel supply exclusively composed of the dissociator product. The engine was cranked at 240 revolutions per minute.

This testing consisted of successively longer fills of the intake manifold runners, each fill followed by 2-3 second cranking periods. The fill periods allowed were of 15, 20, 25, 30, 35, and 40-second lengths. Extended fills of 2, 3, and 4-minute lengths were also tried, followed each time by the cranking sequence referred to above.

During this phase, the boiler element operated at 2.6 amps over 220 volts for 570 watts applied. The superheater operated at 57 amps over 12 volts for a power output of 680 watts. The gas mixture exited the superheater at 450°C. The dissociator element received 55 amps at 12 volts for a power output of 660 watts. Product gas temperature out of the dissociator measured 493°C during cranking.

The methanol vaporization rate in the boiler was measured at 237.4 grams per hour during this testing. H₂ product gas concentration was measured at 7.5 volume percent. A 20 percent yield was determined, equating to a dissociated product flow of .013 grams per second.

The engine failed to start on each attempt. After one fill attempt, that of 30 seconds duration, the engine did fire, but even then on only one revolution. During successively longer fill periods, the engine gave no indication of an ability to start.

The low flowrate provided by the boiler may substantially contribute to this dissociator's inability to start and idle the warmed engine. The dissociated product flowrate to start an engine of similar size has been calculated [5,6] as .3 to .6 grams per second or .45 grams per second. The .013 grams per second achieved here may simply be too low to allow a start and idle. Extended fill periods did not seem to aid the start either. Temperatures into and out of the dissociator appeared adequate to promote the desired reaction. The choice of a platinum catalyst appeared appropriate, and no attempts at scientific determination of the dissociator element's ability to promote the desired reaction were made after this testing.

An air/fuel ratio was calculated at start conditions in order to determine if an appropriate mixture was present to permit cold starting. A summary of this determination is given below.

Air flow through the engine air induction system was measured at 4.7 cfm during cranking with the dissociator feeding product gas into the exhaust gas recirculation ports. Methanol was vaporized in the boiler section at a rate of 3.96 grams per minute, and 6 liters per minute of N₂ carrier gas flowed into the engine during cranking. The dissociation reaction occurred with a yield of 20 percent, which amounted to a total fuel feed stream into the engine from the dissociator of:

- a. .10 grams per minute H₂;
- b. .69 grams per minute CO; and
- c. 3.17 grams per minute vaporized methanol.

An equimolar amount of oxygen is required to oxidize either 1 mole of methanol or its dissociated product; this fact aids the calculation of an air/fuel ratio where the fuel is a mixture of H₂, CO, and vaporized methanol. It may be instructive to view the weight of fuel in terms of "equivalent methanol grams." This term is defined here as grams of specific fuels adjusted by their combustion energies relative to methanol to arrive at methanol equivalent weights. Using the information given in reference 6:

<u>Feed Rate From Dissociator to Engine</u>	<u>Methanol Equivalent Feedrate</u>
3.17 gpm methanol	3.17 gpm methanol equivalents
.69 gpm CO	.33 gpm methanol equivalents
.10 gpm H ₂	.57 gpm methanol equivalents

4.07 grams per minute methanol equivalents is the fuel source during cranking for the test engine.

Using the ideal gas law, the rate of air supplied through the engine's air induction system at cranking is 160 gpm air. N₂ carrier gas is supplied to the engine at a rate of 7 gpm N₂. If air/fuel ratio is then defined as:

$$\frac{\text{Weight of air} + \text{weight of carrier gas}}{\text{Weight of fuel in methanol equivalents}}$$

then air/fuel ratio at cranking would be calculated as (160 + 7)/4.07, or 41, much too lean to start. If the concept of methanol equivalents is neglected and weight of fuel is defined as total fuel weight, regardless of chemical composition, air/fuel ratio is calculated as (160 + 7)/3.96 or 42, much too lean to start.

Further experiments with this technology may make use of the superheater and catalytic dissociator elements. The rate of vaporization prior to superheating will have to be substantially improved before satisfactory results using this technology as a cold start assist for a methanol engine can be achieved.

VII. Conclusions

A low flow methanol dissociator was tested as a cold start assist for a methanol engine. The engine was operated prior to the cold start testing to ensure a most favorable case scenario (fully warmed engine). Dissociated product gas flowing directly from the dissociator comprised the fuel supply; the methanol engine fuel injectors were disabled during the start testing.

The engine was allowed to receive dissociated product gas for various periods of 15 seconds to 4 minutes in duration before cranking was attempted. On each occasion the engine failed to start. The most probable cause of the failure to start was the low flowrate of product gas generated, approximately .013 grams per second. Air/fuel ratio during the attempted start was calculated; this calculated value exceeded 40, too lean to permit a cold start.

Future cold start efforts with this technology may limit the use of the resistively heated ceramic fiber elements to the catalytic dissociator and superheater sections.

VIII. 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.

IX. References

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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.[7,8]

APPENDIX A (cont'd)

Specifications:

Chromatograph model

GOW-MAC Model 69-550

Detector:

Operating principle
 Temperature control
 Carrier gas
 Detector elements
 Noise
 Drift

Thermal conductivity type
 Ambient to 300°C
 N₂
 Four (4) rhenium tungsten elements
 10-micro volts maximum
 40-micro volts/hour maximum

Injection:

Number of ports
 Control
 Operating temperature

Two
 Solid-state, variable-voltage
 phase control
 Ambient to 300°C

Column Oven:

Temperature range
 Control

Ambient to 300°C
 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
 Circuit breaker

105-125 volts, 50/60 H₂
 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.

Compressed Gas Auxiliaries:

Zero gas
 Span gas

N₂
 40 percent H₂/60 percent N₂

Output:

Stripchart recorder

Soltech model 3318

B-1
APPENDIX B

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