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Dissociated Methanol Test Results

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DISSOCIATED METHANOL TEST RESULTS

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ABSTRACT

This paper describes the design and testing of an automotive fuel system that provides hydrogen-rich gases to an internal combustion engine by catalytically cracking, or dissociating, methanol on board the vehicle. The vaporization and dissociation of methanol absorb heat from the engine exhaust and increase the lower heating value of the fuel by approximately 22%. In addition, raising the compression ratio and burning with excess air increase the engine thermal efficiency.

Engine dynamometer test results with dissociated methanol demonstrated improvements in brake thermal efficiency compared to gasoline from 30% to 100% depending on engine speed and torque. Lower speeds and torques produce the largest improvements. This paper presents maps of exhaust temperature and exhaust heat content. The exhaust temperature is almost always high enough for dissociation to occur, but at lower power outputs, there is only enough exhaust energy for partial dissociation of the methanol.

INTRODUCTION

We expect dissociated methanol to offer higher efficiency than conventional liquid fuels because of three factors: (1) the increase in chemical energy due to waste heat recovery, (2) an extended lean misfire limit, and (3) higher allowable compression ratio. Exhaust emissions also are lower.

In the past, many researchers have proposed on-board fuel processing to generate hydrogen for automotive applications (e.g., Breshears, Cotrill, and Rupe, 1974; Houseman and Voecks, 1980; Kester, Konopta, and Camara, 1975; and Sjostrom, Eriksson, and Lindner, 1979). Numerous groups have constructed several experimental automobiles and performed engine tests (e.g., Noguchi and co-workers, 1977; Inagaki, Hirota, and Ueno, 1979; MacDonald, 1976; and Finegold, 1976). Only recently has dissociation of alcohol attracted much serious attention.

Methanol can be dissociated to hydrogen and carbon monoxide or carbon dioxide by strongly endothermic reactions. The reactions occur in the 250°-350°C range, which matches available waste heat in engine exhaust, increasing the enthalpy of the fuels as shown in Table 1. In terms of the energy increase, the dissociation reaction yielding carbon monoxide is more attractive than the steam reforming reaction yielding carbon dioxide. The resultant fuels also

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Table 1. Comparison of Fuel Processing Reactions

| Reaction | Increase in Lower Heating Value |
|--|---------------------------------|
| Methanol | |
| $\text{CH}_3\text{OH} + \text{heat} \rightarrow 2\text{H}_2 + \text{CO}$ | 22% |
| $\text{CH}_3\text{OH} + \text{H}_2\text{O} + \text{heat} \rightarrow 3\text{H}_2 + \text{CO}_2$ | 15% |
| Ethanol | |
| $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} + \text{heat} \rightarrow 4\text{H}_2 + 2\text{CO}$ | 20% |
| $\text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} + \text{heat} \rightarrow 6\text{H}_2 + 2\text{CO}_2$ | 13% |

have a higher energy density since less, or no, water is required. The steam reforming reaction has the advantage of occurring at a lower temperature (~200°C). Methanol has less tendency to coke (lay down carbon) on dissociation than hydrocarbon fuels do.

The methanol dissociation reaction is the reverse of the reaction by which methanol is produced. Although it is strongly endothermic, dissociation is thermodynamically favored because of an increase in entropy, as shown by the equation for free energy:

$$\Delta G_{\text{rxn}} = \Delta H_{\text{rxn}} - T\Delta S_{\text{rxn}} = -39.7 \text{ kJ/gmol} \quad (1)$$

$$\begin{aligned} \Delta H_{\text{rxn}} &= 99.6 \text{ kJ/gmol} \\ \Delta S_{\text{rxn}} &= 243 \text{ J/gmol}^\circ\text{C} \\ T &= 300^\circ\text{C} (573 \text{ K}) \\ P &= 100 \text{ kPa} \end{aligned}$$

Equilibrium favors the reaction going nearly to completion. At 300°C and 150 kPa, equilibrium considerations predict that 99.9% of the methanol will be converted to CO and H₂, discounting side reactions.

In addition to the desired dissociation reaction, many side reactions are possible as shown in Table 2. Most of the side reactions are undesirable. Reactions 2 and 3 consume hydrogen that would have otherwise been available to extend the lean misfire limit. Reaction 5 produces solid carbon that would plug the catalyst bed and destroy the catalyst activity.

Table 2. Methanol Dissociation and Side Reactions

| | | | |
|-----|-------------------------------------|---------------|--|
| (1) | CH_3OH | \rightarrow | $\text{CO} + 2\text{H}_2$ |
| (2) | $2\text{CH}_3\text{OH}$ | \rightarrow | $\text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$ |
| (3) | $\text{CH}_3\text{OH} + \text{H}_2$ | \rightarrow | $\text{CH}_4 + \text{H}_2\text{O}$ |
| (4) | $\text{CO} + \text{H}_2\text{O}$ | \rightarrow | $\text{CO}_2 + \text{H}_2$ |
| (5) | 2CO | \rightarrow | $\text{C}_2 + \text{CO}$ |
| (6) | CH_3OH | \rightarrow | $\text{CH}_2\text{O} + \text{H}_2$ |

The choice of catalyst has a major effect on reaction kinetics and, thus, the composition of the reaction products. A number of catalysts are known to be active for methanol dissociation (e.g., platinum, palladium, copper, zinc). In addition to high activity toward dissociation at low temperatures and low activity toward side reactions, a fuel-reforming catalyst should have a low cost, long life, and be resistant to poisoning by impurities that might be present in fuel-grade methanol.

SYSTEMS DESCRIPTION

The dissociated methanol system comprises a fuel system to dissociate the methanol and a modified internal combustion engine to burn it. They are shown together in a simplified schematic drawing in Fig. 1 and in a comprehensive one in Fig. 2 showing instrumentation locations.

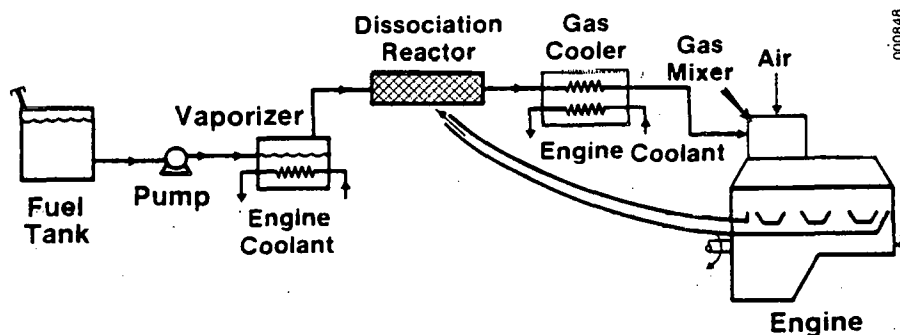


Figure 1. Conceptual Diagram of Automotive System

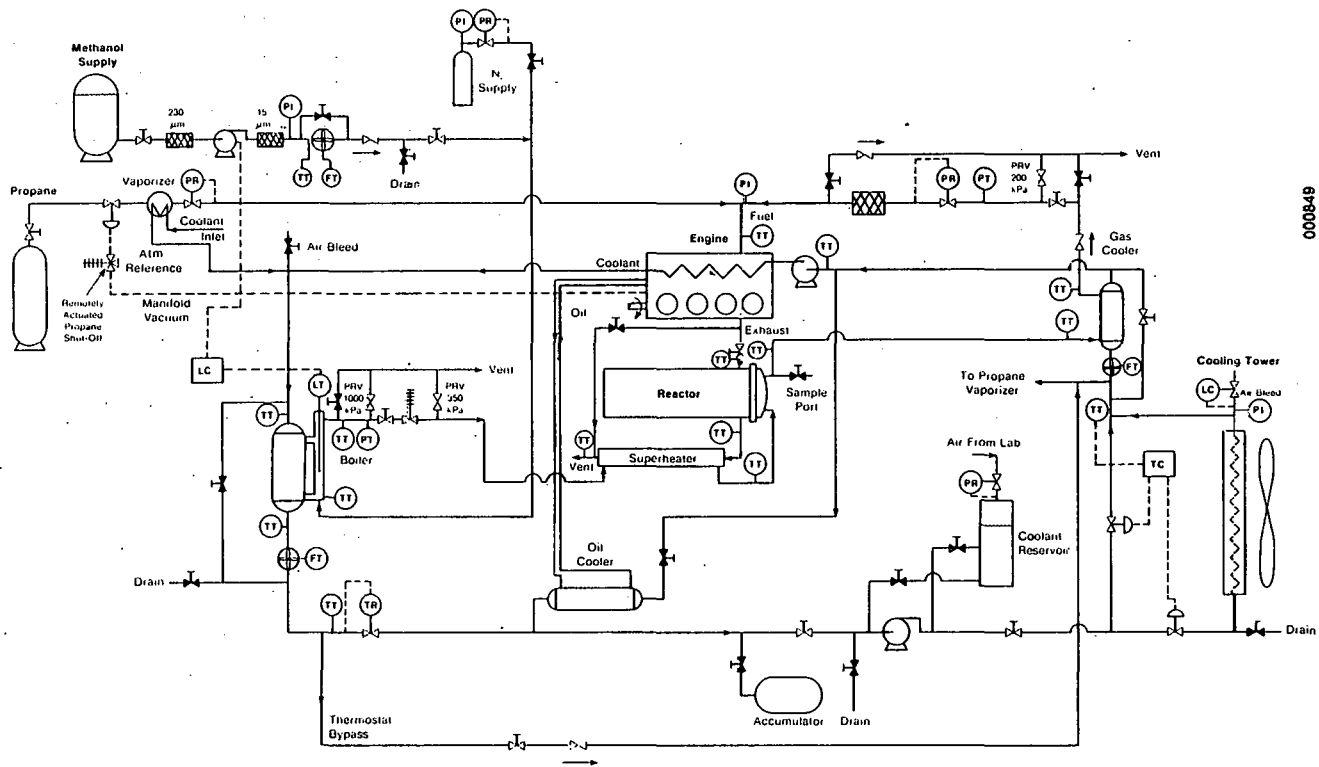
Fuel System

The function of the fuel system is to vaporize and dissociate the methanol and to deliver the hydrogen-rich gases to the engine to be burned. The major components, in order of fuel flow, are the vaporizer, superheater, reactor, and gas cooler. To minimize time and cost, most of the components selected are commercially available, although some were slightly modified. All the components were sized to fit into the engine compartment of a 1980 Chevrolet Citation so the system could be road tested.

Liquid methanol is pumped by a small electric gear pump from a fuel reservoir. It then is filtered to $7\ \mu\text{m}$ using a series of filters. From here the methanol passes through a solenoid valve and into the vaporizer, a vertically-mounted, shell-and-tube heat exchanger with $2200\ \text{cm}^2$ of heat transfer area. Engine coolant, which provides heat for the vaporization, flows through the tubes, and the methanol is vaporized in the shell. A cylinder is mounted directly above the vaporizer and serves as a vapor-liquid separation chamber. A level probe, operating on an electrical capacitance principle, monitors the methanol level in the vaporizer. Cycling the liquid methanol solenoid valve controls the liquid level. The engine coolant temperature and, to a lesser extent, the vaporization rate determine the vaporization pressure. Most of the testing was conducted with the engine coolant in the $90^\circ\text{-}100^\circ\text{C}$ range, producing a methanol vapor pressure of 180-200 kPa.

Methanol leaves the vaporizer as saturated vapor at approximately 80°C . It passes through a solenoid valve and into the superheater, a double-pipe heat exchanger with $880\ \text{cm}^2$ heat transfer area that heats the methanol to approximately 250°C using engine exhaust after it leaves the catalytic reactor. Upon leaving the superheater, the methanol vapor enters the dissociation reactor, where the methanol vapor makes contact with the catalyst and where heat from the engine exhaust drives the endothermic reaction. The reactor was designed, built, and tested by Cerini, Houseman, and Voecks (1980) at the Jet Propulsion Laboratory under contract with the Solar Energy Research Institute (SERI). The reactor is a stainless steel, shell-and-tube heat exchanger, 100 cm long and 18 cm in diameter with $4.0\ \text{m}^2$ of heat transfer area. The 0.8-cm ID tubes are packed with catalyst pellets over which the fuel flows. The engine exhaust flows directly from the exhaust manifold to the reactor. Both fuel and the exhaust sides are two pass flow, and the flow is counter-current. The reaction occurs on the surface of a Cu-ZnO catalyst supported on alumina pellets, United Catalysts #T2107RS.

The gaseous fuel, which consists of hydrogen and carbon monoxide in approximately a 2:1 ratio with small amounts of methanol, methane, and dimethyl ether, leaves the reactor at approximately 300°C . Before entering the engine, the gaseous fuel is cooled to 100°C to improve the volumetric efficiency, lower NO_x emissions, and increase resistance to preignition. The cooling is done using engine coolant from the radiator in a small shell-and-tube heat exchanger (heat transfer area = $1200\ \text{cm}^2$). The decrease in temperature increases the energy density of the fuel from 5.4 kJ/l to 8.3 kJ/l (methane at STP is 34.0 kJ/l). The higher energy density of the fuel allows increased engine power output because the fractional volume required for fuel in the air-fuel mixture is reduced.



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- Valves**
- Hand valve — normally open normally closed
 - Solenoid valve
 - Pneumatic valve
 - XR
 - Self-contained regulator
 - PRV
 - Pressure relief valve
 - Check valve

Legend

Abbreviations

- Prefixes**
- T Temperature
 - P Pressure
 - L Level
 - F Flow
 - Filter

- Suffixes**
- T Transducer
 - I Indicator
 - C Controller
 - R Regulator

Figure 2. Detailed Schematic of Automotive System

A conventional gas regulator upstream of the carburetor controls pressure of this gaseous fuel. The final step in fuel processing is to filter any catalyst fines from the fuel stream to protect the engine. At this point, the carburetor can draw on a supply of cool synthesis gas at a regulated pressure.

Since the fuel processing system requires engine heat to function, a separate start-up system is required. For the test stand, propane was plumbed to the fuel line directly upstream of the carburetor. After the engine is adequately warmed up, the methanol flow is started and the propane flow shut off. A liquid methanol fuel injection system is being installed in the vehicle for startup.

Engine

We used a General Motors 2.5-l, in-line, four-cylinder engine rated at 65 kW from a 1980 Chevrolet Citation. The block and cross-flow head are cast iron. The GM high energy ignition system was used. The engine was modified only slightly to operate on dissociated methanol. The compression ratio was increased from the stock 8.3:1 to approximately 14:1 by installing flat-top pistons with greater compression height and by milling 1.5 mm from the cylinder head. The original carburetor was replaced with an Impco air-valve carburetor, Model 225, designed for propane. No changes were made to valve timing, but we removed the exhaust gas recirculation, exhaust air injection equipment, and the exhaust catalyst.

RESULTS

Figures 3 and 4 show the engine maps for the baseline gasoline engine and the dissociated methanol system, respectively. Note that the peak efficiency for

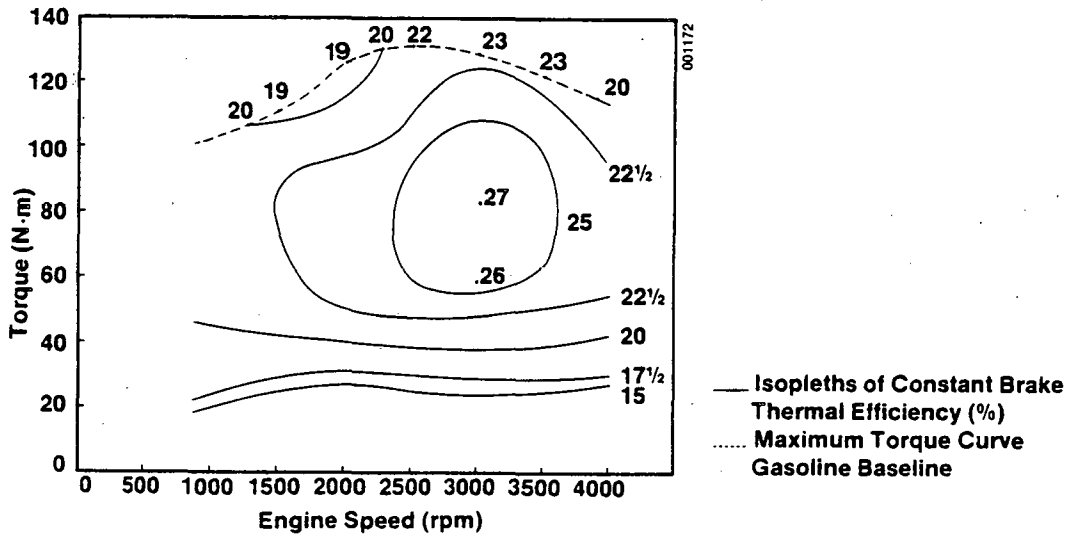


Figure 3. Gasoline Engine Map

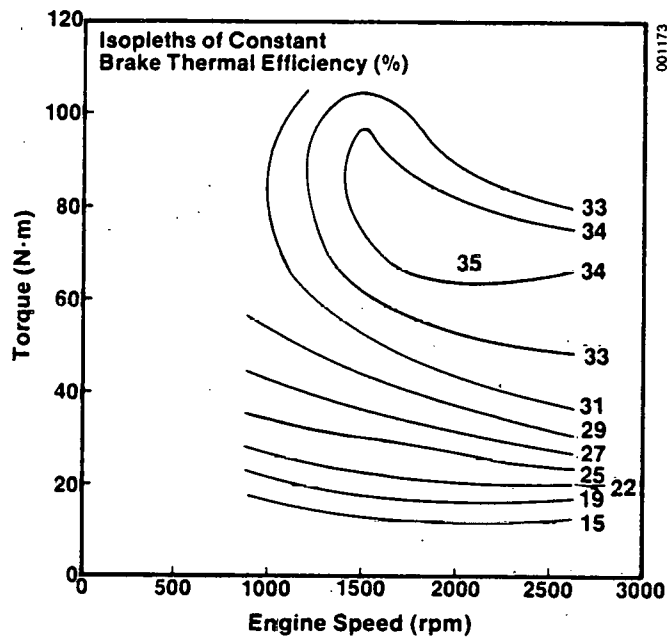


Figure 4. Dissociated Methanol Engine Map

the gasoline system is 27% and for the methanol system, 35%. The peak efficiency for methanol occurs at a lower speed.

Figures 5 and 6 present brake thermal efficiency compared to torque at 1000 and 2000 rpm, respectively, for both the gasoline system and the dissociated

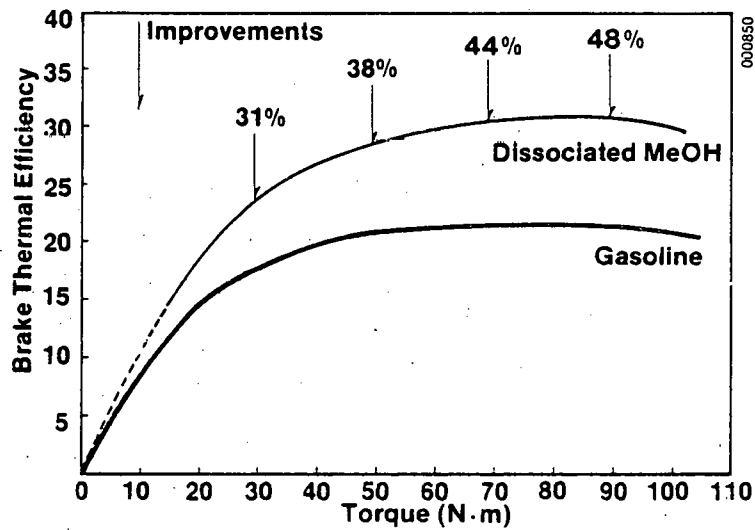


Figure 5. Brake Thermal Efficiency vs. Torque at 1000 rpm

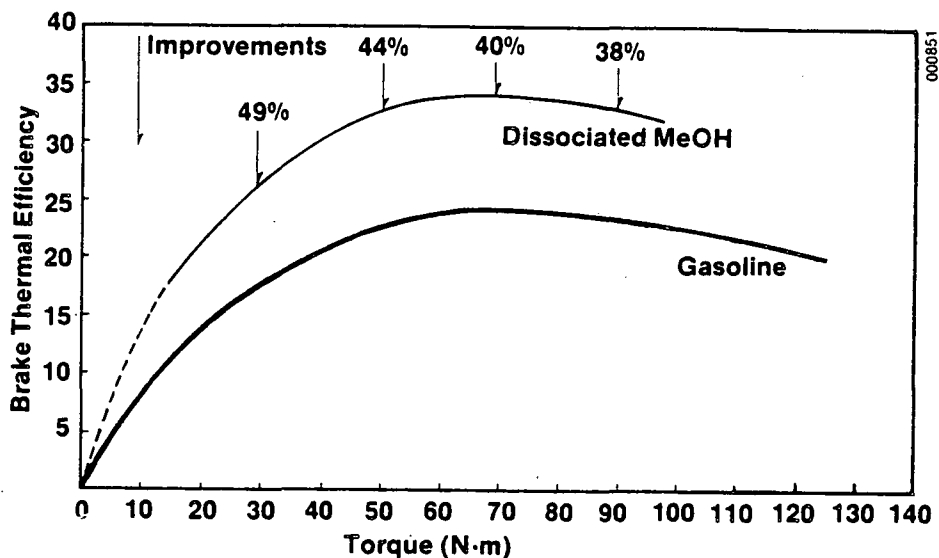


Figure 6. Brake Thermal Efficiency vs. Torque at 2000 rpm

methanol system. The improvement is in the range of 31% to 48% at 1000 rpm and from 38% to 49% at 2000 rpm.

Figures 7 and 8 show maps of exhaust temperature and exhaust heat content relative to that required for 100% dissociation of the inlet methanol. With the Cu/ZnO catalyst, the effective lower temperature limit for reaction is 250°-300°C. At the lower power points, the exhaust temperature and heat content are only high enough to dissociate part of the methanol. In practice, this is not a problem. Even with a small fraction of the methanol dissociated, there is enough hydrogen generated to gain the desired lean-burn advantages. Some of the possible chemical energy gain, however, is not realized.

DISCUSSION

The data presented in the previous section shows substantial improvements in brake thermal efficiency for the dissociated methanol system when compared to the gasoline system. We attribute the improvements to three basic differences: (1) the chemical energy increase of the fuel resulting from the vaporization and subsequent catalytic dissociation of methanol into hydrogen and carbon monoxide; (2) the increase in engine efficiency resulting from the use of a very high compression ratio; and (3) the use of very low equivalence ratios.*

*Equivalence ratio (ϕ) is the actual fuel/air ratio divided by the stoichiometric fuel/air ratio. It is the inverse of the excess air ratio (λ).

The chemical energy increase of the fuel is greatest under high loads when the most thermal energy is present in the exhaust. Despite this, the improvements relative to gasoline are greatest under low loads.

The increased compression ratio is made possible by the high resistance to preignition of the hydrogen-rich fuel. High compression ratios (expansion ratios) allow more work to be extracted from a given charge on the expansion stroke, thus increasing the thermodynamic efficiency. The magnitude of the increase may be estimated from the equation for air-standard cycle efficiency:

$$\eta = 1 - \left(\frac{1}{CR}\right)^{\gamma-1} \quad (2)$$

where

- η = thermal efficiency
- CR = compression ratio
- γ = ratio of specific heats (C_p/C_v).

Excess air combustion causes higher thermal efficiency for several reasons: reduced throttling losses, cooler combustion temperatures, and decreased heat capacity of the combustion products. Excess air combustion is possible because of the wide flammability limits of hydrogen, the major constituent of the fuel. The optimum equivalence ratio was as low as $\phi = 0.3$ ($\lambda = 3.3$) depending on engine speed and load.

Throttling losses are reduced in a lean-burn engine because manifold pressures are much higher for a given power output; thus, the engine does not need to expend as much shaft power in pumping the air/fuel mixture into the cylinders. For example, a 2.5-l engine operating at 2500 rpm with a manifold pressure of 70 kPa (9-in. Hg vacuum) wastes approximately 1 kW of shaft power pumping air across the partially closed throttle. An engine fueled with hydrogen or hydrogen-rich gases can operate under most conditions with the throttle almost or completely wide open. Power is modulated by controlling fuel flow once wide-open throttle at low equivalence ratios is attained.

Low equivalence ratios reduce peak combustion temperatures because of the diluent effect of the excess air. The most obvious effect is that heat losses to the cylinder walls are lowered, allowing more heat to be converted to work. Two more subtle effects are changes in heat capacity with temperature and dissociation of water and carbon dioxide at high temperature. For example, from 100° to 2500°C the C_v of water vapor increases 55%. The result is that a given amount of heat increases combustion temperatures more at a lower temperature and, thus, is more effective. High combustion temperatures cause a fraction of the water vapor and carbon dioxide to endothermically dissociate at the start of the expansion stroke, absorbing some of the energy of combustion. The water vapor and carbon dioxide recombine and release the energy, but it is released later in the expansion stroke where it is less effective. The dissociation is a very strong function of temperature and pressure.

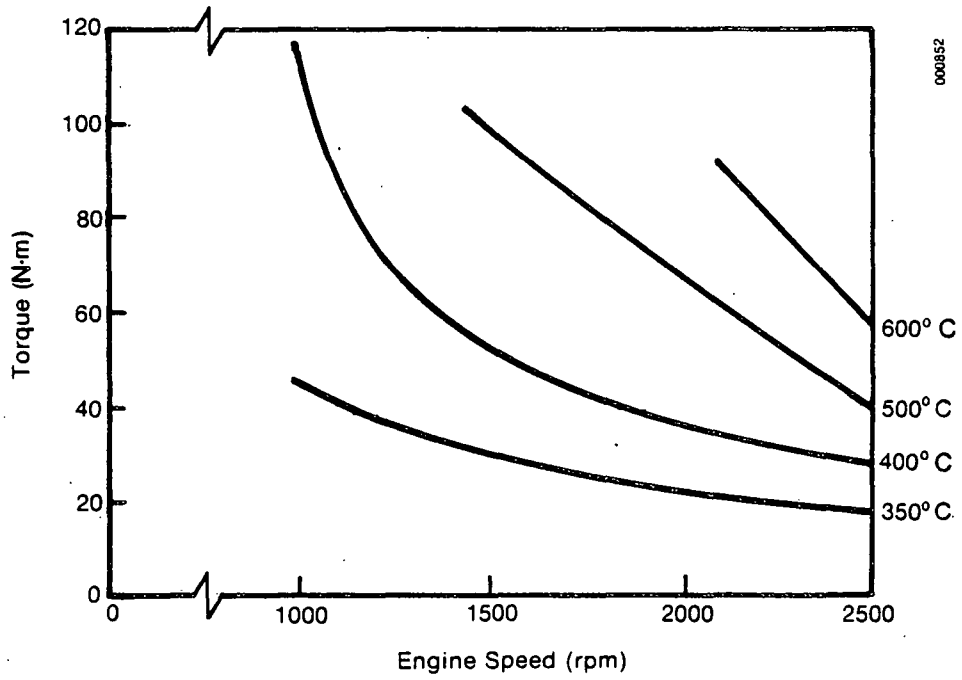


Figure 7. Exhaust Temperature Map

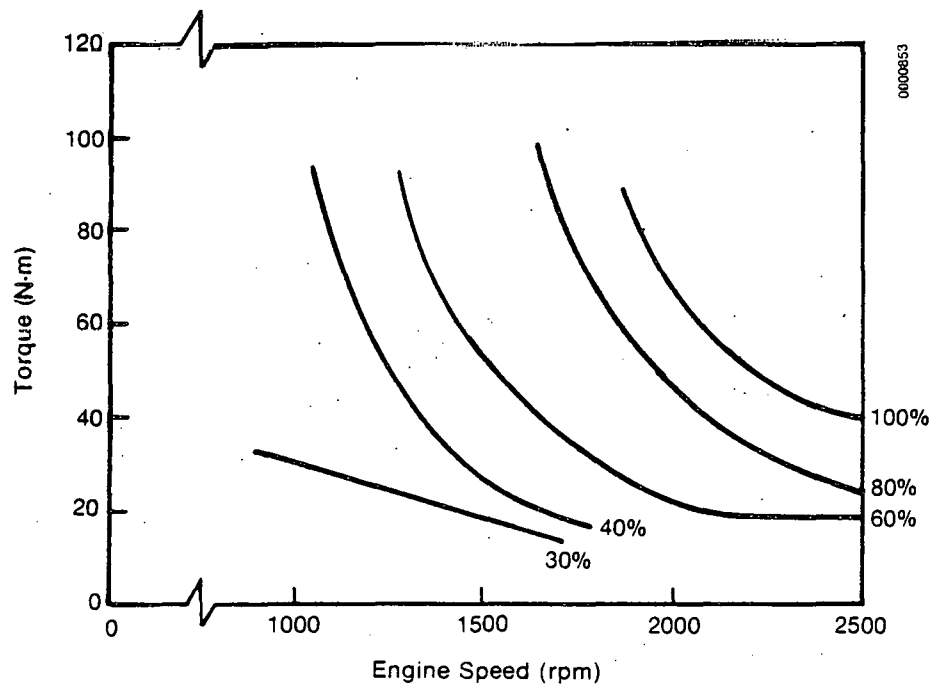


Figure 8. Percentage of Fuel Methanol That Can Be Dissociated with Exhaust Heat

The heat capacity of the combustion products of a lean-burn engine is further reduced because air has a lower heat capacity than water and carbon dioxide. This allows higher combustion temperatures for a given heat input. Equation 2 also shows this effect since γ increases as C_v decreases.

The power of the dissociated methanol engine was comparable to the gasoline engine at low engine speeds. The energy density of the fuel is approximately one-fourth that of methane and one-tenth that of propane, but less air is required to burn the dissociated methanol. Thus, the energy density of the air/fuel mixture is approximately the same for all these gaseous fuels and is about 10% less than gasoline/air mixtures. The increased compression ratio brings the power of gasoline and dissociated methanol engines to about the same level.

VEHICLE INSTALLATION

The entire system was installed in the engine compartment of the Citation for road testing and EPA emissions testing. The methanol vaporizer was replaced with a shell-and-tube heat exchanger with 3300 cm^2 of heat transfer area, 50% larger than the original one, allowing the coolant thermostat setting to be lowered to $\sim 85^\circ\text{C}$. The methanol vaporizes in the shell, and the coolant flows in a two-pass configuration in the tubes. The heat exchanger is mounted vertically as was the one on the test stand. A larger capacity filter with a more favorable shape for vehicle installation was used. The fuel regulator was replaced with a larger capacity one to allow more precise pressure regulation. No muffler is used on the vehicle as the reactor adequately silenced exhaust noise.

SUMMARY

A dissociated methanol fuel system was designed, built, and tested. Improvements in the brake thermal efficiency of 30%-100% over gasoline were obtained from engine dynamometer tests even though the fuel generally did not completely dissociate. Vehicle tests are currently underway, and we are designing a second generation system to solve the problems encountered in the first system and to explore the benefits of design improvements.

ACKNOWLEDGMENTS

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