April 1994 • NREL/TP-425-6357

Advanced Hydrogen/Methane Utilization Technology Demonstration

Final Report

F. Lynch
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Hydrogen Consultants, Inc.
Littleton, Colorado

National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401-3393
A national laboratory of the U.S. Department of Energy
Operated by Midwest Research Institute
for the U.S. Department of Energy
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ADVANCED HYDROGEN/ METHANE UTILIZATION TECHNOLOGY DEMONSTRATION

SUBMITTED TO

NATIONAL RENEWABLE ENERGY LABORATORY

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1.0 Introduction and Executive Summary

This is the Phase I Final Report under contract XR-2-11175-1, "Advanced Hydrogen/Methane Utilization Demonstration" between the National Renewable Energy Laboratory (NREL), Alternative Fuels Utilization Program, Golden, Colorado and Hydrogen Consultants, Inc., Littleton, Colorado. Brent Bailey and Chris Colucci were Technical Monitors for NREL.

The overall objective of the work was to seek homogeneous blend ratios of H_2/CH_4 that provide "leverage" with respect to exhaust emissions or engine performance. The "leverage" sought was a reduction in exhaust emissions or improved efficiency in proportions greater than the percentage of hydrogen energy in the blended fuel gas mixture.

The steady-state study was conducted with a 5.7 liter General Motors (GM) V-8 engine equipped with a manually controlled Impco gas mixer and a secondary mixing device to reduce cylinder-to-cylinder mixture variations. Hydrogen/methane blends were mixed, real time, from commercial purity compressed gases supplied without charge to the project by Air Products and Chemicals, Inc. A GM high energy ignition system was manually adjusted to "minimum best torque" spark advance at each test point. A catalyst, donated by Englehard Corp., was seasoned by 18k miles of gasoline, natural gas and Hythane®[1] operation prior to installation on the test engine. The catalyst, specially formulated for methane oxidation, was used both as an oxidation catalyst in the lean range and as a three-way catalyst with stoichiometric mixtures.

The scope of the study included the range of air/fuel mixtures from the lean limit to slightly richer than stoichiometric. This encompasses two important modes of engine operation for emissions control; lean burn pre-catalyst (some NG engines have no catalyst) and post-catalyst, and stoichiometric with three-way catalyst. A brief discussion of each of these modes is presented below.

1.1 Lean Burn

Hydrogen has strong effects on the combustion properties of methane in the lean range of air/fuel ratios. Near the lean limit of combustion with methane, the addition of hydrogen reduces incomplete combustion products (CO, HC) and increases engine torque. The catalyst is virtually 100% efficient for CO oxidation under all lean burn test conditions. For engines equipped with good oxidation catalysts, the HC vs. NOx tradeoff is the main issue. Hydrogen is effective for increasing thermal efficiency and reducing post-catalyst HC emissions near the lean limit.

Improved engine efficiency and power were observed with increasing hydrogen content at ultra lean equivalence ratios. The improvements are attributed to the increased combustion efficiency that is apparent in the emissions data. To a lesser extent, lean hydrogen/air mixtures have an energy density advantage over lean

[1] Hythane is a registered trademark of Hydrogen Consultants, Inc.

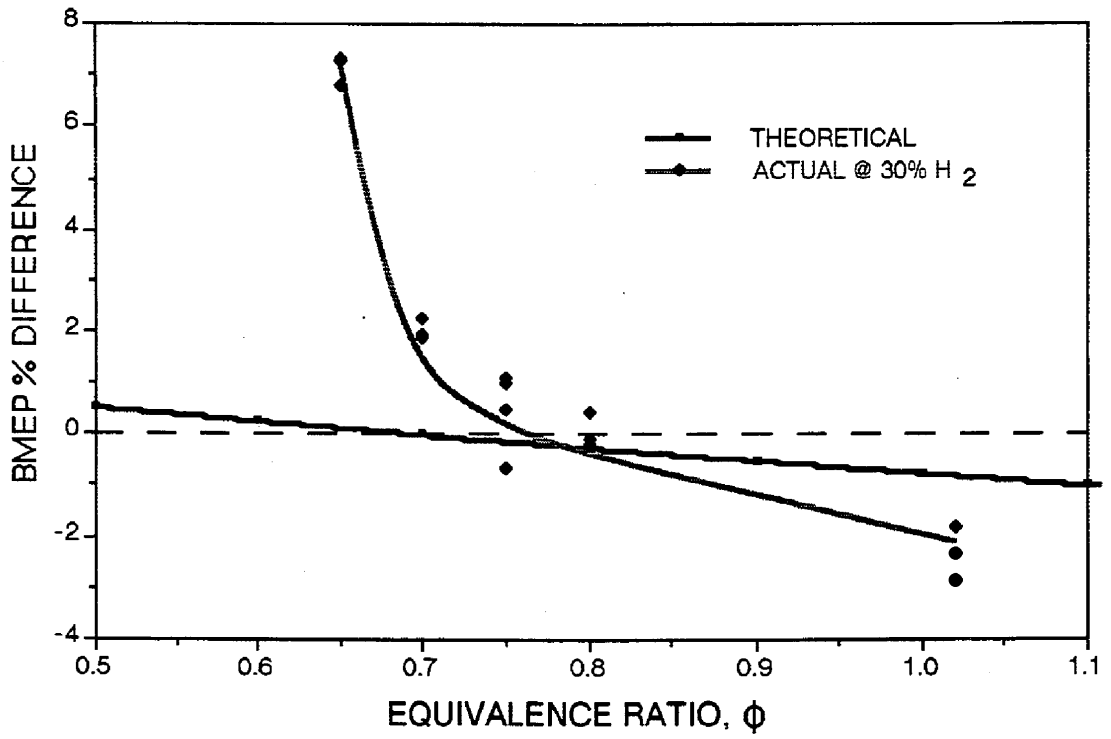

Figure 1-1. Comparison between theoretical and actual BMEP improvement with 30% H_2 in CH_4 at 80 kPa MAP.

methane/air mixtures ($\phi \leq 0.7$). Figure 1-1 compares the theoretical and actual percent difference in BMEP for pure methane and 30% hydrogen in methane at wide-open throttle. The significant performance advantage with hydrogen in the lean range, apparent in Figure 1-1, may be sacrificed for a NOx advantage over pure methane, as discussed below.

In Figure 1-1, the slight decrease in BMEP at $\phi = 1$ pertains to the 30% hydrogen data only. BMEP data for 5% and 15% hydrogen are equal, within limits of error, to pure methane.

The sluggish combustion process near the lean limit with pure methane does not produce as much NOx as the more stable combustion that occurs with hydrogen addition. However, if the excess torque (BMEP), gained through hydrogen addition is sacrificed by retarding the spark and/or leaning the mixture, it is possible to have lower HC and NOx at the same BMEP[2] (e.g., Figure 1-2).

With pure methane, lean burn NOx emissions below 1 gram/kW-hr are accompanied by high HC emissions. With 15-30% hydrogen, both NOx and post-catalyst HC can be held to 1 gram/kW-hr or less. This effect is even stronger in pre-catalyst emissions. Getting below 1 gram/kW-hr of NOx with pure methane fuel comes at the expense of pre-catalyst HC emissions on the order of 10 grams/kW-hr.

[2] The torques were exactly equal on the day of the retard test. Averaging with methane data from earlier tests resulted in the small difference in BMEP shown in Figure 1-2.

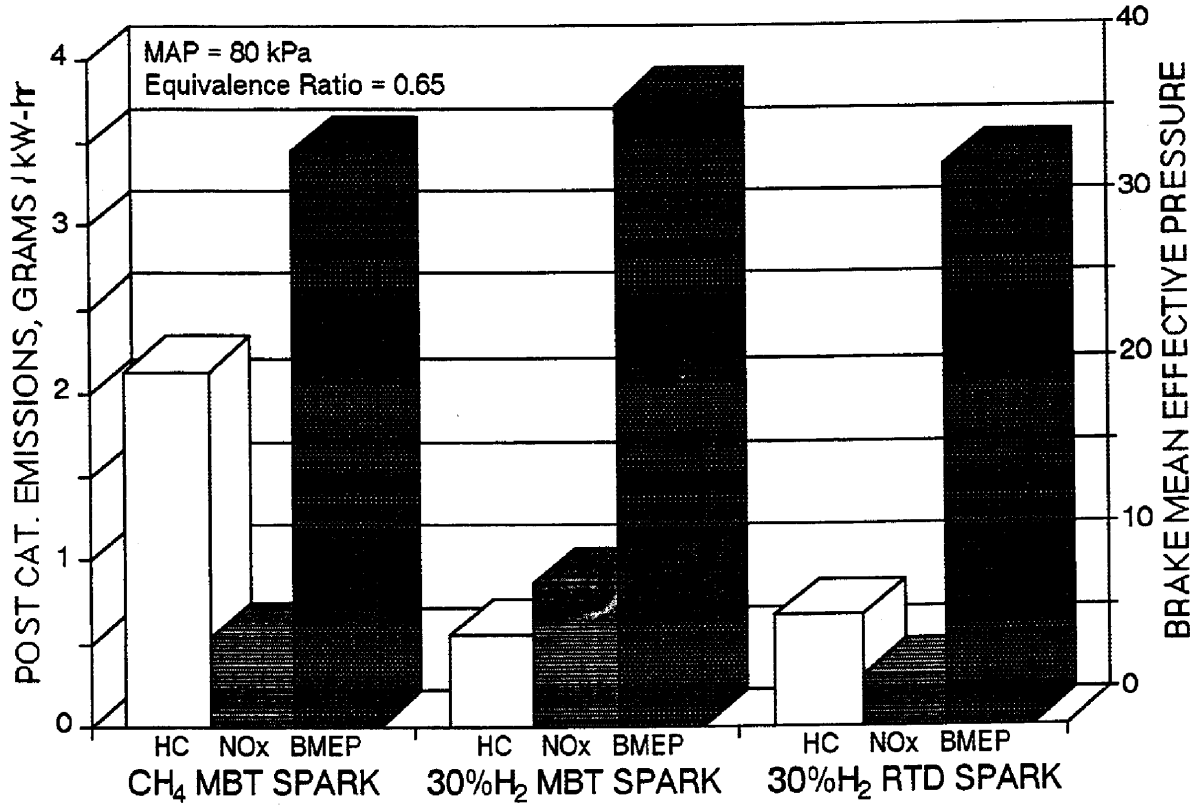

Figure 1-2. At comparable BMEP, NOx and HC are less with 30% H_2 than with pure CH_4.

NOx increase with hydrogen content pertains only to wide-open throttle operation at equivalence ratios approaching 1. All other test conditions show minor (±) variations of NOx with hydrogen content. The effect of equivalence ratio is much stronger than that of hydrogen content. Since hydrogen permits leaner operation than methane, any part load condition can be served by opening the throttle (higher MAP) and leaning the mixture to get equal BMEP with lower NOx.

1.2 Stoichiometric with Three-way Catalyst

With near stoichiometric air/fuel mixtures, pre-catalyst emissions show a downward trend in HC emissions with hydrogen content regardless of MAP. Surprisingly, the CO emissions are unaffected by hydrogen, within the limits of resolution of the tests. NOx increased steadily with hydrogen content at wide-open throttle, but not at part load conditions. Up to 15% hydrogen has a small, perhaps beneficial, effect on pre-catalyst NOx data under part load conditions.

Near stoichiometric post-catalyst emissions data are much more significant because pre-catalyst emissions are too high to meet modern emissions standards, regardless

of hydrogen effects. Equivalence ratio had, by far, the strongest effect on near stoichiometric post-catalyst emissions. Figure 1-3 shows how suddenly the emissions change near the optimum equivalence ratio, 1.005.

NOx heads rapidly toward zero on the approach to stoichiometric equivalence ratio from the lean side. Along the downward NOx trend, some of the CO measurements are slightly negative, challenging the limits of error of the instruments. Just past stoichiometric, as CO passes 1 g/kW-hr, NOx is too low to measure precisely. Slightly negative NOx readings are occasionally observed, due to zero drift of the instruments.

At the optimum equivalence ratio, post-catalyst NOx and CO emissions are so low that test-to-test scatter clouds the effects of hydrogen content, if any. Below $\phi = 1.005$, CO emissions data are sometimes negative, indicating instrument zero drift. The same is true of NOx emissions data above $\phi = 1.005$.

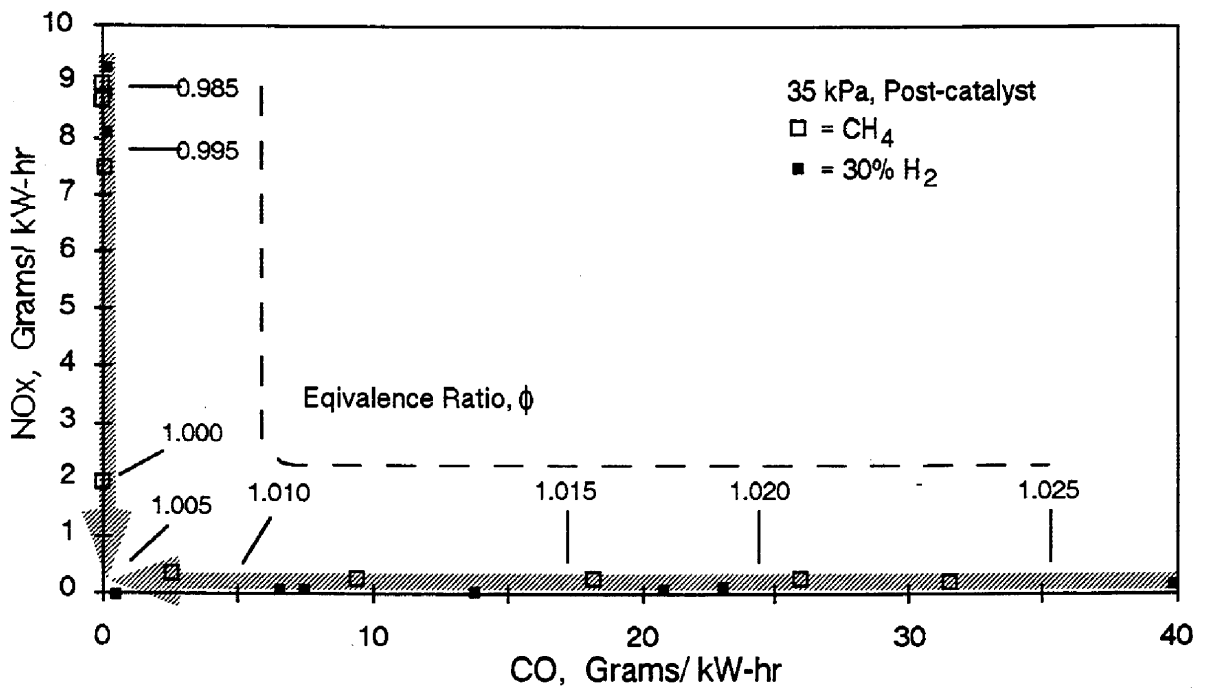

Figure 1-3. NOx vs. CO characteristic of the three-way catalyst. The dominant variable is equivalence ratio. Any difference between 0 and 30% hydrogen is within test-to-test scatter.

As equivalence ratio approaches the optimum 1.005 from either direction, differences between pure methane and 30% hydrogen on the order of 50% are well within the range of test-to-test scatter. Inclusion of data for 5 and 15% hydrogen would only confirm the scatter. The data in Figure 1-3 are for MAP = 35 kPa. Including data for wide-open throttle would not be conspicuous on this plot. Figure 1-3 is a catalyst characteristic that has little to do with engine operating parameters, other than ϕ, at any temperature well above "light-off".

The main conclusion to be drawn from Figure 1-3 is that very precise control of equivalence ratio can limit post catalyst emissions of CO and NOx to such low levels that measurement becomes difficult. Such precise control is possible in steady state operation with wide range oxygen sensors and electronic feedback control, precisely at $\phi = 1.005$. This is the automatic equivalent of the manual control applied in this project. Hybrid electric vehicles or stationary engines may be controlled in this way. Identification of hydrogen effects, if any, will require better instrumentation. Variations of ± 50% are within the scatter of the test equipment at such low emission levels.

It is apparent in Figure 1-3 that equivalence ratio variations are extremely important during transient operation of motor vehicles. Any tendency of a control system to slew to one side more rapidly than the to the other will have major influence on NOx and CO emissions.

Typical zirconia oxygen sensors cannot control methane or Hythane engines at the optimum equivalence ratio for a three-way catalyst. They can come close if the control system is adjusted near the saturation voltage of the sensor (ca. 800 mV). The zirconia-based wide range oxygen sensor used in the test work was also miscalibrated for methane or Hythane by about 1.5% at stoichiometric. This is a huge error that causes NOx to be an order of magnitude higher than it is at the optimum mixture.

Figure 1-4 shows the effects of ±1% errors from the optimum equivalence ratio, 1.005.

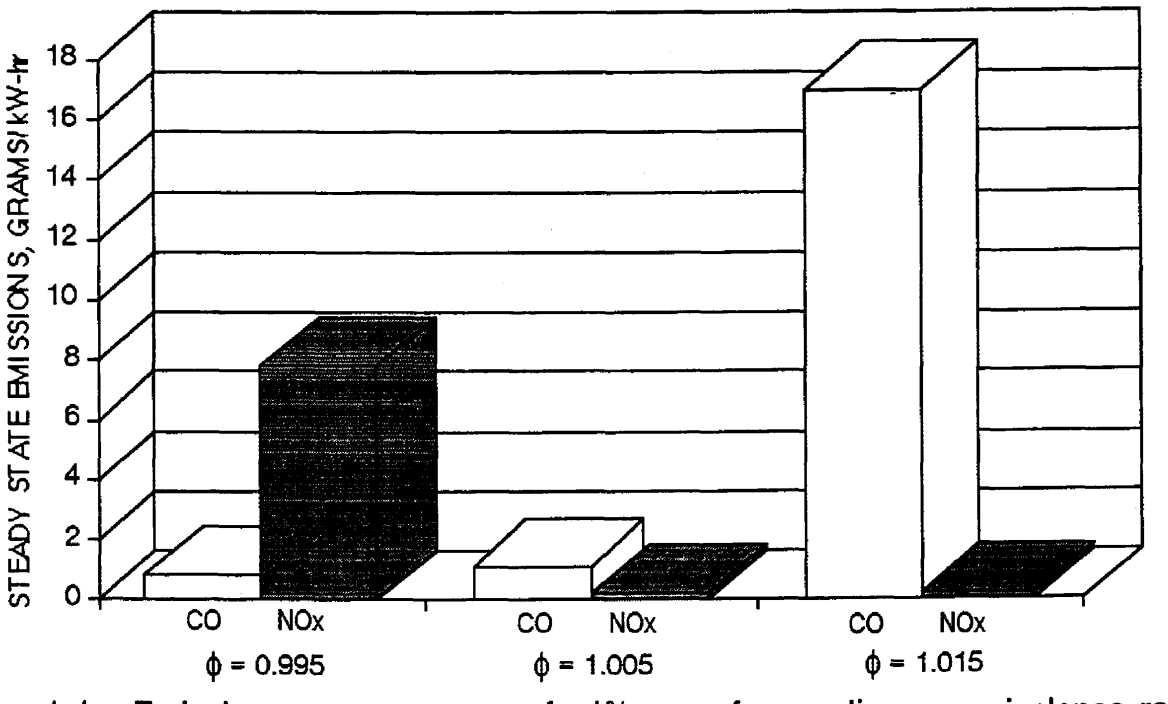

Figure 1-4. Emissions consequences of ±1% error from optimum equivalence ratio for three-way catalysis.

Appendix A on vehicle emissions tests should be read with this extreme sensitivity to control precision in mind. The results of this study support the hypothesis that the strong effects of hydrogen in light-duty vehicle Federal emissions tests[3] may be caused by the reaction of closed loop control systems, especially oxygen sensors, to the presence of hydrogen in the fuel and/or in the exhaust.

Worst case HC emissions at the optimum equivalence ratio, $\phi = 1.005$, observed at light loads, were around 2.3 grams/kW-hr. By simple methane dilution, NMHC emissions with natural gas will be an order of magnitude below this. Further reduction in NMHC results from increased catalyst efficiency on heavier hydrocarbons. The catalyst used in this study has repeatedly produced speciated NMHC emissions of 0.01 grams/mile in light duty vehicle Federal emissions tests on Hythane and natural gas. NMHC is therefore somewhat of a non-issue for stoichiometric natural gas vehicles with good three-way catalysts, regardless of hydrogen content.

1.3 Conclusions

The following detailed report, literature citations and Appendix A support the following conclusions about the effects of hydrogen on methane as a fuel for internal combustion engines operated with MBT spark timing;

- Hydrogen enables leaner operation. Between 15 and 30% H_2 extends the lean limit of CH_4 fuel by enough to realize strong emissions leverage.
- Hydrogen strongly decreases pre-catalyst HC and CO emissions in the lean range of operation.
- Post-catalyst CO emissions are extremely low, with or without hydrogen additions, throughout the lean range of operation.
- Post-catalyst HC emissions are reduced significantly by hydrogen near the lean limit.
- Lean burn NOx increases with hydrogen content at wide open throttle only.
- At light loads, small ± variations of NOx with increasing hydrogen content are observed.
- Hydrogen increases BMEP in the lean burn range.

[3] Four vehicles with three different catalyst formulations and three different engine types have been variously tested at California Air Resources Board, Colorado Department of Health, U.S. Environmental Protection Agency, Impco and National Center for Vehicle Emissions Control and Safety. All testing to date indicates strong hydrogen influence, as discussed in Appendix A.

- Increased BMEP can be sacrificed to get lower NOx than pure methane.
- Near stoichiometric pre-catalyst HC emissions decrease with hydrogen content but no improvement in post-catalyst HC emissions is apparent.
- The optimum equivalence ratio for emissions control with a three-way catalyst is $\phi = 1.005$, regardless of hydrogen content.
- Zirconia based oxygen sensors read 1.5% rich, relative to true stoichiometry, thereby causing lean operation and excessive NOx with methane or Hythane.
- $\pm 1\%$ deviation from optimum mixture ($\phi = 1.005$) causes order of magnitude increases in NOx ($\phi = 0.995$) or CO ($\phi = 1.015$).
- The latter observation may be responsible for the strong influence of hydrogen in transient emissions tests of natural gas vehicles.

2.0 Terminology

The terminology used to describe the test results is standard among automotive engineers. However, since those who are not specialists in engine testing may have an interest in the results, the following section is offered to clarify the terminology.

The abbreviations used for "hydrocarbon", "carbon monoxide", and "nitrogen oxides" are HC, CO and NOx respectively. All emissions data are expressed in "brake specific" (BS) units, i.e., grams per kilowatt-hour (g/kW-hr). For example, BSCO = 2 g/kW-hr means that the engine emits 2 grams of carbon monoxide for each kilowatt-hour of work dissipated into the "brake" or dynamometer. The only hydrocarbon in the fuel supplied to the engine was methane, CH_4. However, since CH_4 has a very low reactivity in ozone-producing reactions in the atmosphere, occasional reference will be made to non methane hydrocarbon emissions, NMHC.

Manifold air pressure (MAP) indicates the absolute air pressure in kPa. Most of the data were taken with MAP = 35 kPa. This indicates that the engine was throttled to a vacuum of about 20 inches of mercury or 5.1 pounds per square inch absolute. Additional data were taken at MAP = 80 kPa. This indicates wide-open-throttle operating conditions at the 1539 meter (5050 ft) altitude of Colorado State University, Fort Collins, Colorado.

The conversion of fuel energy into work output by the engine is characterized by "brake thermal efficiency" or BTE. BTE = 0.25 means that 25% of the lower heat value of the fuel was converted to work, available at the crankshaft of the engine. Engine performance is also characterized by "brake mean effective pressure", BMEP. BMEP is a fictious pressure that is presumed to act on the piston throughout the expansion stroke. It is proportional to engine torque but, unlike torque, it is independent of engine size. A 4-liter engine produces twice the torque of a 2-liter engine at the same BMEP.

A "stoichiometric" mixture has chemically correct proportions of fuel and air wherein complete combustion occurs with no excess oxygen. Stoichiometric combustion equations for hydrogen and methane in air are as follows;

$$2H_2 + O_2 + 3.77N_2 \rightarrow 2H_2O + 3.77N_2$$

$$CH_4 + 2O_2 + 7.54\ N_2 \rightarrow CO_2 + 2H_2O + 7.54\ N_2$$

where N_2 represents nitrogen plus other inert gases in air.

Equivalence ratio, ϕ, indicates the relative amounts of fuel and air. The definition of ϕ is; stoichiometric air/fuel ratio ÷ actual air/fuel ratio. For example, $\phi = 0.7$ means that the engine is burning lean with 70% of the fuel that could theoretically be burned by the air flowing into the engine. With $\phi = 1.03$, the engine is burning rich at 103% of the stoichiometric fuel flow.

The ϕ's indicated in the analysis were read directly from the AFRecorder. One of the significant conclusions of this work is that this zirconia-based air/fuel analyzer reads richer than actual stoichiometry by 1.5%. The less expensive zirconia exhaust gas oxygen sensors used in gasoline automobiles have also proven to read rich when operating on natural gas or Hythane[1]. This results in slightly lean closed loop engine control and inefficient conversion of NOx on three-way catalysts.

"Percent H_2" in the following discussion means "percent by volume", defined as the ratio of "standard"[2] volume of H_2 to the total "standard" volume of CH_4 plus H_2. This definition ignores any non-ideal consequences of mixing of the two gases or super compressibility effects. Figure 2-1 shows the relationship between hydrogen content by volume and by lower heat value.

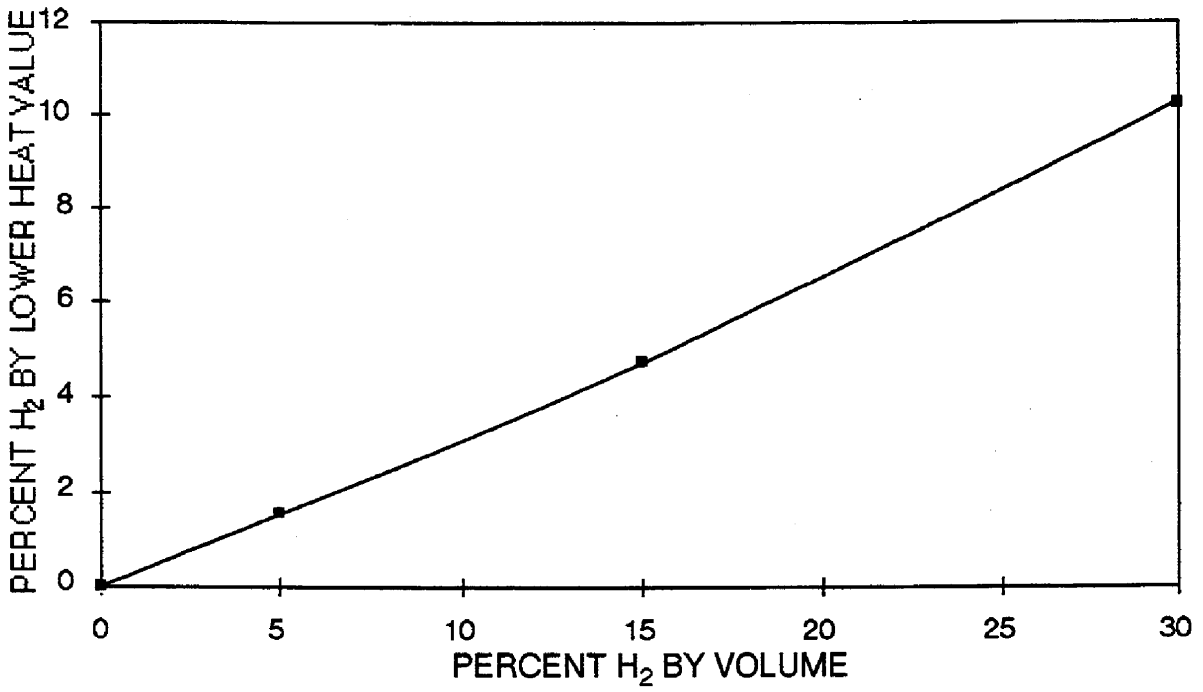

Figure 2-1. Hydrogen energy content vs. volume percent in methane.

[1] Hansel, J. et al. "Hythane: A Status Report", National Hydrogen Assn, 4th Annual Meeting, Washington, D.C. (1993)

[2] American Gas Association "standard" conditions are 60°F and 14.3 psia.

3.0 Experimental

3.1 Emissions Analysis

Hot exhaust samples were diluted with filtered room air to avoid water condensation and potential solution of emissions in condensate water. The dilution ratio was calculated from CO_2 in the raw exhaust and CO_2 in the diluted exhaust.

The exhaust emission analyzer bench consists of instruments for measuring emissions of carbon monoxide (CO), raw carbon dioxide (CO_2), dilute carbon dioxide, total hydrocarbons (THC), and oxides of nitrogen (NO-NO_X). Table 3-I lists the instruments in the analyzer bench.

Table 3-I. Emission Analysers

Gas	Model	Type
CO	Horiba AIA-21-AS, 500 mm, Version 3	Infrared
CO_2	Horiba AIA-21, 200 mm Version 1	Infrared
THC	Horiba FIA-21	Flame Ionization
NOx	Thermo Electron 44	Chemiluminescent

An eleven point curve was fit to each analyzer range to make accurate voltage to parts per million (ppm) conversions with the data acquisition system. Each curve point was found by supplying the analyzer with a known mixture of span gas and zero gas. These mixtures were created with a gas divider which was capable of diluting the span gas from 0% to 100% by 10% steps. The voltage output from the analyzer at each point was entered into a software package which generated a polynomial curve fit to the data. These curve fits were then used by the data acquisition program to interpret the analyzer output.

Emissions analysis requires a regular recalibration process to reduce errors caused by drift. The original procedure was to check zero and span at each data point, however this became quite time consuming. Further observation showed that recalibrating once per hour was often enough that the analyzers stayed within acceptable limits.

To calibrate the instruments, a set of procedures for zeroing and spanning with the computer software was followed, checking for 1% of full scale tolerances. First, all instruments were zeroed in all ranges and then the instruments were spanned in all ranges. Following span adjustments, the zero's were rechecked to verify that span adjustments did not move the original zero position.

The calibration gases used are traceable to NIST Class S weights and/or NIST Gas Mixture Standard Reference Materials (SRM's) - Reference SGD Field Directive Book I Part A-3.

The flame ionization detector (FID) fuel for the hydrocarbon analyzer was hydrogen in nitrogen. Methane, instead of the normal propane, was used as the calibration gas for the hydrocarbon analyzer to ensure accuracy with the measurements of methane hydrocarbon emissions. The ozone required for the NO-NOx instrument's operation is produced using oxygen instead of dry air which is normal. This was done to achieve a larger linear range; 10,000 ppm NO-NOx on the high end with oxygen compared to 2000 ppm using air. The calibration zero gases used were zero grade nitrogen for the CO and CO_2 analyzers and zero grade air for the HC and NO-NOx analyzers.

3.2 Dynamometer

The engine was placed on a SuperFlow waterbrake test stand, model SF-1. The absorber on the SF-1 has the following specifications:

- Torque: 1000 ft-lb maximum
- Speed: 10,000 RPM, brief 12,000 RPM is possible
- Power: 1000 horsepower maximum

The SF-1 test stand uses the SF-730 as the electronic base for dynamometer control and data acquisition. The SF-730 uses a Motorola MC6809 micro-processor for its controller. The SF-1809 is the controller for the stepper motor / servo valve on the water outlet of the absorber unit. The SF-1809 is connected to the SF-730 and controls engine speed or torque depending on which mode is selected in the SF-730.

3.3 Air Fuel Ratio Meter

The ECM (Engine Control and Monitoring) Air Fuel Ratio Meter (AFRecorder 2400A) provided the means for measuring equivalence ratio, spark timing, engine speed and manifold absolute pressure (MAP). The specifications and limits are listed in Table 3-II below.

Table 3-II. Air Fuel Ratio Meter Specifications

Data	Units	Range
A/F Ratio	AFR	10.0 - 30.0*
	PHI	0.50 -1.45
	LAMBDA	0.70 - 2.0
Spark Timing	Degrees	60 BTDC-30 ATDC
Speed	RPM	100 - 9999
MAP	kPa	0 - 172

* Ranges given for gasoline.

The sensor for measuring the air to fuel ratio is a zirconia-based NTK oxygen sensor. Spark Timing is sensed through an inductive pick-up placed on a spark plug wire. Engine Speed and position is measured by amagnetic pick-up, located on the crank dampener. Manifold absolute pressure was sensed by a vacuum port on the GM throttle body housing.

3.4 Data Acquisition

Data acquisition was done using a DOS personal computer with a data acquisition card. A custom software package was written to monitor all testing parameters and display them in real time on the PC screen. This software has the ability to control all necessary functions of the analyzer bench through mouse commands. The data acquisition system consists of the following;

- 486-DX Personal Computer
- 200 Mb hard drive
- 8 Mb RAM
- SVGA Monitor
- 2 National Instruments Lab-PC cards
- 8 multiplexed analog inputs (12 bit successive-approximation)
- 24 lines of TTL-compatible digital I/O
- 6ea. 16-bit counter/timer channels

The software included;

- National Instruments LabWindows development system
- Graphical User Interface, Control panels, Display panels
- Data Acquisition Card subroutines for setup and I/O
- Compiler for subsets of QuickBASIC and C languages

The data acquisition software allowed the user to monitor recorded data and adjust the emissions analyzers. A screen displays groups of data in a clearly organized format. This data included:

- engine: speed, torque, power, manifold absolute pressure, timing
- ambient: air temperature, air pressure, relative humidity
- fuel: hydrogen to carbon ratio
- equivalence ratio: measured, calculated
- background, raw, dilute: CO, CO_2, HC, NO_x ppm

All of the above data were displayed in real time. The screen update rate was limited to about once per second. The slow step in the update was an algorithm for communicating serially with the Air Fuel Ratio Meter.

The data acquisition program was also required to change analyzer settings. To operate the analyzers accurately, they must be monitored and adjusted often. To speed this process, the acquisition program user has the ability to change the analyzer source from background to exhaust or switch any of the analyzer ranges from the software display screen. This design allowed a single user to control all necessary functions of the analyzers with a mouse while test data is concurrently visible in the same display screen.

The exhaust analyzers need periodic span and zero checks. The software program contained a calibration interface which would allow the user to route zero or span gas through the analyzers and automatically check for out of range instruments.

3.5 Preparation of Standard Hydrogen/Methane Mixtures

Known methane/hydrogen gas mixtures were required to calibrate the thermal conductivity comparator used for real-time indication of the Hythane blend fed to the engine. The "recipe" for these span gas mixtures requires only simple pressure measurements and a constant temperature environment. Generating the recipe itself required the following:

1) a lightweight high pressure vessel for which the internal volume is known as a function of pressure

2) thermophysical data tables for hydrogen

3) the standard density for methane (CGA uses 14.7 psia, 70°F = 0.0416 lbs/scf)

4) a precise scale

5) a precise absolute pressure gauge

6) a constant temperature laboratory.

The method is as follows:

1) weigh the evacuated vessel with all fittings required to couple it to high pressure gas sources and gauges (empty mass)

2) charge the vessel with a measured pressure of H_2 and wait for thermal equilibrium, repeat if necessary to achieve desired initial H_2 pressure

3) determine the volume of the vessel from the equilibrium pressure, and determine the mass of H_2 from the volume, pressure, temperature, and NIST hydrogen tables

4) weigh the vessel to roughly confirm the NIST mass determination

5) determine the volume of hydrogen at standard conditions from NIST tables (scf H_2)

6) add methane, wait for thermal equilibrium, and record pressure

7) weigh the vessel (total mass)

8) calculate the mass of methane added:

$$CH_4 \text{ mass} = \text{total mass} - \text{empty mass} - H_2 \text{ mass}$$

9) calculate the standard volume of methane in vessel from mass and density (scf CH_4)

10) calculate volume% hydrogen in mixture:

$$\text{volume\% } H_2 = [\text{scf } H_2 \div (\text{scf } CH_4 + \text{scf } H_2)] \times 100$$

11) calculate energy% hydrogen in mixture:

$$\text{energy\% } H_2 = \{268.9 \text{ Btu/scf} \times \text{scf } H_2 \div [(895.2 \text{ Btu/scf} \times \text{scf } CH_4) + (268.9 \text{ Btu/scf} \times \text{scf } H_2)]\} \times 100$$

The entire procedure was repeated for each data point to prevent any one error from affecting several measurements. The experiments were begun with an initial H_2 pressure of 400 psia. The range of gases observed at reasonable mixture pressures was 12 to 60 volume% H_2 as shown in Figure 3-1. Lower hydrogen content span gases were desired, so a set of experiments was also run at an initial H_2 pressure of 200 psia. This data covers a range of 7 to 16 volume% H_2 (Figure 3-2). The corresponding plots of energy% H_2 are also shown in Figures 3-3 and 3-4.

Six span gases in the range from from 6.4 to 50 volume% H_2 were used to calibrate the thermal conductivity comparator. The calibration curve is shown in Figure 3-5.

With the thermal conductivity comparator attached to the blending unit shown in Figure3-6, it was possible to blend and control the Hythane mixture supplied to the engine at any ratio from 0 to 50% H_2 in CH_4.

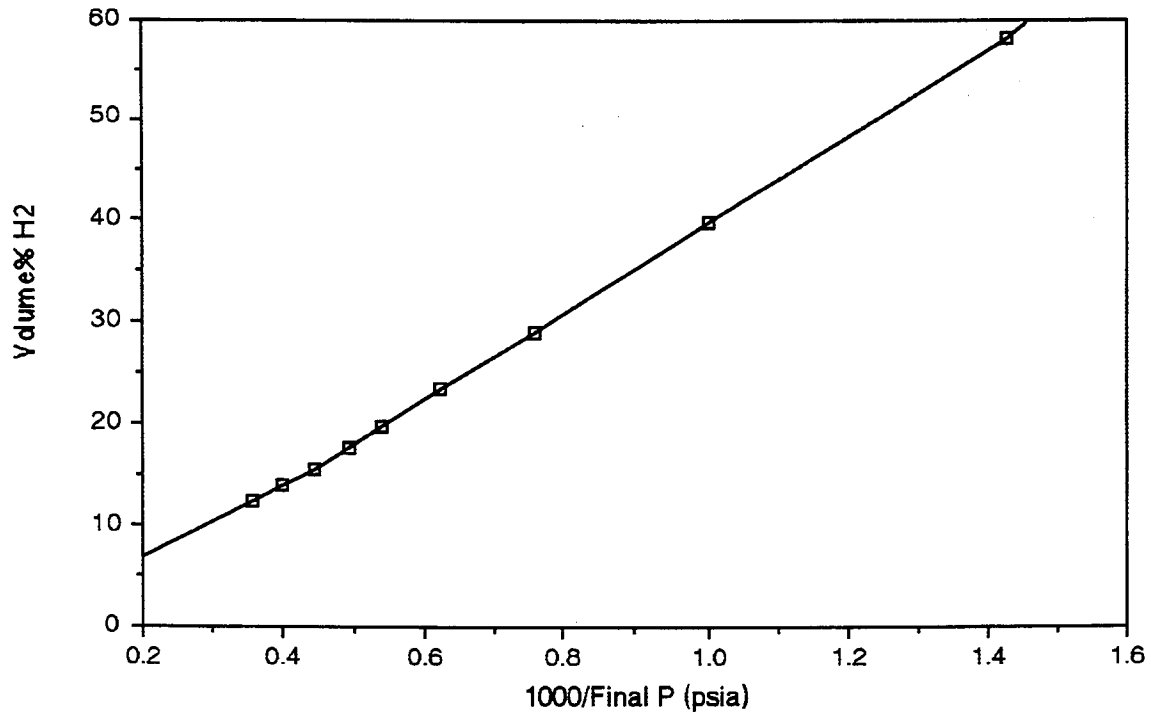

Figure 3-1. Volume% H_2 vs. inverse mixture absolute pressure for 400 psia H_2 initial pressure experiments.

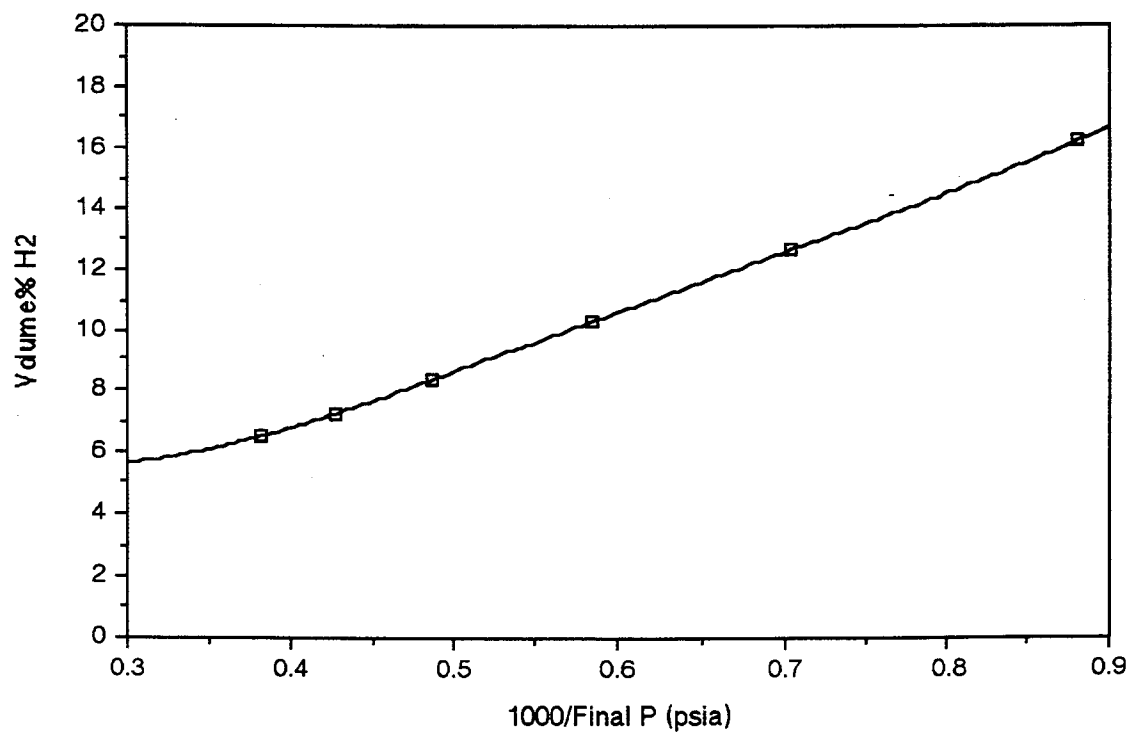

Figure 3-2. Volume% H_2 vs. inverse mixture absolute pressure for 200 psia H_2 initial pressure experiments.

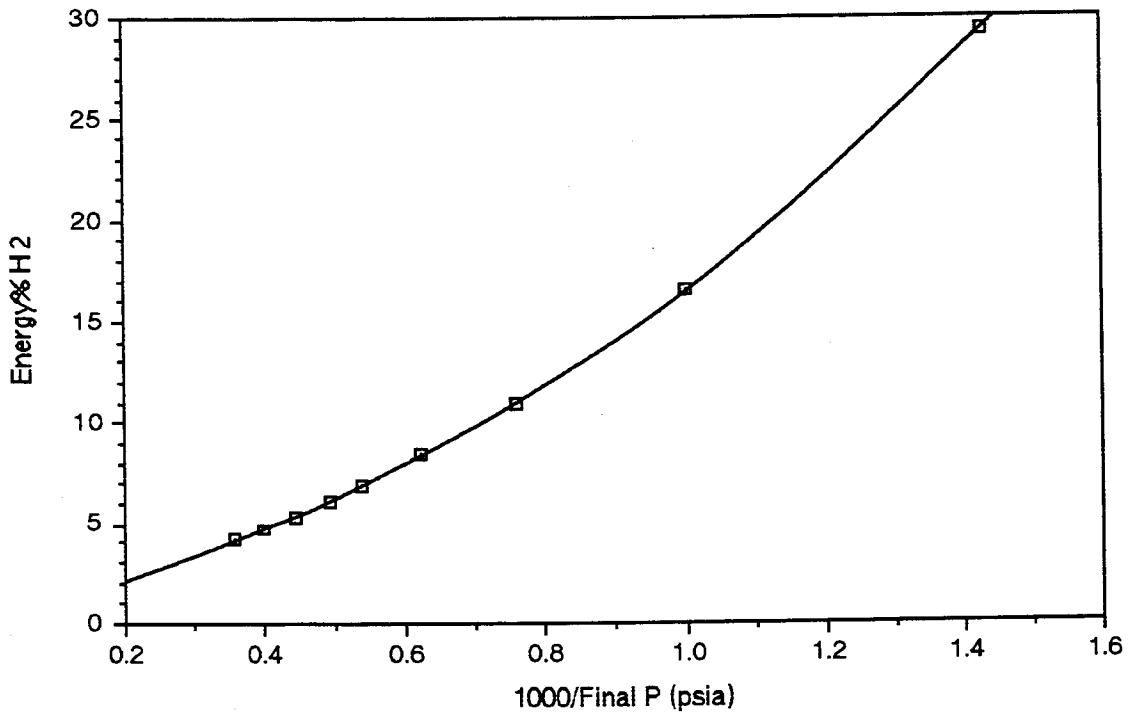

Figure 3-3. Energy% H_2 vs. inverse mixture absolute pressure for 400 psia H_2 initial pressure experiments.

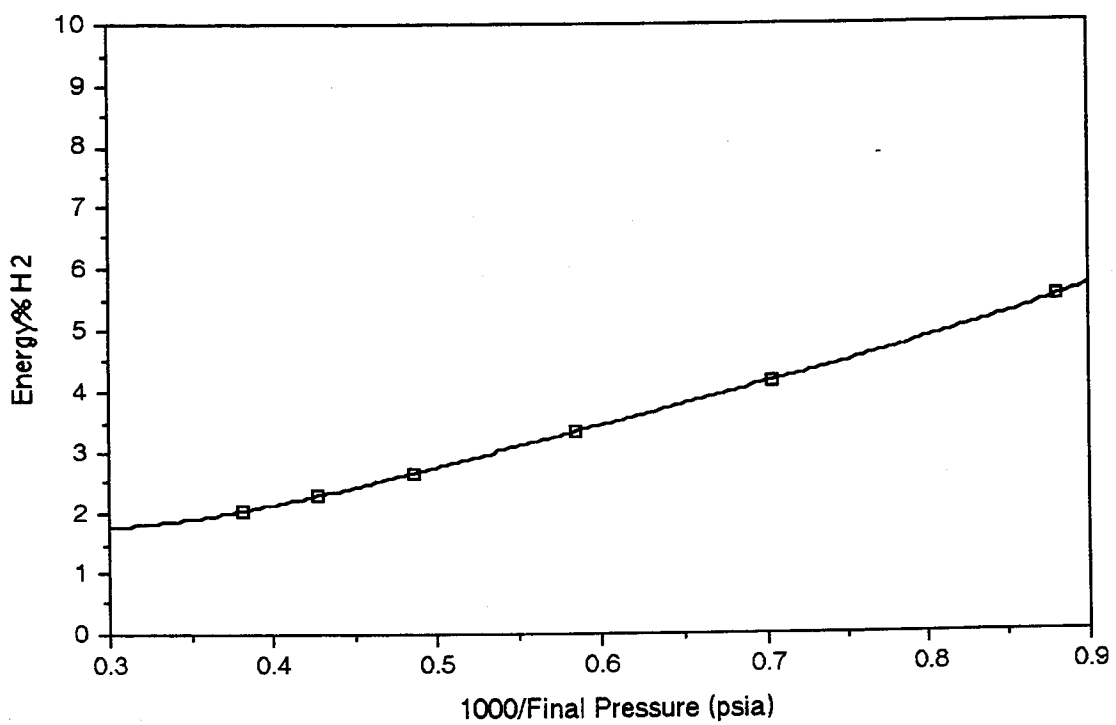

Figure 3-4. Energy% H_2 vs. inverse mixture absolute pressure for 200 psia H_2 initial pressure experiments.

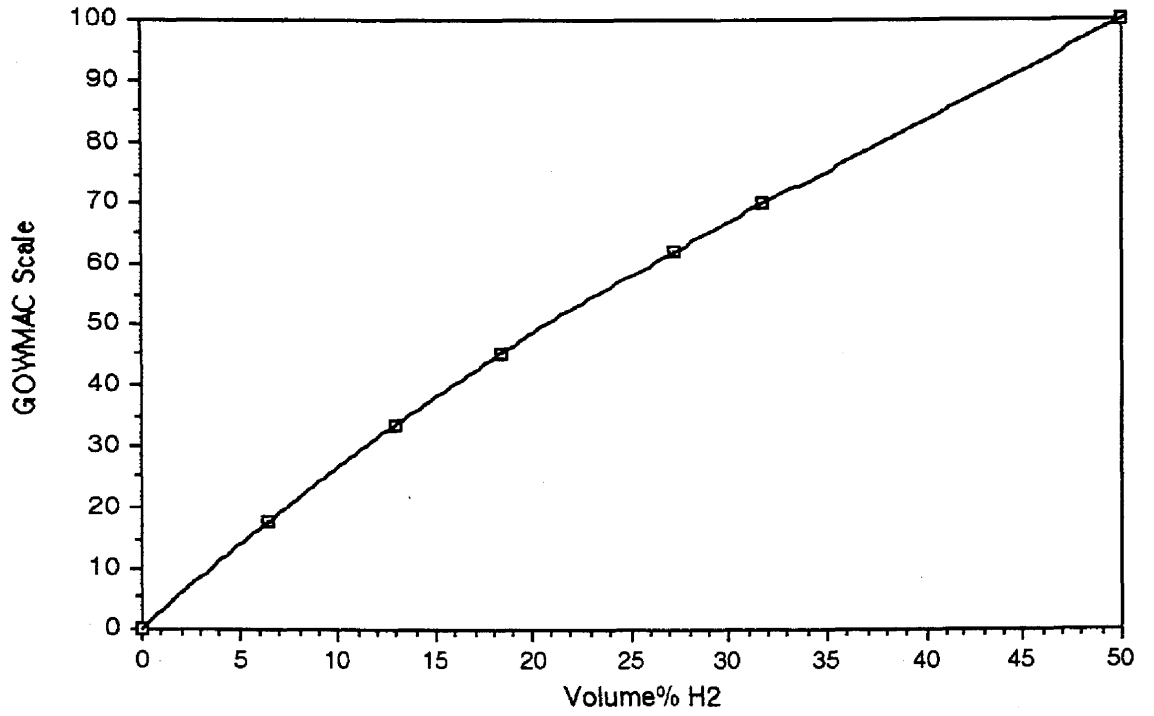

Figure 3-5. Gow-Mac thermal conductivity comparator response vs. volume% H_2 for six prepared span gases.

3.6 Hythane Span Gas Error Analysis

The accumulation of errors in the determination of hydrogen percentages by the above method is derived below. NIST densities are regarded as absolutely accurate with a precision of ± the least significant digit published. Calculations are regarded as absolutely precise. These two assumptions make volume fraction, weight fraction and energy fraction of equal certainty because, to convert from one to the other, only calculations and published densities are required. The uncertainty in weight fraction hydrogen is calculated as follows:

$$\text{let } R = \text{weight fraction } H_2 = \frac{W_{H2}}{W_{H2} + W_{CH4}}$$

$$\frac{\partial R}{\partial W_{H2}} = \frac{W_{CH4}}{(W_{H2} + W_{CH4})^2} \quad , \quad \frac{\partial R}{\partial W_{CH4}} = \frac{W_{H2}}{(W_{H2} + W_{CH4})^2}$$

$$\Delta R = \left| \frac{\partial R}{\partial W_{H2}} \right| \Delta W_{H2} + \left| \frac{\partial R}{\partial W_{CH4}} \right| \Delta W_{CH4}$$

$$= \left[\frac{W_{CH4}}{(W_{H2} + W_{CH4})^2} \Delta W_{H2} + \frac{W_{H2}}{(W_{H2} + W_{CH4})^2} \Delta W_{CH4} \right] \quad (I)$$

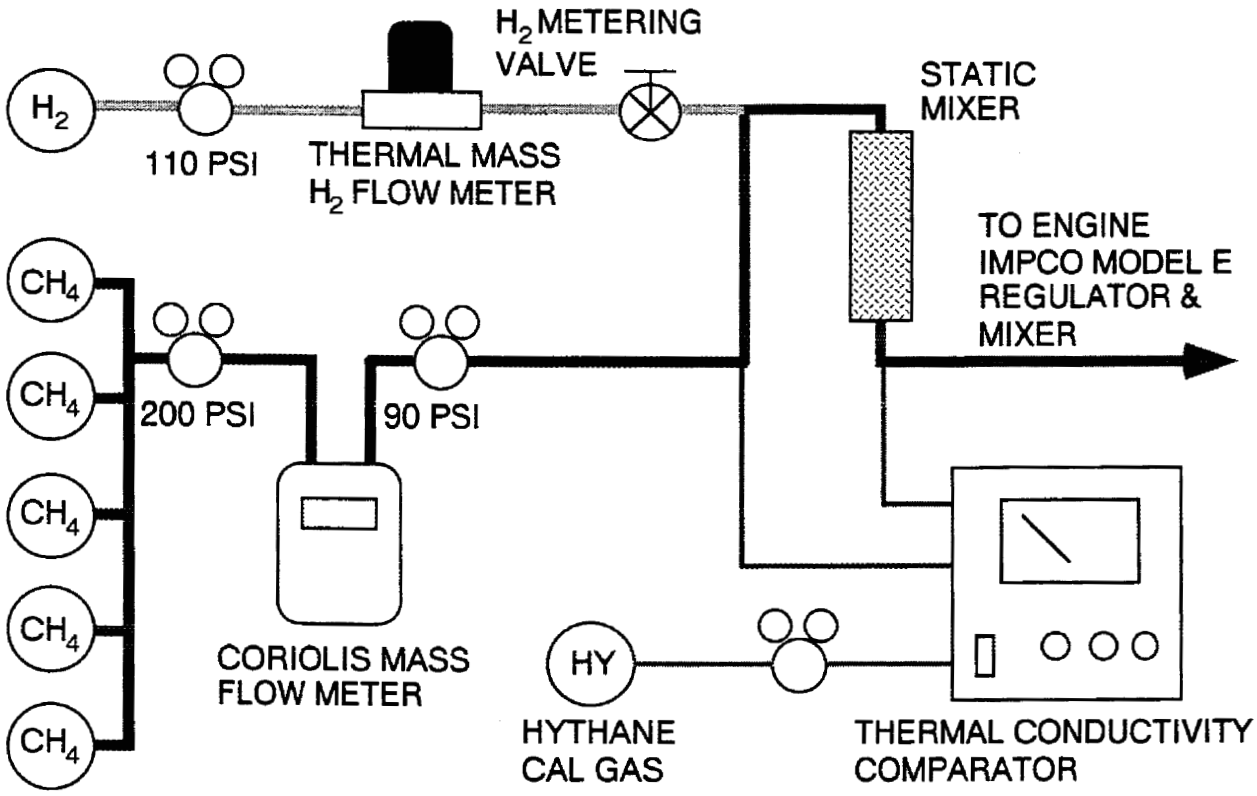

Figure 3-6. Diagram of methane/hydrogen fuel blending equipment using the Gow-Mac Model 20-260 thermal conductivity comparator.

The uncertainty in H_2 weight is linearly related to the uncertainties in pressure vessel volume, absolute pressure gauge reading and absolute temperature reading.

$$\Delta W_{H2} = W_{H2}\left[\frac{\Delta V}{V}+\frac{\Delta P}{P}+\frac{\Delta T}{T}\right]$$

The uncertainty in pressure vessel volume, V, results from scale uncertainty during weighings empty and filled with water at various pressures. Water pressure was measured with a 5000 psia transducer whose uncertainty is ±0.1% of full scale or ±5 psi (34 kPa). Water pressure uncertainty is a second order effect not included in this error analysis. An Ohaus triple-beam balance was calibrated with standard weights prepared via Metler electronic balance weighings. The volume of the pressure vessel was found to increase linearly with pressure due to strain according to;

$$V \text{ in cc} = (767.2282 + 0.00058 \times \text{ kPa gauge}) \pm 0.2.$$

where the ± 0.2 cc error results from two 0.1 gram uncertainties in tank weight.

For example, at 500 psig (3448 kPag);

$$V \text{ in cc} = [767.2282 + (0.00058 \times 3348 \text{ kPag})]$$

$$V \text{ in cc} = 769.2 \pm 0.2$$

$$\frac{\Delta V}{V} = 0.0003$$

Hydrogen pressure was measured with an 800 psig Weksler bourdon tube gauge whose uncertainty is ± 0.25% of full scale. A median hydrogen pressure of 300 psig carries an uncertainty of ± 2 psig;

$$\frac{\Delta P}{P} = 0.007$$

HCI's temperature controlled Sieverts laboratory is monitored to ± 0.1°C on certified mercury thermometers. At a laboratory temperature of 23.0°C or 296.15 K;

$$\frac{\Delta T}{T} = 0.0003$$

The uncertainty in hydrogen weight in the cylinder at 300 psig is therefore;

$$\Delta W_{H2} = 2.18\ (0.0003 + 0.007 + 0.0003) = \pm 0.013 \text{ grams.}$$

The uncertainty in methane weight results from two ± 0.1 gram weighings, before and after adding methane. Therefore,

$$\Delta W_{CH4} = 0.2 \text{ grams}$$

A typical weight difference between the two readings is about 100 grams in the pressure range of interest (up to 10 weight% hydrogen in 3000 psi methane) so, the methane weight uncertainty ranges around ±0.2%.

The accumulation of errors for the set of 6 span gases varies somewhat, depending on the particular values of pressure and weight. Applying equation I above within the range of the 6 span gases showed;

$$\Delta R/R = 1\text{-}2\%.$$

This does not mean an uncertainty of 1-2% hydrogen. It means 1-2% of the stated concentration, e.g., 10.00%±0.15% by weight, volume, energy, etc.

3.7 Test Engine Setup

The test engine setup was built around a General Motors Goodwrench long block, part number 10147954. This is a stock assembly for 1991 GMC 3/4 ton Sierra Pick-up Trucks. The long block has the following specifications:

- displacement: 350 cubic inch
- bore: 4.00 inch
- stroke: 3.48 inch
- compression ratio: 9.1:1
- crank: stock
- camshaft: stock
    - intake lobe lift: 0.2565 inches
    - exhaust lobe lift: 0.2690 inches
    - cylinder heads: stock
    - intake valves: 1.94 inches
    - exhaust valves: 1.50 inches

The intake manifold used is for a 1991 GMC 3/4 ton Sierra Pick-up Truck, throttle body injected, part number 14102183. A throttle body housing was also used, part number 17112516.

The gaseous fuel control system consisted of the following items;

- 2 Meco Type PID Primary Pressure Regulators with Engine Coolant Heated Meco Envirocaps (1 for H_2, 1 for CH_4).

- Fuel Blending/Composition Control System (Figure 3-6)

- Impco Model PEV Final Pressure Regulator

- Impco Model 200D Gas Mixer ("carburetor")

- Kenics Model 001-04962 Static Gas Mixer

- General Motors Throttle Body (sans exhaust recycle, idle speed controller and gasoline injector).

As illustrated in Figure 3-7, air and fuel come together in the Impco 200D gas mixer, analogous to a gasoline carburetor. The 200D is equipped with an air-bleed idle mixture control screw and a power valve that restricts the fuel inlet tube. Additional control of air/fuel ratio was applied by varying spring tension and dome air pressure in the Impco PEV final pressure regulator (not shown).

The Kenics static mixer contains two vanes in series, each of which divide the flow in half and swirl it in opposite directions. The purpose of the static mixer is to minimize cylinder-to-cylinder variations in air/fuel ratio. The effectiveness of the static mixer has been verified in previous work with pure hydrogen and during this work by placing two identical NTK sensors before and after the Y that joins the two exhaust headers of the V-8 engine. No difference in equivalence ratio was observed.

A standard GM throttle body was used to control manifold air pressure (MAP) via the Super Flow control lever. The exhaust gas recycle and idle air controls were disabled

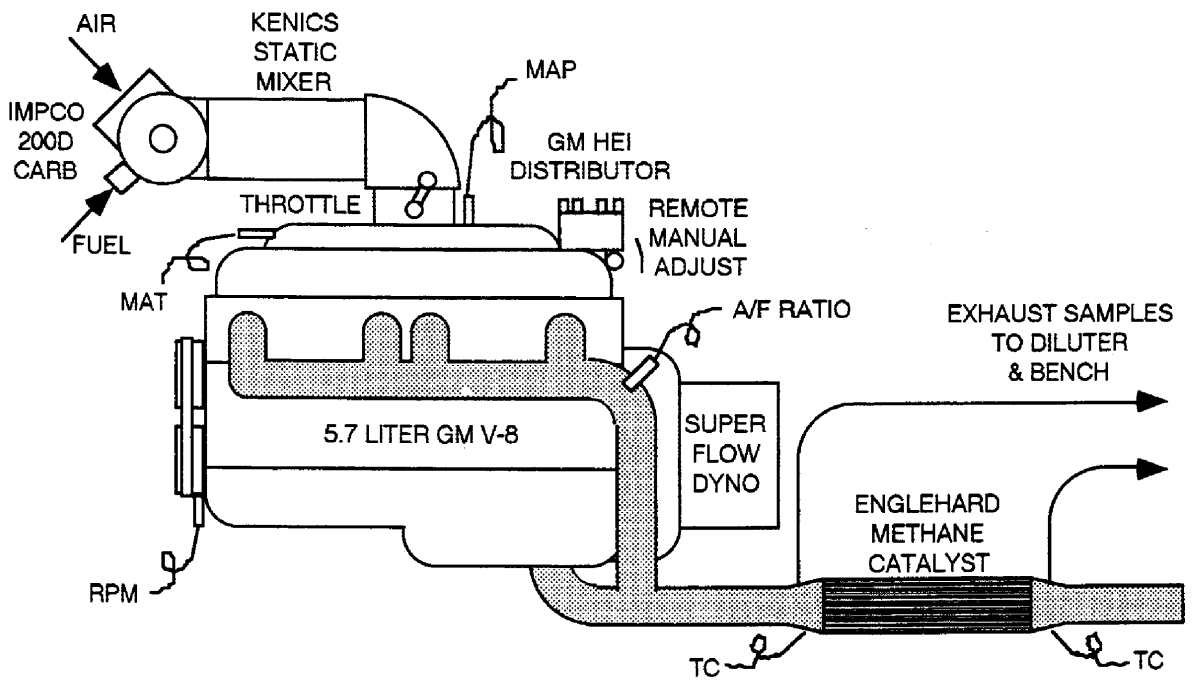

Figure 3-7. Test setup.

in the test engine. The gasoline injectors were removed. Manifold air temperature (MAT) was monitored with a LM335 temperature sensor integrated circuit epoxied into a metal tube.

A General Motors High Energy Ignition (HEI) distributor and coil was equipped with a manual adjustment screw, linkage and cable that allowed the test operator to rotate the distributor while monitoring the spark timing on the AFRecorder, outside the test cell.

The NTK wide range oxygen sensor, supplied with the AFRecorder, was located in the standard location in the exhaust manifold on the 1,3,5,7-side of the engine. In this location the sensor is unable to indicate any side-to-side air/fuel ratio variations in the V-8 engine. However, as discussed above in this section, the combined mixing effects of the Impco "carburetor" and the Kenics static mixer rendered such variations insignificant.

The exhaust from the two sides of the engine are joined in a Y-pipe and fed into an Englehard monolithic catalyst. The catalyst has a Pd-Rh formulation designed to have a methane "light-off"[1] temperature of about 400°C. The catalyst was removed from an HCI test vehicle that had accumulated 18,000 miles of combined use on gasoline, natural gas and Hythane. The catalyst, at the 7000 mile point, produced ULEV emissions levels on Hythane and natural gas at the California Air Resources Board Laboratory in El Monte, CA.

[1] "Light-off" temperature for a catalyst is the temperature where its efficiency of conversion for a particular species, methane in this case, reaches 50%. This information was supplied by John Mooney of Englehard.

The inlet and outlet of the catalyst are fitted with thermocouples and emissions sample tubes that communicate with the analyzer Bench via the dilution controller.

3.8 Engine Test Procedure

For all testing, an engine operating speed of 2500 rpm was held constant by the dynamometer controls. This speed is near the torque peak but is not an unusually high operating speed. The ignition timing was set by generating a torque vs. timing curve and finding the minimum advance at which 1% of the peak torque is lost. In this way, a real-world operating condition was maintained. These timing curves are shown in Figures 3-8 thru 3-14. The test matrix included equivalence ratios from 0.6 to 1.1 for four different fuel compositions (0, 5, 15, and 30% H_2) at two different manifold absolute pressures (MAP's of 35 and 80 kPa).

The initial test procedure was decided upon in order to take data as quickly as possible. Changes in fuel delivery for different equivalence ratios could be made very quickly with the carburetor adjustments; however, different fuel hydrogen concentration adjustments were relatively slow due to the response time and precision of the thermal conductivity instrument. Therefore, the procedure for our first sets of data at 35 kPa MAP held a constant fuel composition and varied the equivalence ratio. Although this was the quickest possible technique, the number of different equivalence ratios and the response delay of the sampling system when switching between pre- and post- catalyst exhaust made any given curve require almost a day of testing.

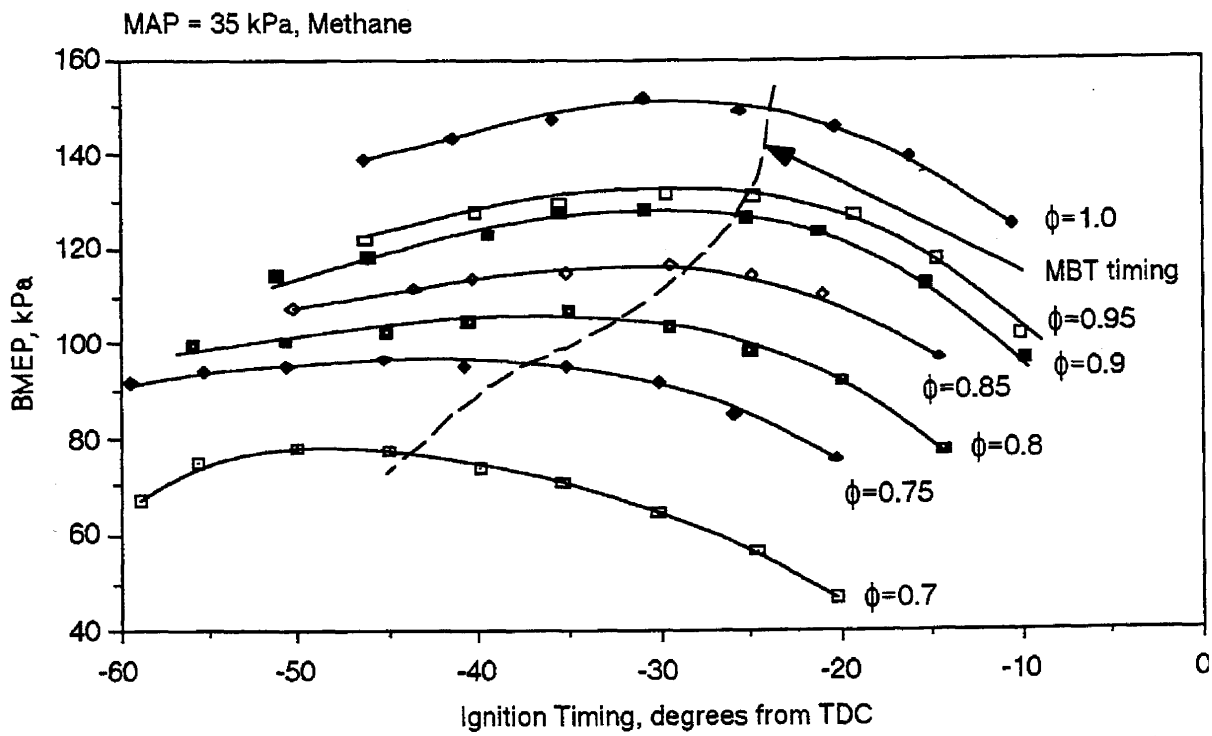

Figure 3-8. BMEP vs. ignition timing for various equivalence ratios with engine conditions of 2500 rpm, 35 kPa MAP, and pure methane fuel.

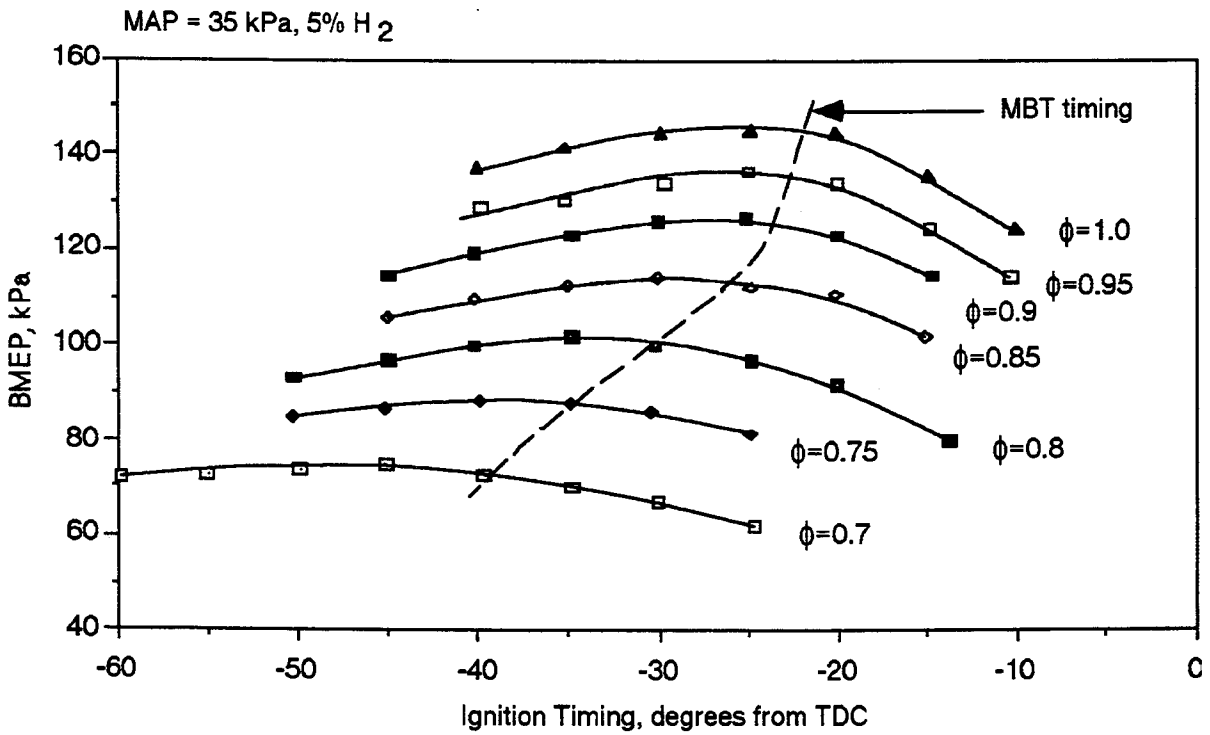

Figure 3-9. BMEP vs. ignition timing for various equivalence ratios with engine conditions of 2500 rpm, 35 kPa MAP, and 5% hydrogen in methane fuel.

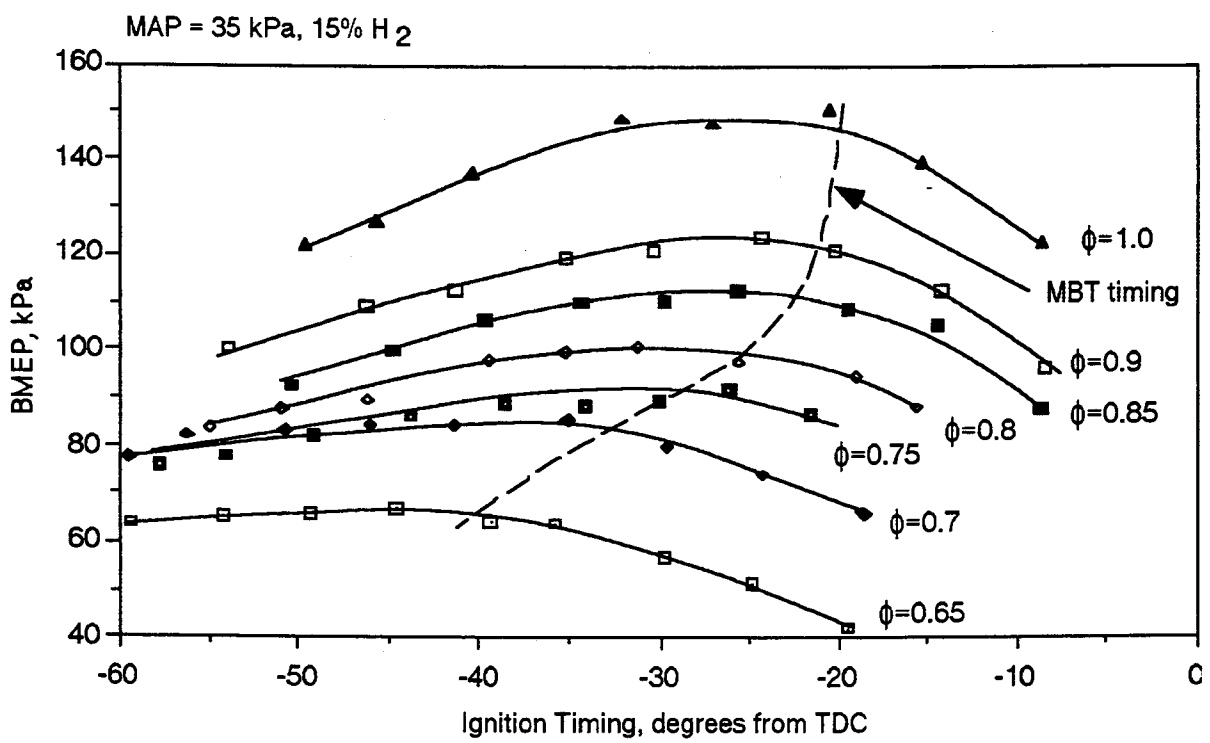

Figure 3-10. BMEP vs. ignition timing for various equivalence ratios with engine conditions of 2500 rpm, 35 kPa MAP, and 15% hydrogen in methane fuel.

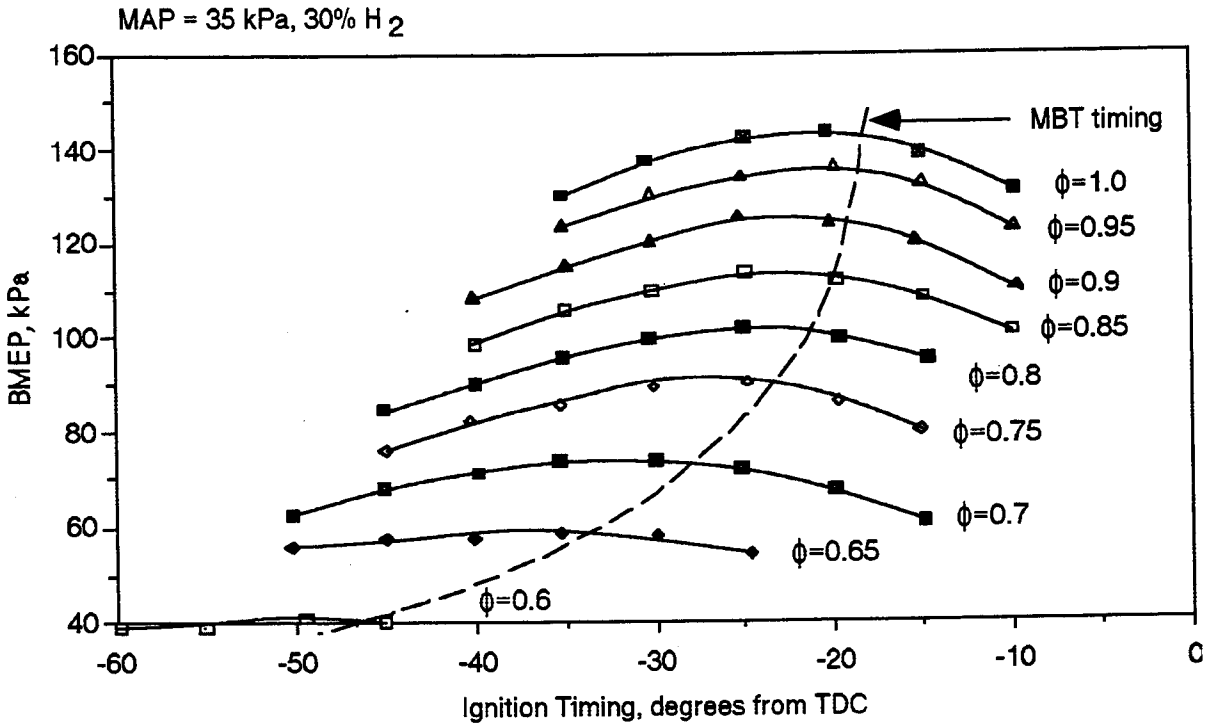

Figure 3-11. BMEP vs. ignition timing for various equivalence ratios with engine conditions of 2500 rpm, 35 kPa MAP, and 30% hydrogen in methane fuel.

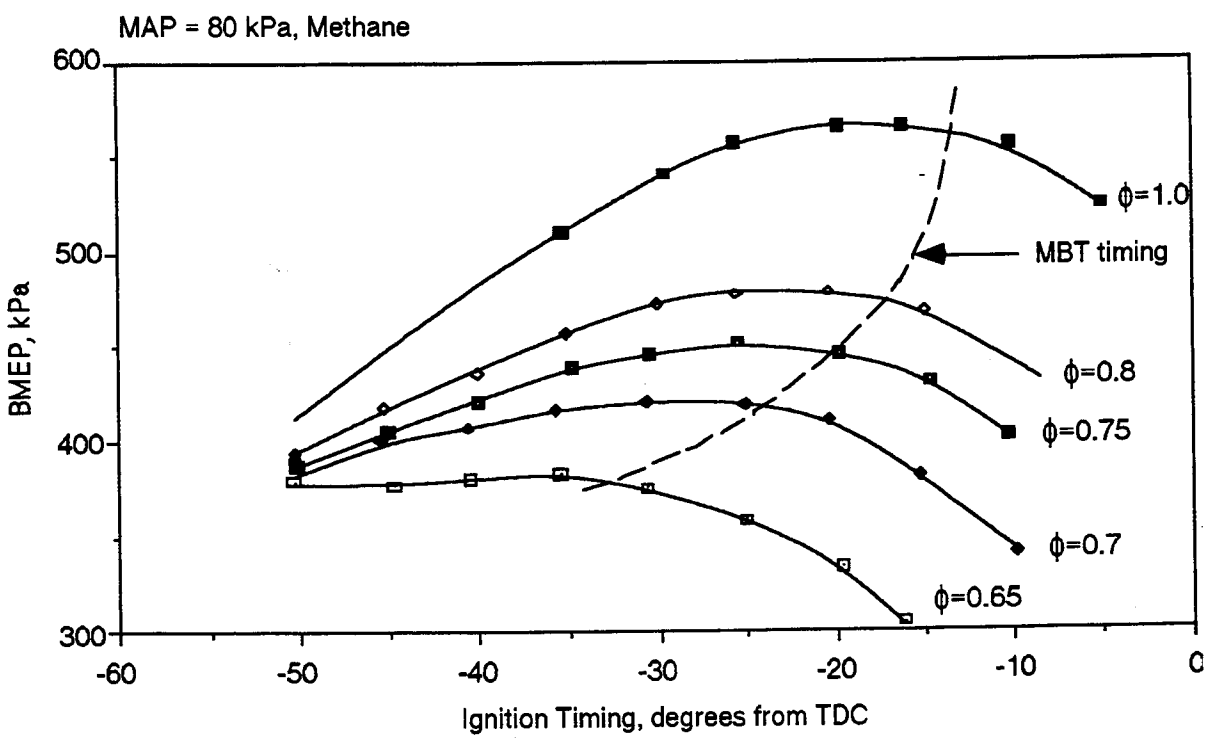

Figure 3-12. BMEP vs. ignition timing for various equivalence ratios with engine conditions of 2500 rpm, 80 kPa MAP, and pure methane fuel.

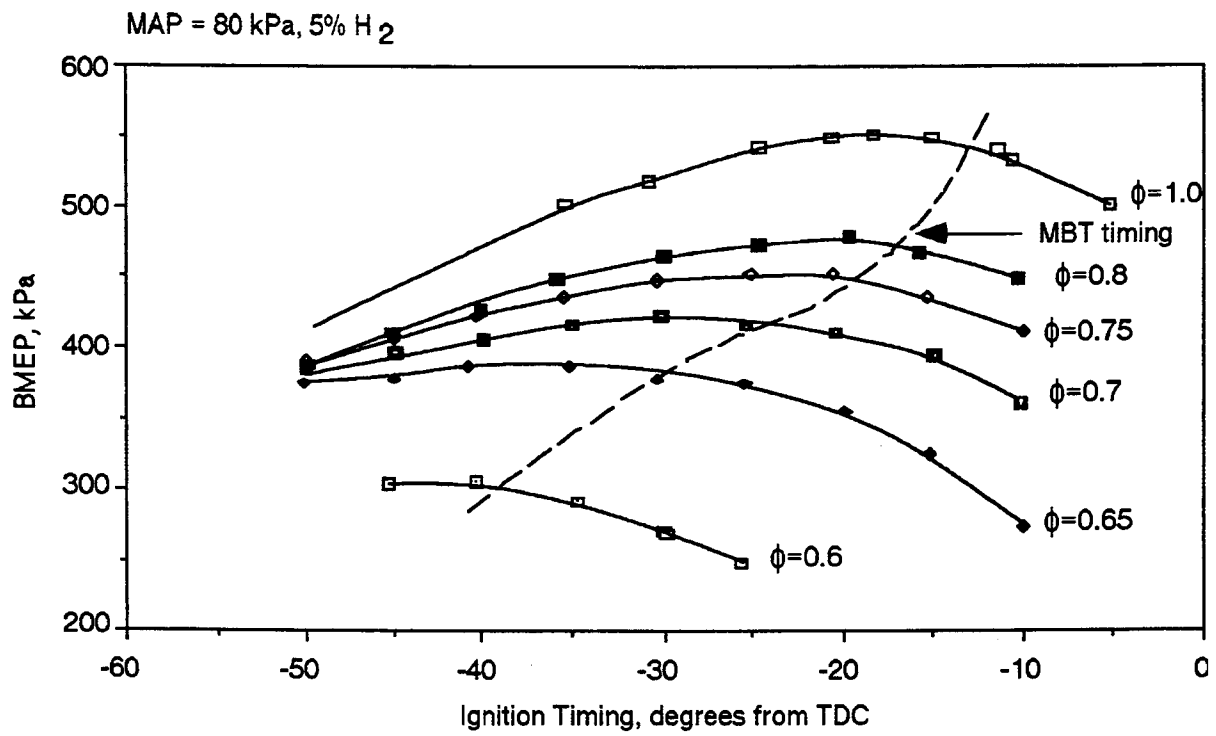

Figure 3-13. BMEP vs. ignition timing for various equivalence ratios with engine conditions of 2500 rpm, 80 kPa MAP, and 5% hydrogen in methane fuel.

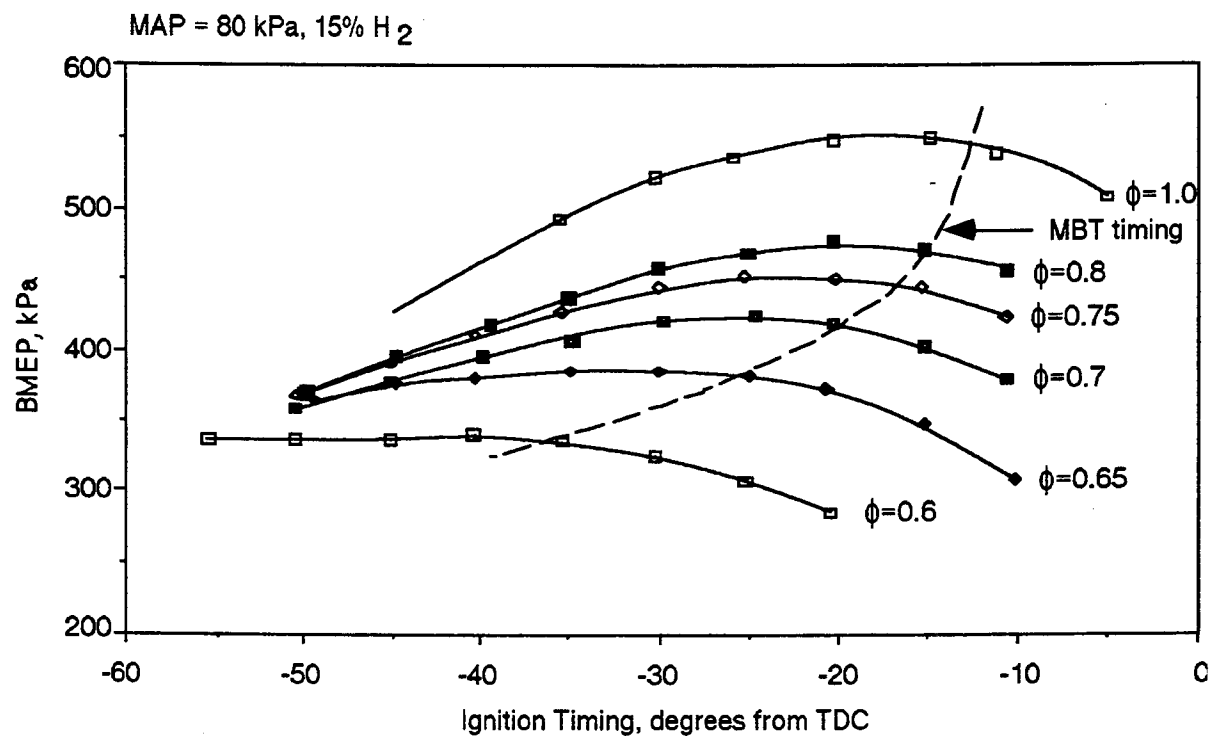

Figure 3-14. BMEP vs. ignition timing for various equivalence ratios with engine conditions of 2500 rpm, 80 kPa MAP, and 15% hydrogen in methane fuel.

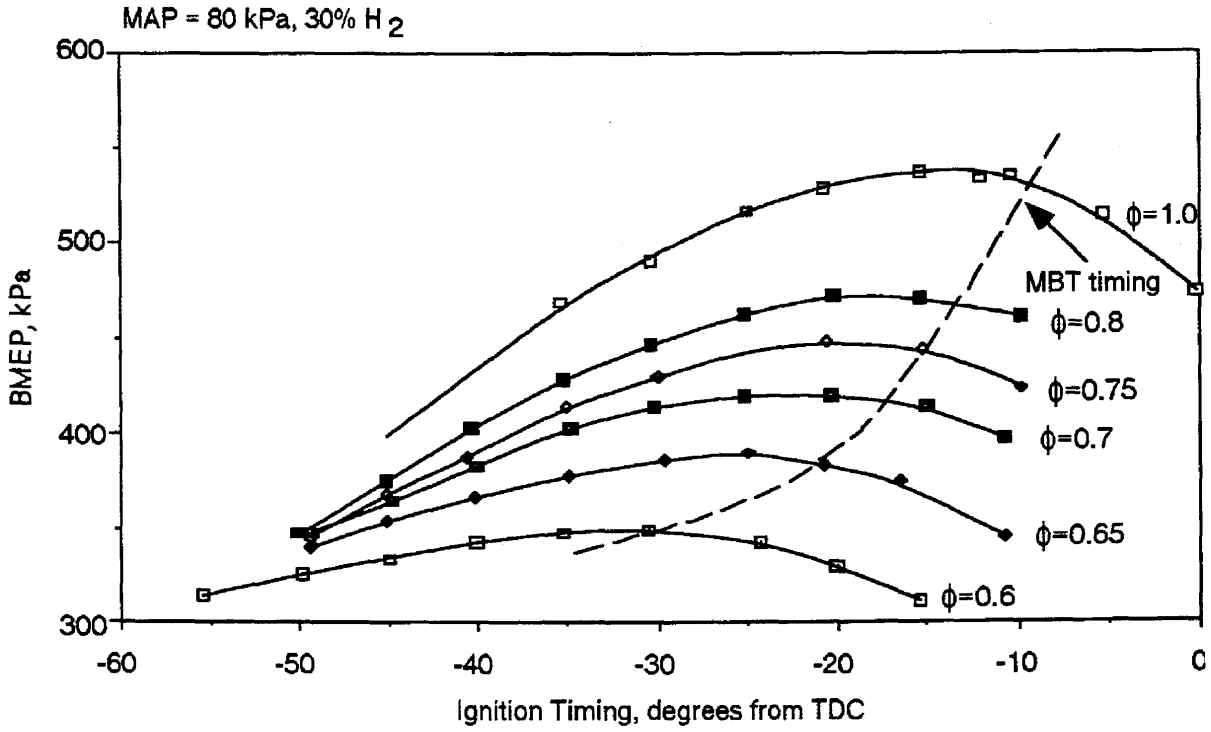

Figure 3-15. BMEP vs. ignition timing for various equivalence ratios with engine conditions of 2500 rpm, 80 kPa MAP, and 30% hydrogen in methane fuel.

Upon analysis of this data, day-to-day variations in air intake temperature and humidity made major effects on NOx data. Therefore, we modified the test procedure to try to minimize the effects of ambient variations on the data. Equivalence ratio was thereafter held constant, and the fuel compostion varied within a set of data. This new procedure involved taking data on pure methane, then adding hydrogen in the 5, 15, and 30% compositions while maintaining a constant equivalence ratio, then repeating those compositions back down to pure methane. When the data going up to 30%H_2 matched the data coming back down to pure methane, it was assumed that any change in ambient conditions wsas too small to affect the emissions data. Although this was not the fastest way to take data, the results represent only the effect of hydrogen addition on the engine--not ambient variables.

Before any set of data was taken, the emission instruments were zeroed and spanned with reference gases, and the thermal conductivity analyzer was calibrated with pure methane, 50%H2, and an intermediate mixture to verify the calibration curve. At least every week, the dynamometer was calibrated with a torque arm and known weights. Engine speed was held constant by the dynamometer and verified by the AFRecorder. The ignition timing was changed by a cable mechanism attached to the distrubutor, measured by the AFRecorder, and verified occasionally with an automotive timing light.

4.0 Emissions Test Results

The discussion of test results will be divided into two major subsections--lean burn and near stoichiometric--because they represent two distinct approaches to emissions control. On the lean side, NOx emissions are reduced by burning at relatively low peak temperatures. The useful range of lean-burn equivalence ratios is bounded on the lean side by erratic combustion near the lean limit where HC begins to rise beyond acceptable levels. An oxidation catalyst extends the usable leanburn range, but high HC emissions and poor thermal efficiency still put bounds on the lean burn range.

The alternative to lean-burn is to burn richer, more powerful mixtures and rely on an advanced emissions control system to meet emissions standards. Near the chemically correct equivalence ratio for complete combustion with no excess oxygen, i.e., "stoichiometric", emissions are simultaneously reduced by three-way (HC, CO, NOx) catalysis.

A second reason for separating lean burn and near stoichiometric results is that the range of equivalence ratios of interest for lean burn is much wider than that for three-way catalysis. The discussion of lean burn involves equivalence ratios from the NOx peak, near $\phi = 0.9$, to the lean limit, about $\phi = 0.7$ with pure methane and lower with Hythane. The focus for three-way catalysis is from stoichiometric, $\phi = 1$, to a few percent rich. In graphics that show the whole range of equivalence ratios, it is difficult to see the interesting effects observed in post catalyst emissions over small ranges of equivalence ratio near stoichiometric.

Within each major subsection, the results are broken down into "Pre-catalyst" and "Post-catalyst" emissions. The Englehard catalyst is designed to work with near stoichiometric mixtures as a three-way catalyst, but it is also effective as an oxidation catalyst in the lean range. In some cases, pre- and post-catalyst emissions cannot be shown clearly on the same scale, i.e., variations in post-catalyst emissions are too small to see clearly on a pre-catalyst scale.

4.1 Methodology

Early tests showed significant scatter. The scatter was traced to a number of problems discussed in Section 2.8, including changes in ambient temperature and humidity. To get accurate information despite such scatter required an unusual approach to data acquisition and analysis. The method adopted consists of taking data sets over short periods of time at constant equivalence ratio, scanning up and down in hydrogen content (i.e., 0%, 5%, 15% and 30%, 30%, 15%, 5% and 0% by volume). During these short periods of time the uncontrolled laboratory environment changed very little. The effects of changes that did occur are mitigated by averaging data from the up and down H_2 scan[1] to isolate the effect of the H_2 from indeterminate errors.

[1] This approach was borrowed from Ron Ragazzi of the Colorado Department of Health who uses similar methods in to confirm repeatability of trends in Federal urban driving cycle tests.

In this way, emissions trends versus H_2 content were established over short periods of time with relatively small indeterminant and ambient induced errors.

4.2 Lean Burn BSHC Emissions

4.2.1 Pre-catalyst BSHC Emissions

The lines in Figure 4-1 are sets of data taken at 35 kPa MAP and constant equivalence with variable H_2 content (i.e., 0%, 5%, 15% and 30%, 30%, 15%, 5% and 0% by volume). Each set of data was collected over a period of about 30 minutes to minimize ambient variations. With 0% or 5% hydrogen, the engine was not stable enough to obtain data with ϕ below 0.7. There is a clear downward trend in CH_4 emissions with increasing H_2 content. However, even with 15% and 30% hydrogen content, high pre-catalyst hydrocarbon emissions signal the approach of the lean limit of combustion below $\phi = 0.65$ under these light load conditions.

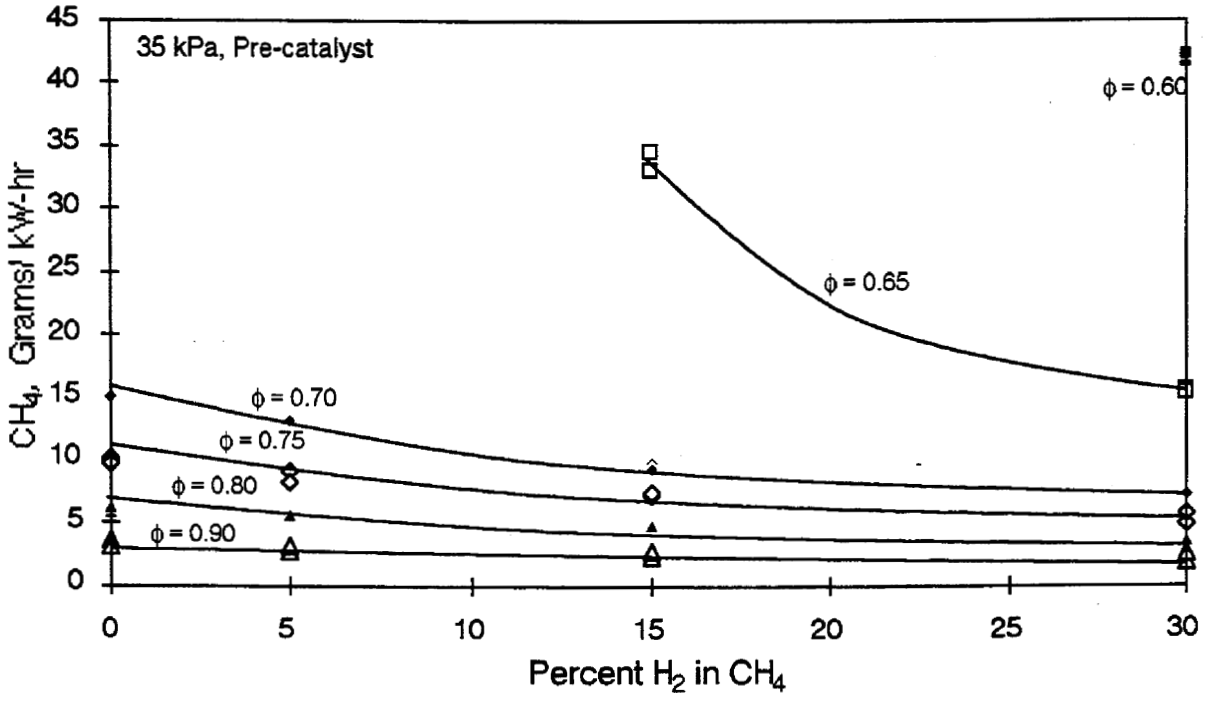

Figure 4-1. Variation of pre-catalyst CH_4 emissions in the lean range vs. H_2 % and ϕ at 35 kPa of MAP.

Figure 4-2 shows the pre-catalyst CH_4 emissions at wide open throttle with 80 kPa of MAP. The CH_4 emissions are generally lower at higher manifold pressures. The same downward trend vs. H_2 content is observed at wide open throttle. It is noteworthy that the percent reduction in CH_4 emissions is significantly greater than the percent increase in hydrogen energy content. At 30 volume percent H_2, about 10% of the fuel energy is coming from H_2. At ϕ =0.7 the unburned CH_4 emissions are cut to less than half of the emissions observed with pure CH_4. A 50% reduction with 10% H_2 energy shows a "leverage" factor of 5 relative to burning 100% hydrogen with zero CH_4

emissions. Similar leverage is expected with non methane hydrocarbons (NMHC) in natural gas.

For purposes of NOx control, $\phi < 0.7$ is a particularly useful range of operation. It is noteworthy that most of the improvement in CH_4 emissions at $\phi = 0.7$ was obtained with just 15 volume % H_2 or 5% by energy content. A 35% reduction in BSHC with 5% H_2 energy gives a leverage factor of 7.

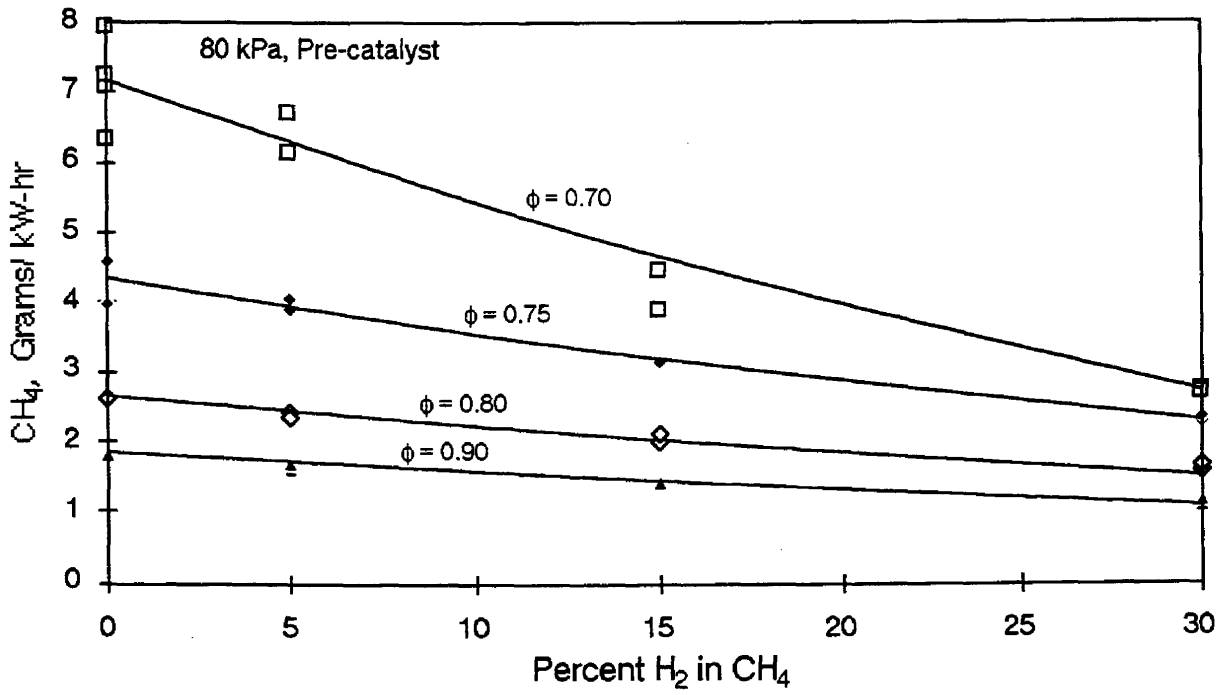

Figure 4-2. Variation of pre-catalyst CH_4 emissions in the lean range vs. H_2% and ϕ at 80 kPa of MAP.

4.2.2 Post-catalyst BSHC Emissions

The catalyst used in the tests has demonstrated a high efficiency for oxidizing non methane hydrocarbons (NMHC) in speciated vehicle emissions tests. As a stoichiometric, three-way catalyst in transient vehicle tests, total hydrocarbon emissions are typically 50 times greater than non methane hydrocarbons when the test vehicle burns natural gas or Hythane. Since the fuel burned in the following tests is composed of hydrogen and pure methane, NMHC emissions are thought to be truly negligible.

Figure 4-3 shows that the unburned CH_4 observed in Figure 4-1 has been reduced by roughly an order of magnitude by the catalyst for $\phi > 0.7$. At the lower exhaust temperatures corresponding to 35 kPa and $\phi = 0.65$ or less, the conversion efficiency falls off rapidly. Comparing Figures 4-1 and 4-3 indicates a conversion efficiency below 40% at $\phi = 0.65$ and about 12% at ϕ=0.6. Although NMHC conversion efficiency should be considerably higher, it appears that light loads are best met with $\phi > 0.7$.

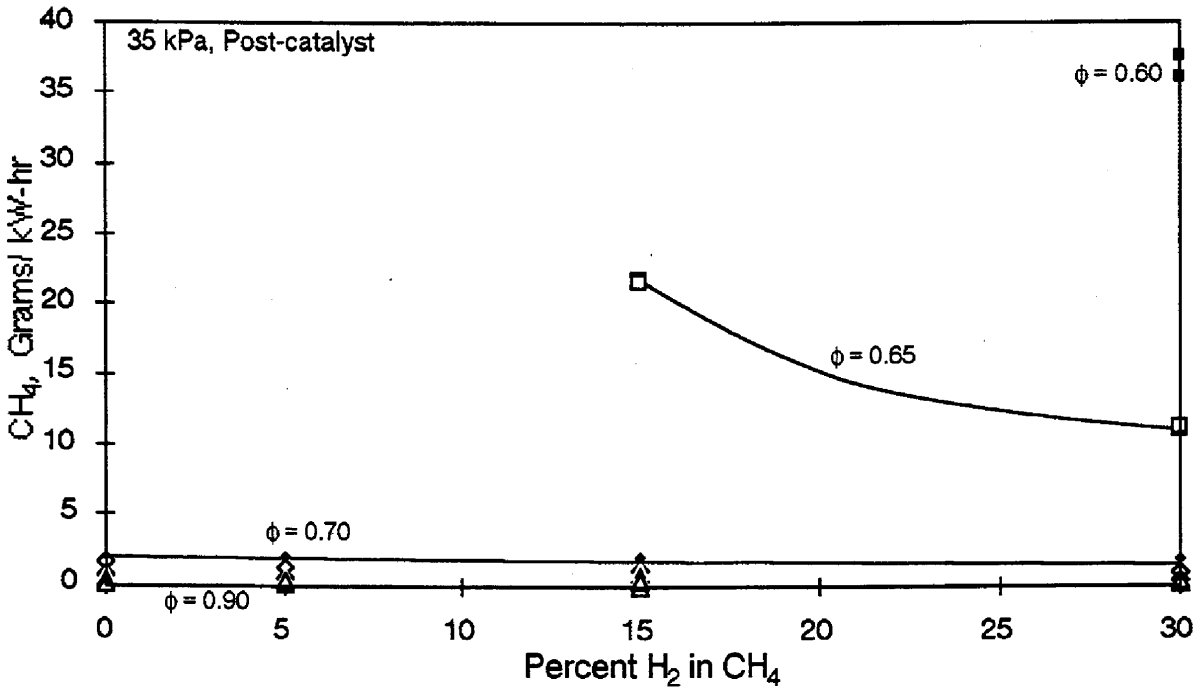

Figure 4-3. Variation of post-catalyst CH_4 emissions in the lean range vs. H_2% and ϕ at 35 kPa of MAP.

Figure 4-4 shows that unburned CH_4 remains low at $\phi > 0.65$ for all H_2 concentrations at wide-open throttle. Adding hydrogen up to about 15% by volume at $\phi = 0.65$ reduces post catalyst BSHC by about 40%. Recalling that 15% by volume is about 5% by energy content, the leverage factor is $40 \div 5 = 8$.

With $\phi = 0.6$, CH_4 emissions begin to rise rapidly. The data scatter is attributed to combustion instability at this ultralean equivalence ratio. However, NMHC with ordinary natural gas will be considerably lower, partly by simple methane dilution and partly because catalyst efficiency is higher on NMHC. The engine ran well at $\phi = 0.6$ with 15 or 30 volume % hydrogen (high BTE) so this ultralean operating regime, enabled by H_2, may be accessible for NOx control despite the high CH_4 emissions.

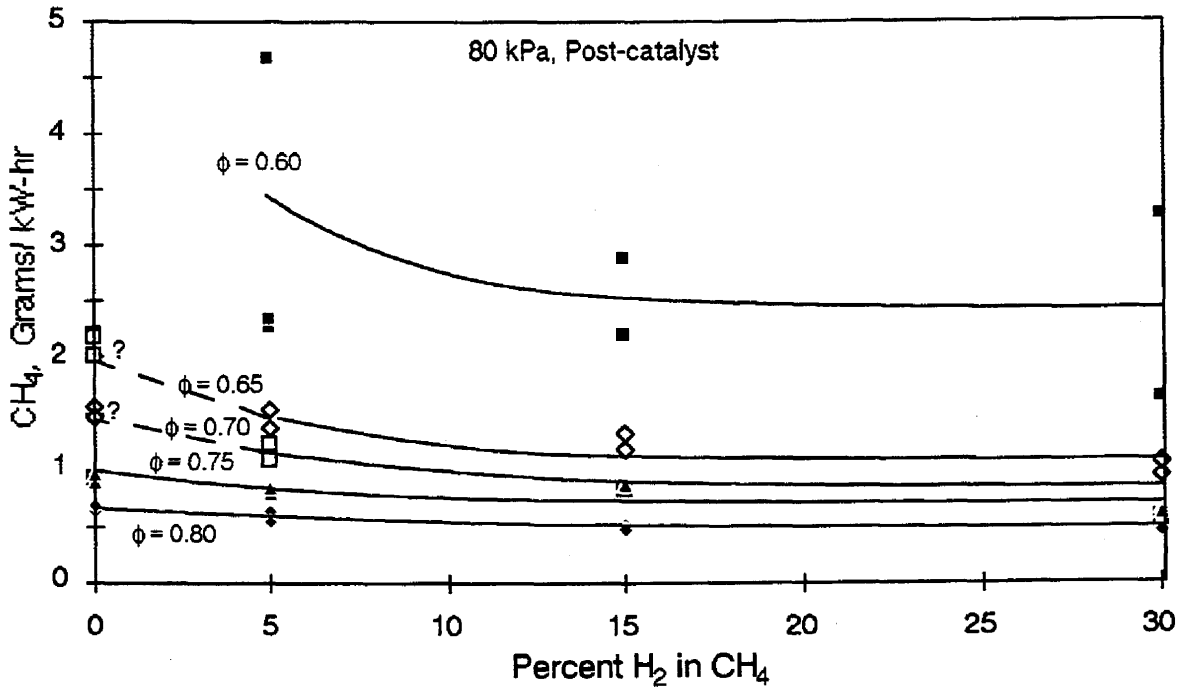

Figure 4-4. Variation of post-catalyst CH_4 emissions in the lean range vs. H_2 % and ϕ at 80 kPa of MAP. The data for pure methane at $\phi = 0.65$ and $\phi = 0.70$ may be reversed.

4.3 Lean Burn BSCO Emissions

4.3.1 Pre-catalyst BSCO Emissions

Figure 4-5 shows that CO increases with the onset of combustion instability near the lean limit. The trends are similar to Figure 4-1 because both CO and HC emissions result from incomplete combustion. With ϕ = 0.8 or 0.9, the effect of H_2 on CO emissions is approximately that of dilution, i.e.; pure H_2 can make no CO, so 10% H_2 by energy content (30% by volume in Figure 4-5) gives about 10% reduction in CO. The effect of H_2 as a combustion stimulant is apparent with $\phi < 0.8$. For example, with $\phi = 0.70$, supplying 10% of the fuel energy in the form of H_2 (30% by volume) reduces CO emissions by about 40%, relative to pure CH_4--a leverage factor of 4.

At $\phi = 0.65$ the CO emissions with 30 volume percent H_2 are similar to CO emissions with pure CH_4 at ϕ =0.9. This indicates good combustion stability that is reflected in the thermal efficiency data discussed below. However, at $\phi = 0.6$ and 30% H_2 by volume, combustion instability is apparent at 35 kPa of MAP.

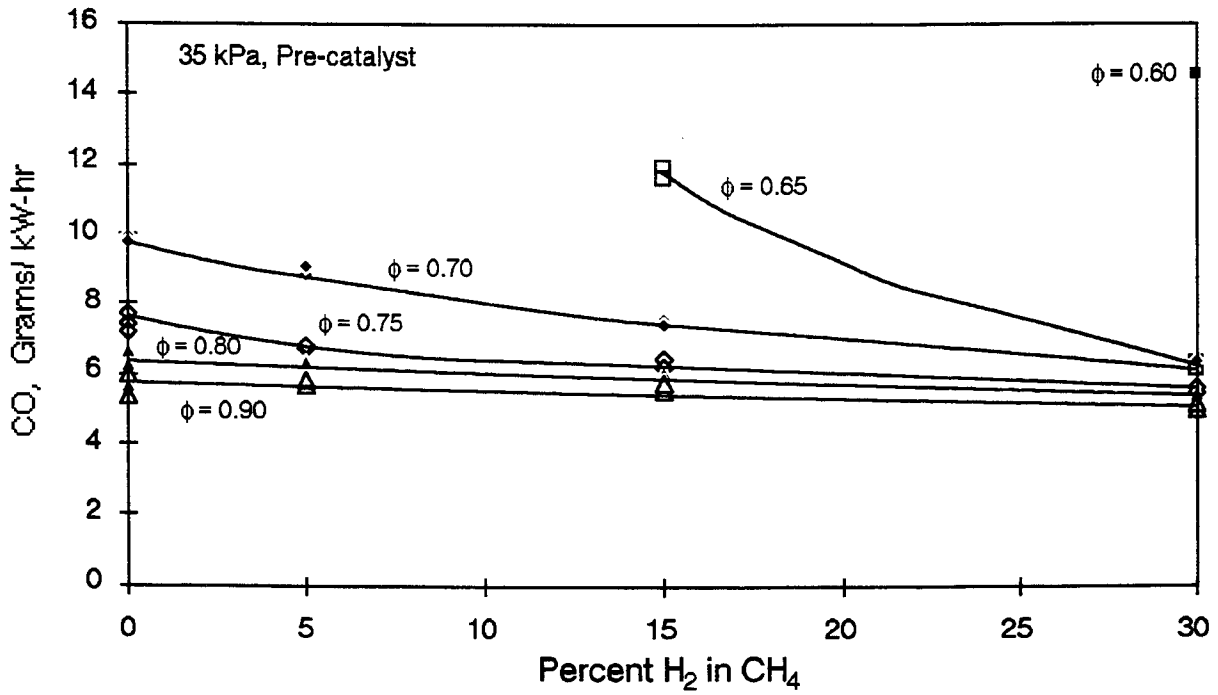

Figure 4-5. Variation of pre-catalyst CO emissions in the lean range vs. H_2 % and ϕ at 35 kPa of MAP.

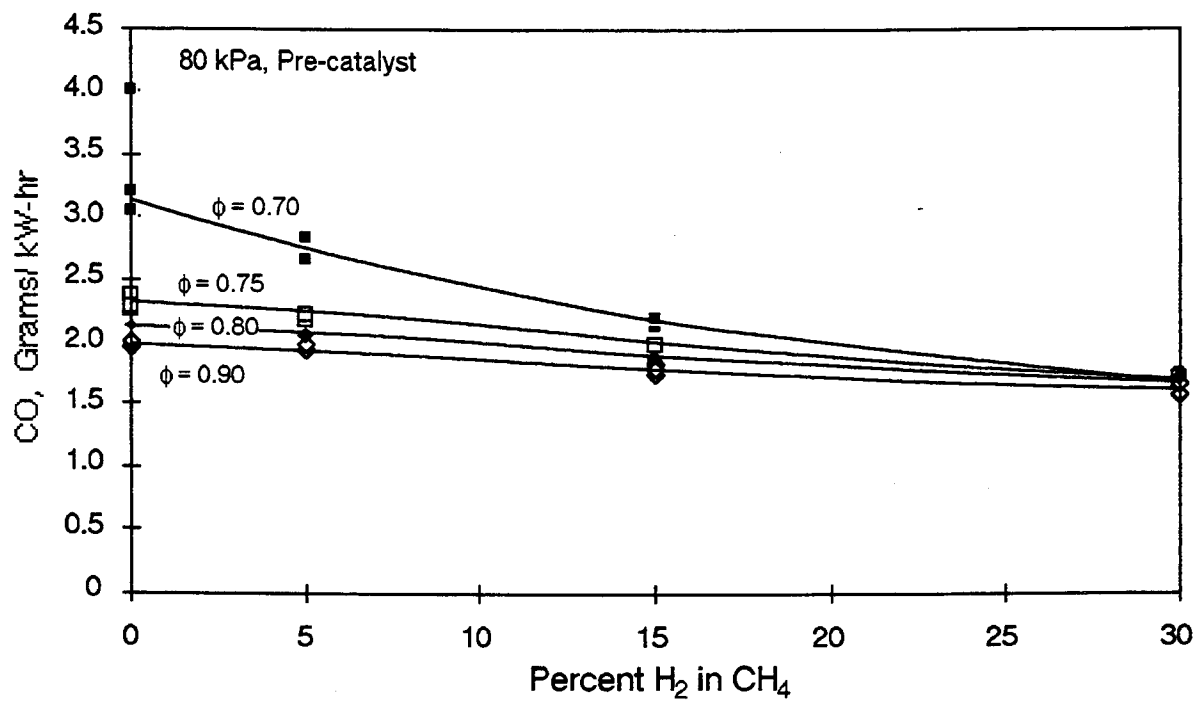

Figure 4-6. Variation of pre-catalyst CO emissions in the lean range vs. H_2 % and ϕ at 80 kPa of MAP.

Figure 4-6 shows the precatalyst CO emissions at wide open throttle. Within the limited range of equivalence ratios investigated, CO remains at acceptably low levels. The influence of H_2 as a combustion stimulant is none-the-less apparent as each constant equivalence ratio data set slopes downward with increasing H_2 content.

4.3.2 Post-catalyst BSCO Emissions

Post catalyst CO emissions are very low. The entire data set consists of small positive and negative numbers, indicating instrument drift around zero. Even at $\phi = 0.6$ where precatalyst CO emissions were highest and the catalyst temperature is lowest, the catalyst conversion efficiency is virtually 100%.

4.4 Lean-Burn BSNOx Emissions

In the lean range of equivalence ratios, the catalyst has little, if any, effect on NOx emissions. The distinction between pre- and post-catalyst NOx emissions is therefore largely just a formality, indicating where the data were taken. Figures 4-7 and 4-8 may be thought of as companion data sets at 35 kPa, each confirming the other.

Both temperature and time affect the formation of NOx in combustion processes. This is apparent in Figures 4-7 and 4-8. Adiabatic flame temperature calculations indicate that increasing H_2 concentration in CH_4 increases the flame temperature and, based on that alone, an increase in NOx is anticipated. However, H_2 also increases the flame speed and, therefore, requires less spark advance. The time-at-temperature relationship may be responsible for the minor, sometimes negative, changes in NOx with H_2 content at 35 kPa of MAP.

A much stronger trend is observed in NOx versus ϕ. The region of greatest interest for lean-burn emissions control is $\phi < 0.8$. In this range, Figures 4-7 and 4-8 show rapid decrease in NOx with equivalence ratio. The coarse scale employed in Figures 4-7 and 4-8 should not obscure the fact that NOx is cut approximately in half as ϕ falls from 0.70 to 0.65, with 15% H_2, or to 0.60, with 30% hydrogen. Pure CH_4 combustion was too unstable to allow operation below $\phi = 0.70$ at 35 kPa of MAP. The hydrogen additions may, therefore, be regarded as *enabling* with respect to the NOx reductions. Cutting NOx emissions in half with 5% of the fuel energy supplied as hydrogen (15% by volume) results in a leverage factor of about 10.

Figures 4-9 and 4-10 are pre- and post-catalyst NOx data at wide open throttle. NOx increases steadily with H_2 content at higher equivalence ratios ($\phi \geq 0.75$). However, at $\phi = 0.70$ and less the trends are weak versus H_2 content and strong versus ϕ. Operation was possible at $\phi = 0.65$ with pure CH_4. As little as 5% H_2 by volume (<2% by energy content) enabled operation at $\phi = 0.60$ (see Figure 4-10). Going from $\phi = 0.65$ to $\phi = 0.60$ cuts NOx approximately in half, so the leverage is about 50%÷2% = 25.

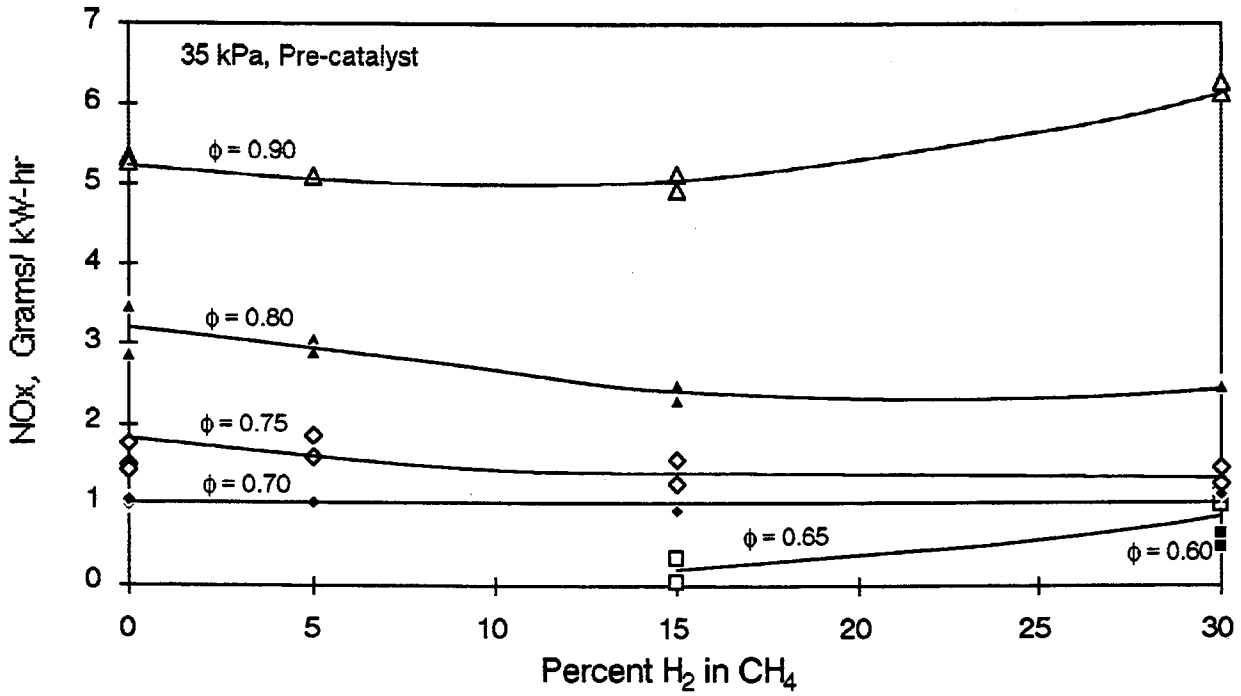

Figure 4-7. Variation of pre-catalyst NOx emissions in the lean range vs. H_2 % and ϕ at 35 kPa of MAP.

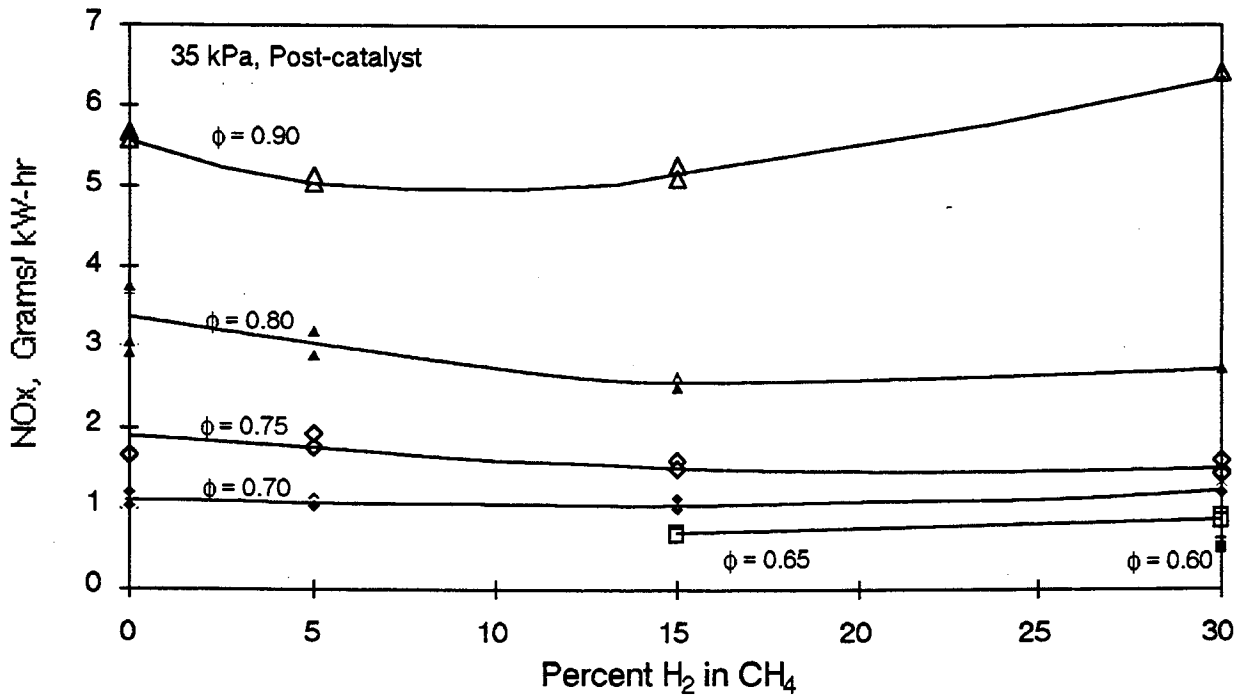

Figure 4-8. Variation of post-catalyst NOx emissions in the lean range vs. H_2 % and ϕ at 35 kPa of MAP.

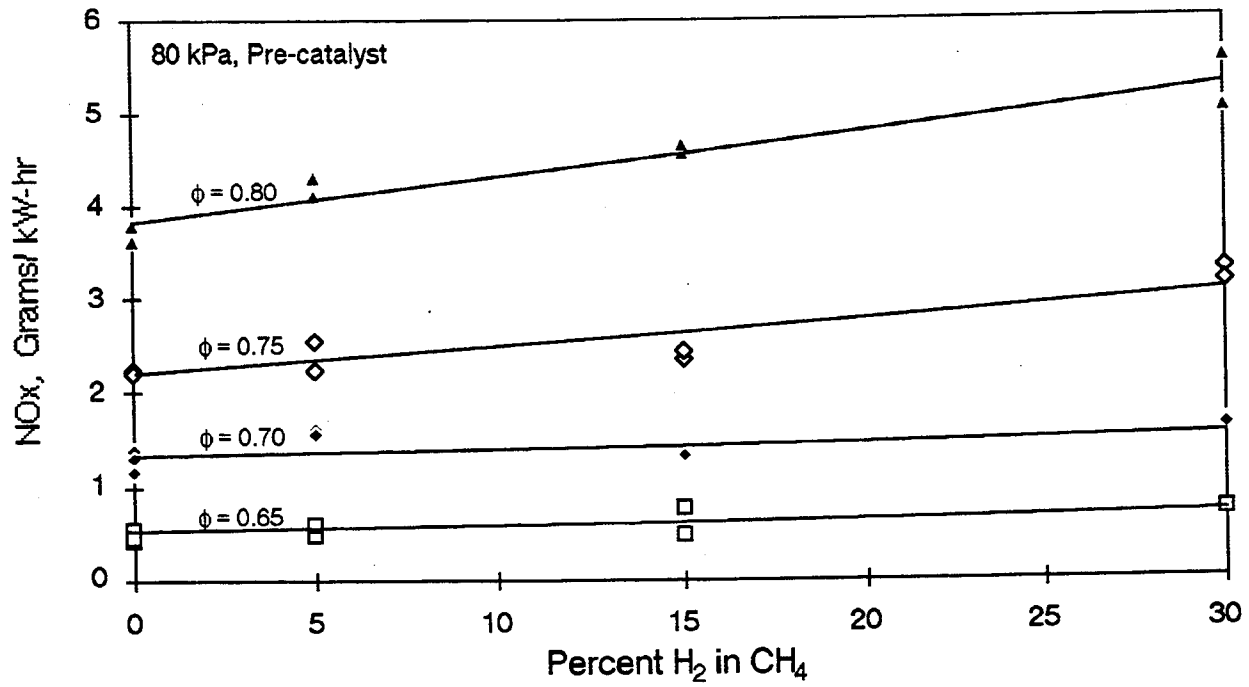

Figure 4-9. Variation of pre-catalyst NOx emissions in the lean range vs. H_2 % and ϕ at 80 kPa of MAP.

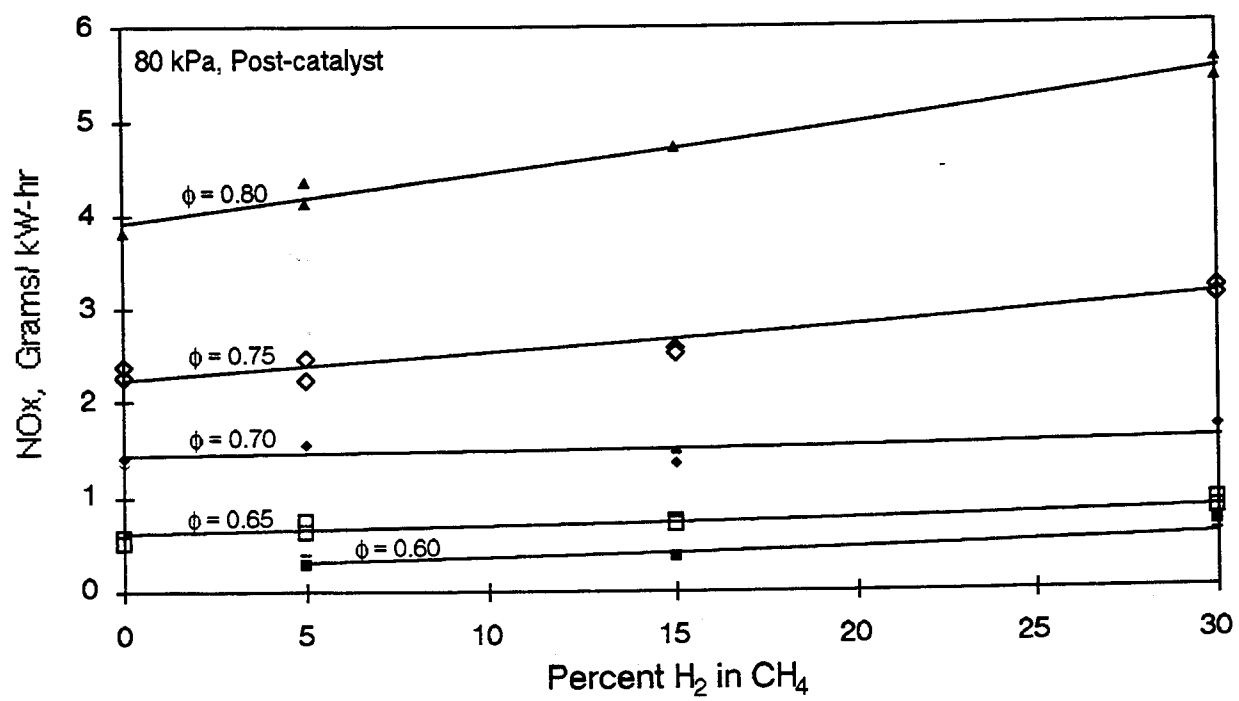

Figure 4-10. Variation of post-catalyst NOx emissions in the lean range vs. H_2 % and ϕ at 80 kPa of MAP.

4.5 Lean Burn NOx, HC and Performance Tradeoffs

Figure 4-11 shows brake-specific NOx vs. THC with varying amounts of hydrogen in methane at light load. As the mixture is leaned from ϕ = 0.9 to ϕ = 0.7, NOx falls rapidly at the expense of increased THC. Leaning out the mixture to reduce NOx emissions to 1 gram/kW-h with methane corresponds to THC emissions of about 15 grams/kW-h. As hydrogen content increases, the THC emissions fall. At the 1 gram/kW-h NOx level, the THC emissions are cut in half somewhere between 15 and 30 volume % hydrogen (5 and 10 energy %).

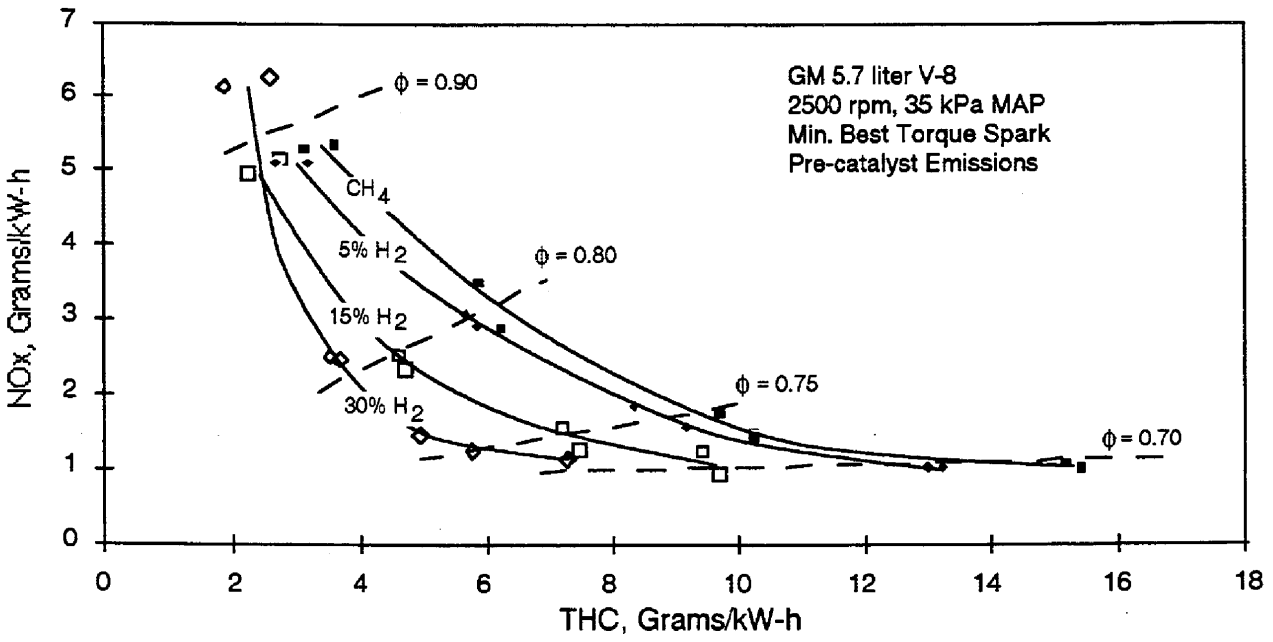

Figure 4-11. At any given NOx level, THC emissions are significantly less with Hythane. The dashed lines indicate the equivalence ratio corresponding to each set of points.

Comparing light load data of Figure 4-11 with wide open throttle data of Figure 4-12 shows generally lower THC emissions. It is nonetheless apparent that the hydrogen additive enables lower THC emissions at any given NOx level or, conversely, lower NOx emissions at any given THC level.

Something that is not apparent in Figures 4-11 or 4-12 is that, below ϕ = 0.7, adding H_2 increases BMEP. This is discussed further in Section 5.1. This advantage was sacrificed by retarding the spark until the engine torque with 30% H_2 was the same as with pure CH_4. The results are shown in Figure 4-12. At the same torque, NOx is less with 30% H_2 than with pure CH_4.

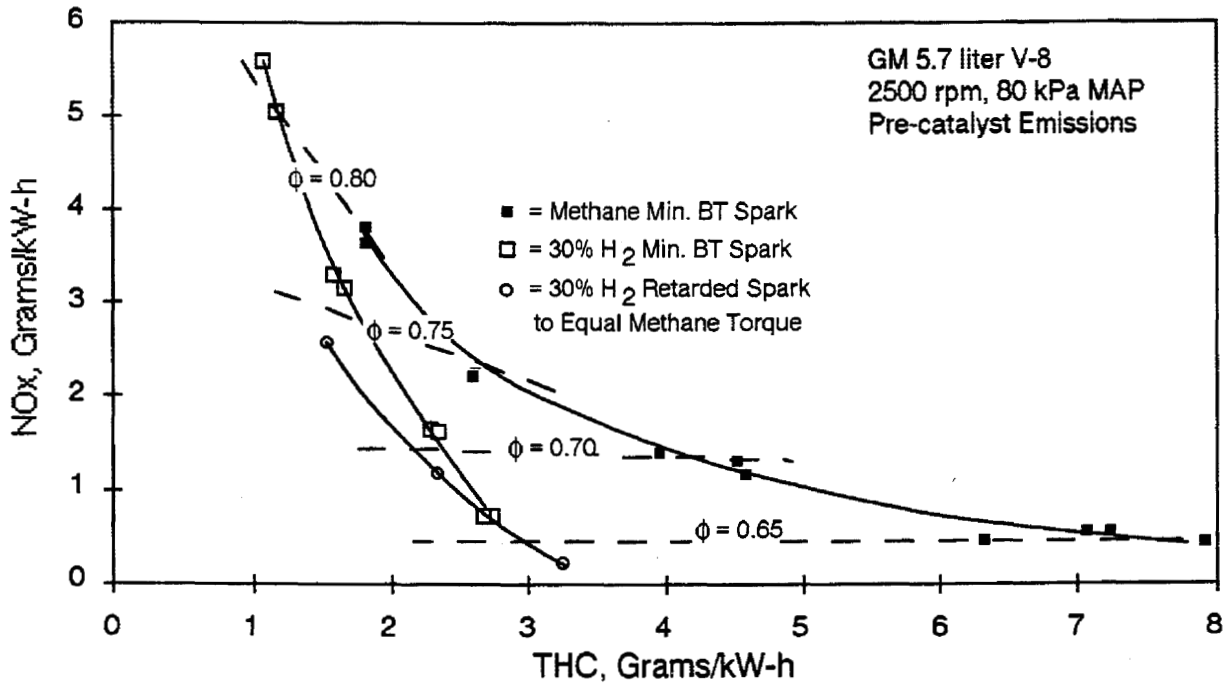

Figure 4-12. At wide open throttle (MAP = 80 kPa), the torque advantage of Hythane may be sacrificed to reduce NOx with minor THC emissions consequences.

4.6 Lean-burn Emissions Conclusions

The addition of H_2 to CH_4 as fuel for a spark ignition engine reduces emissions of HC and CO. This effect is especially strong as the equivalence ratio approaches the lean limit. The relationship between H_2 content and NOx is complicated. With 35 kPa of manifold air pressure (MAP), there is no definitive relationship between H_2 content and NOx. Both small decreases and increases are observed. The lean limit is extended by H_2, thereby allowing lower part load NOx via lower ϕ and increased MAP. Post-catalyst CO emissions were always in the noise level of the instruments. Therefore HC and NOx are the main issues for lean burn engines with good catalysts.

At wide-open throttle, NOx increases with H_2 content. At $\phi \leq 0.7$ this effect is relatively weak. Engine torque with minimum best torque spark advance increases with H_2 content. H_2 enables lower NOx emissions at wide-open throttle by sacrificing this torque advantage. This may be done by running leaner, retarding the spark or both. In either case, HC emissions increase, so care must be taken in applying these strategies. No tests were performed with exhaust gas recycle (EGR), however, sacrificing the extra torque to EGR should also be effective for NOx reduction.

4.7 Stoichiometric BSHC Emissions

In the following discussion, "stoichiometric" means the optimal operating condition for

the three-way catalyst used in this project. The analysis discussed in Section 4.9, shows that the equivalence ratio for optimal performance is $\phi = 1.005$.

4.7.1 Pre-catalyst BSHC Emissions

The effect of H_2 on unburned CH_4 emissions is much less pronounced at stoichiometric operating conditions than it is near the lean limit. Figure 4-13 shows a linear decrease in BSHC with H_2 content. The effect goes beyond simple dilution. Only 10.2% of the total fuel energy is supplied by H_2 at 30 % by volume. The decrease in BSHC is 18%, indicating a leverage factor of 1.8. Figure 4-14 shows the same trend at 80 kPa of MAP. The leverage factor at this wide-open throttle condition is 2.3.

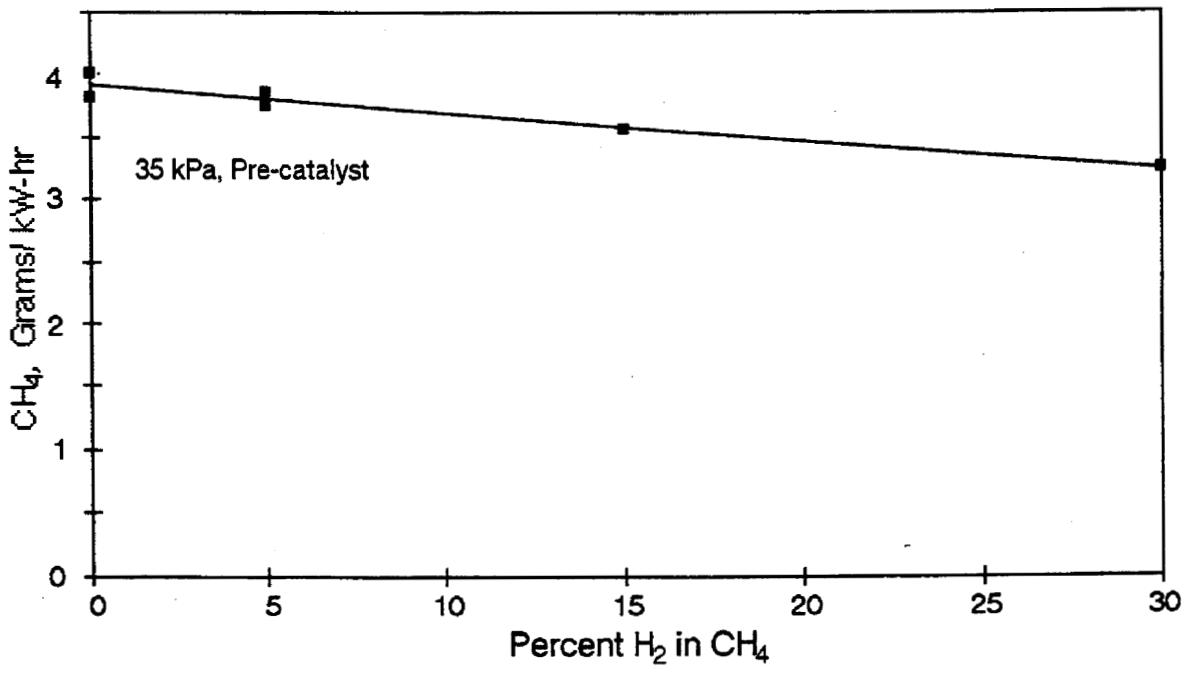

Figure 4-13. Pre-catalyst BSHC emissions vs. H_2 content at 35 kPa MAP.

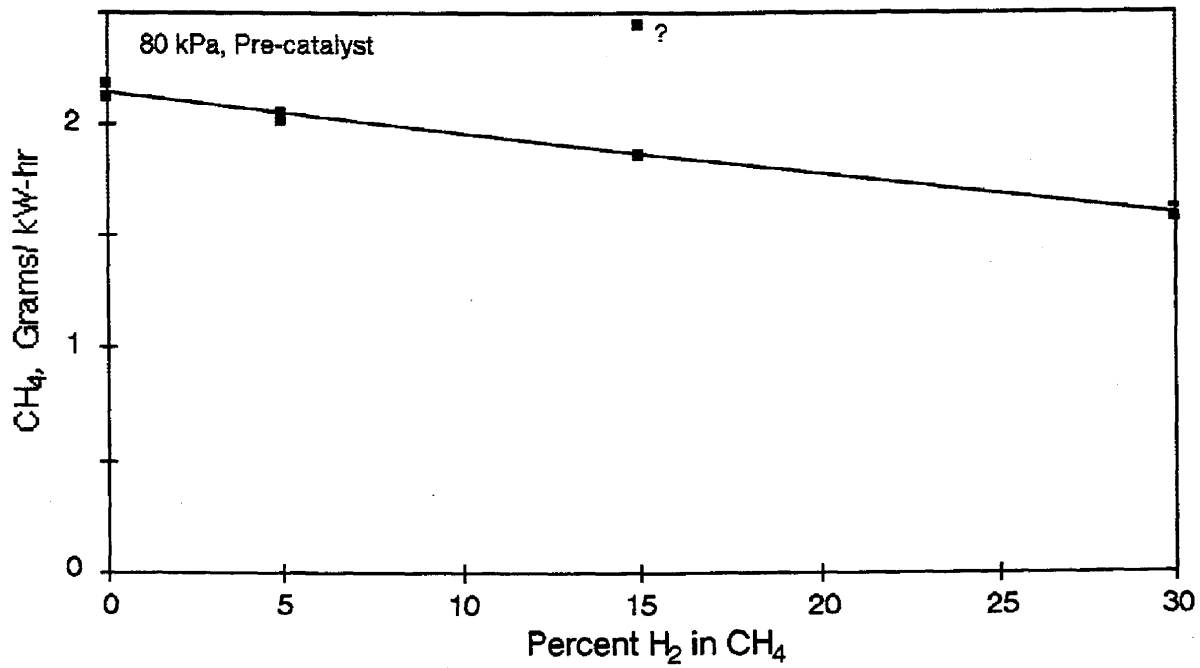

Figure 4-14. Pre-catalyst BSHC emissions vs. H_2 content at 80 kPa MAP.

4.7.2 Post-catalyst BSHC Emissions

At 35 kPa of MAP, post catalyst BSHC emissions were unaffected by H_2. All of the data, regardless of H_2 content, grouped around 2.3 grams/kW-hr. No trend was observed at 80 kPa of MAP either, but the emissions were much lower, grouping around 0.33 g/kW-hr. This indicates higher catalyst efficiency. The catalyst used in this study was previously installed on a 2.5 liter, 4-cylinder engine in a Chevrolet S-10 pickup truck. Several Federal light duty vehicle tests (FTPs), conducted by the California Air Resources Board in 1991 (see Appendix A), non-methane hydrocarbon emissions were approximately 0.01 grams per mile, with or without adding hydrogen. At such low levels, hydrocarbon emissions are not a major issue with this catalyst.

4.8 STOICHIOMETRIC BSCO EMISSIONS

4.8.1 Pre-catalyst BSCO Emissions

There appears to be a slight downward trend in pre-catalyst BSCO emissions with increasing H_2 content. However, any such trend is within the range of scatter of the data and hence insignificant. The pre-catalyst BSCO data averaged 15.1 grams/kW-hr at 35 kPa of MAP and 8.2 grams/kW-hr at 80 kPa of MAP.

4.8.2 Post-catalyst BSCO Emissions

There appears to be a slight downward trend in post-catalyst BSCO emissions with increasing H_2 content. However, any such trend is within the range of scatter of the

data and hence insignificant. The post-catalyst BSCO data averaged 1.1 grams/kW-hr at 35 kPa of MAP and 0.59 grams/kW-hr at 80 kPa of MAP.

4.9 STOICHIOMETRIC BSNOx EMISSIONS

4.9.1 Pre-catalyst BSNOx Emissions

The 35 and 80 kPa pre-catalyst BSNOx data are combined in Figure 4-15. The apparent trends are only slightly greater than the test-to-test uncertainty. It is interesting that, at 35 kPa, precatalyst BSNOx emissions show no increase between 0 and 15% H_2. This particular data set grouped so tightly that the apparent decrease with 5% H_2 may be worthy of further study. At 80 kPa, pre-catalyst NOx increased continuously with increasing H_2 content. At 30% H_2 both data sets indicate an increase in BSNOx of about 10%.

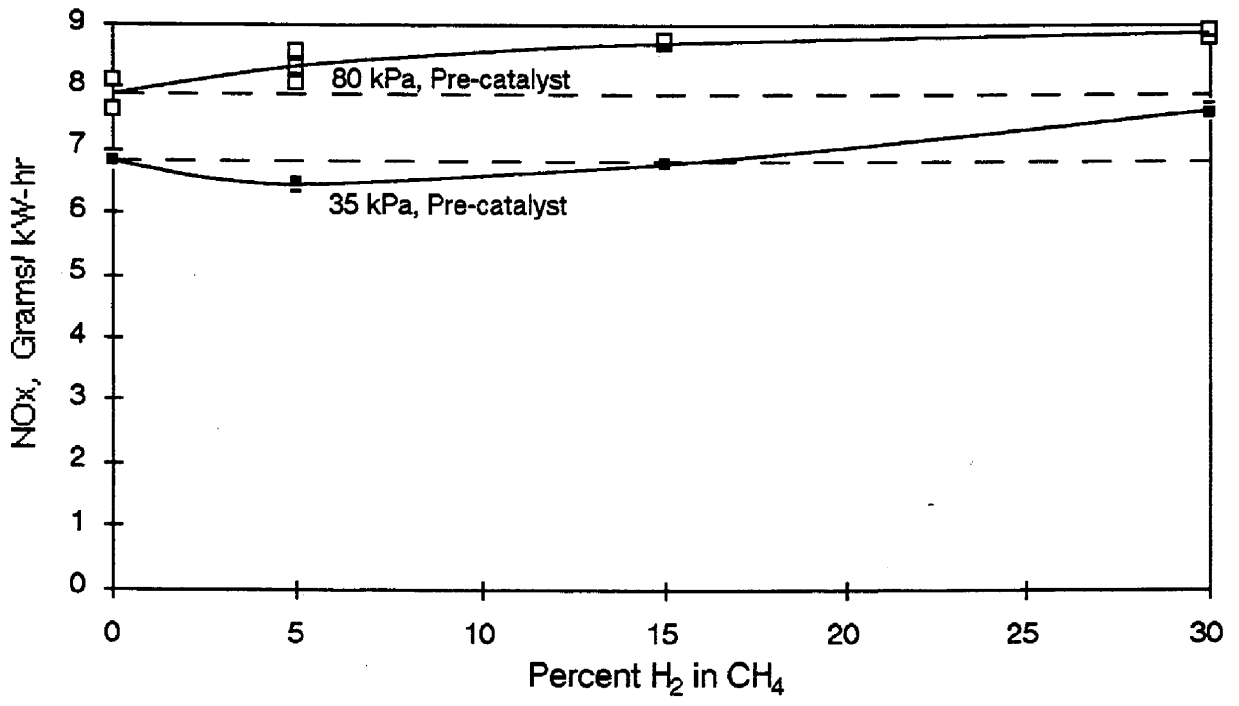

Figure 4-15. Pre-catalyst NOx emissions vs. H_2 content at 35 and 80 kPa MAP.

4.9.2 Post-catalyst BSNOx Emissions

Post-catalyst NOx emissions were so low that the zero drift of the instrumentation was a problem. Occasionally, negative values were observed--with or without adding H_2. The 35 and 80 kPa MAP data may be interpreted to indicate about 0.2 grams per kW-hr of NOx. The variation with H_2 content could not be resolved. A much more important variable is carbon monoxide, as shown in the following section.

4.10 NOx/CO Tradeoff on the Three-way Catalyst

One of the most remarkable observations of this study is how low post-catalyst NOx and CO can be when the engine is controlled precisely at the optimum equivalence ratio. Large changes in emissions occur over very small changes in equivalence ratio. Therefore, before discussing this further, it is necessary to examine the measurement of equivalence ratio more closely.

The post-catalyst CO_2 peak should correspond to the true stoichiometric equivalence ratio because the total of NOx, CO and unburned CH_4 is on the order of 0.1% by volume when this peak is observed, i.e., very complete combustion. Figure 4-16 shows the relationship between peak CO_2 concentration and AFRecorder indication. A median H_2 concentration of 15% is characterized in the chart. Similar effects were observed 0, 5 and 30% H_2. The CO_2 data fall slightly short of the theoretical curve for complete combustion but the peak is none-the less valid as an indication of stoichiometric equivalence ratio. The AFRecorder reads about 1.015 at peak CO_2.

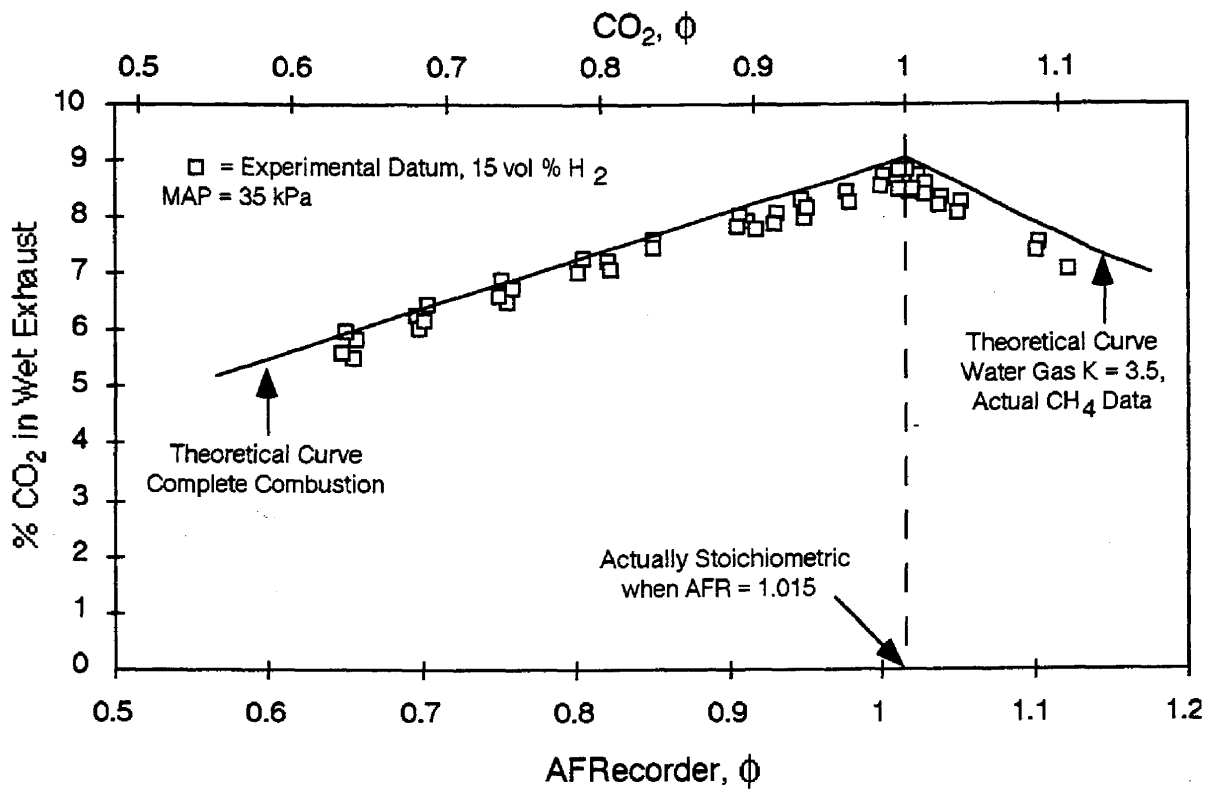

Figure 4-16. Stoichiometric equivalence ratio determination by CO_2 vs. AFRecorder.

Further evidence of this slight miscalibration is apparent in examination of CO emissions. There is a discontinuity near an AFRecorder reading of 1.015, as Shown in Figure 4-17. Rough confirmation of the AFRecorder error is also apparent in Figure 4-18. The average peak exhaust temperature is at ϕ = 1.01, according to the AFRecorder.

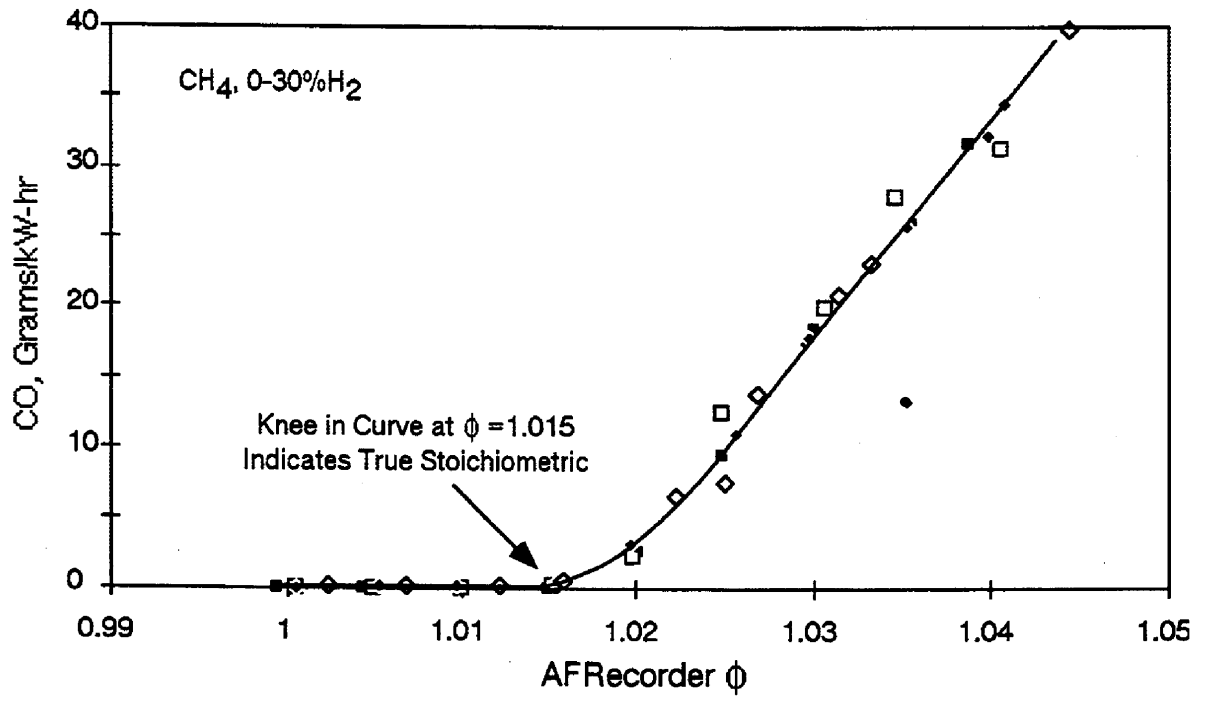

Figure 4-17. Stoichiometric equivalence ratio determination by CO vs. AFRecorder reading.

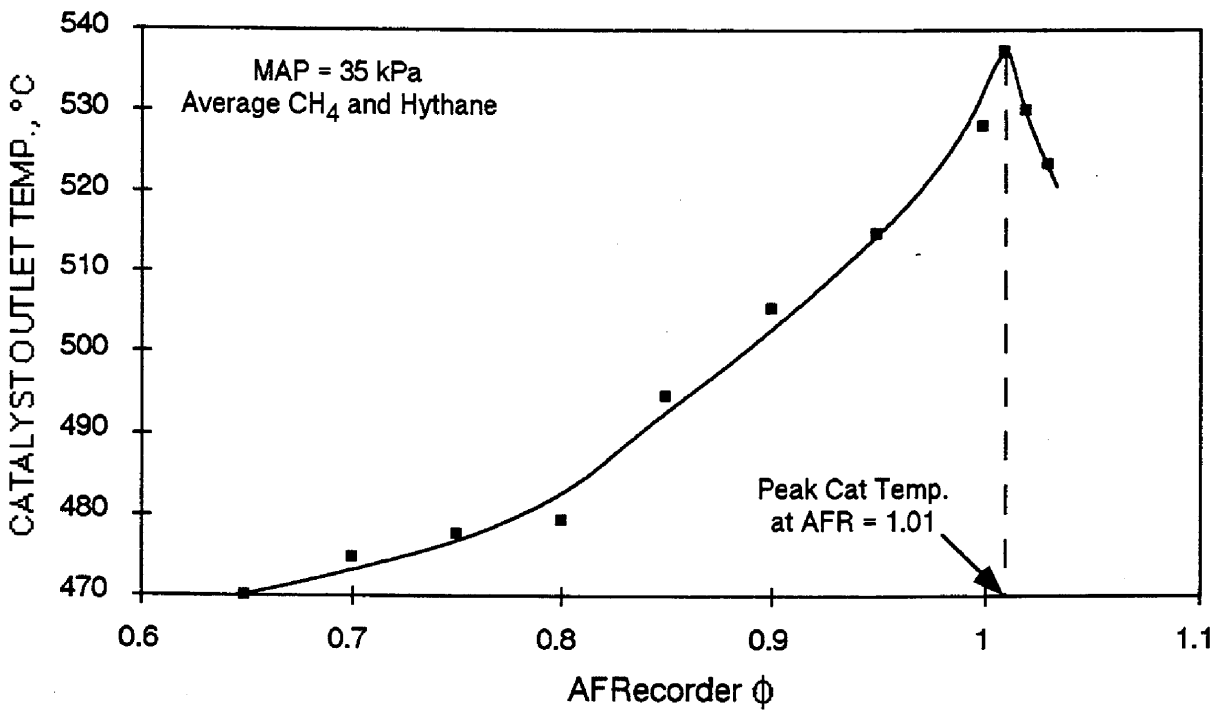

Figure 4-18. Average exhaust temperature vs. AFRecorder equivalence ratio.

Figure 4-19 shows that data for pure CH_4 and 30% H_2 are virtually indistinguishable. This suggests that the NOx vs. CO relationship is more a characteristic of the catalyst than of the fuel composition. Clearly, the best equivalence ratio for simultaneous minimization of NOx and CO is near ϕ = 1.005.

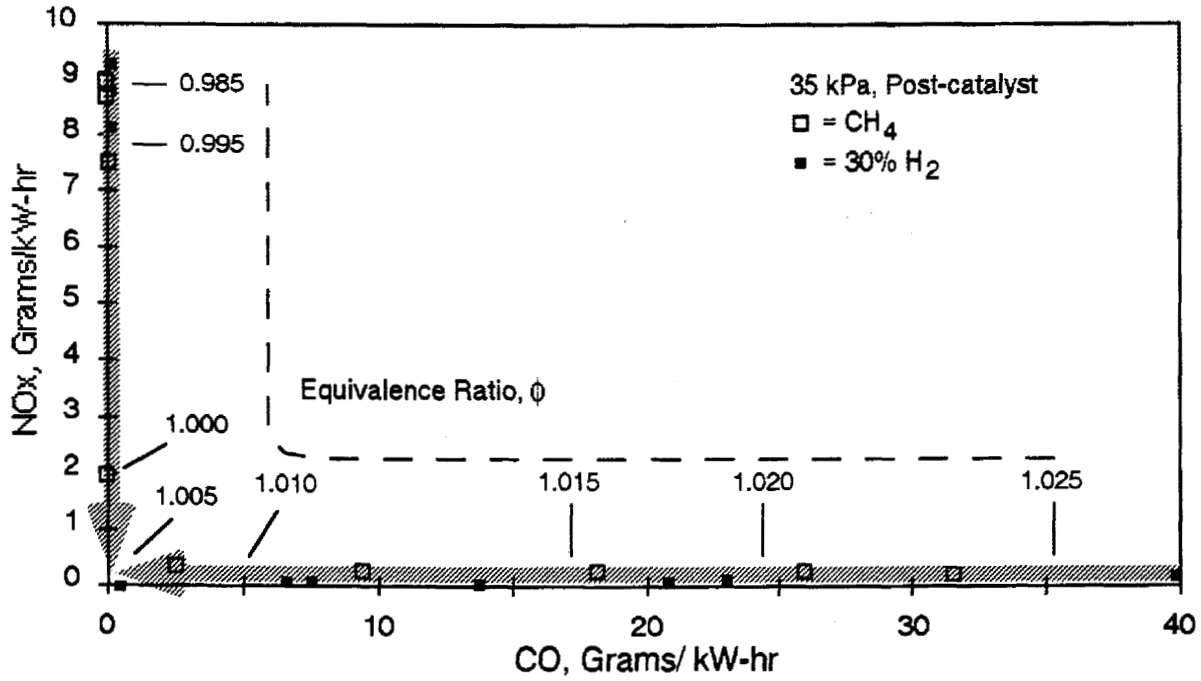

Figure 4-19. NOx vs. CO characteristic of the three-way catalyst.

NOx heads rapidly toward zero on the approach to stoichiometric equivalence ratio. Along the downward NOx trend, some of the CO measurements are slightly negative, challenging the limits of error of the instruments. Just past stoichiometric, as CO passes 1 g/kW-hr, NOx is too low to measure precisely. Slightly negative NOx readings are occasionally observed, due to zero drift of the instruments.

Most of the NOx data at ϕ = 1.005 or greater group around 0.2 grams/kW-hr with no observable trend with respect to H_2 concentration. In Figure 4-19, the NOx emissions appear slightly higher with pure CH_4 than with 30% H_2. This is thought to be caused by an ambient change between the two experiments because no such trend is observed in the data set as a whole.

4.11 Stoichiometric Emissions Conclusions

Hydrogen effects are most apparent in pre-catalyst emissions. There is a general downward trend in pre-catalyst CH_4 that exceeds the effects of simple H_2 dilution. There was no significant change in pre-catalyst CO with H_2 addition, not even what might be expected from dilution. This is a puzzling result that is contrary to recent findings in another study[2]. Pre-catalyst NOx emissions, in general, go up with H_2 content. An exception to this is at 35 kPa where up to 15% hydrogen could be added with no increase in NOx. There may be a small decrease in NOx with 5% H_2.

[2] Swain, M. R. et al., "The Effects of Hydrogen Addition on Natural Gas Engine Operation", SAE Paper No. 932775 (1993)

The post-catalyst emissions results are more significant because stoichiometric natural gas or Hythane engines must be equipped with three-way catalysts to meet emissions standards. Direct effects of hydrogen on post-catalyst emissions are not apparent. It is none-the-less interesting to look at the extremely low emissions that can be attained via precise mixture control with an eye toward how hydrogen can have the effects commonly observed in dynamic tests with closed-loop control systems[3] .

Worst case post-catalyst CH_4 emissions were observed at 35 kPa of MAP. The 2.3 grams/kW-hr observed corresponds closely to THC emissions data from Federal urban driving cycle tests with the same catalyst on HCI's Chevrolet S-10 pickup (see Appendix A). Assuming that the S-10 requires about 0.2 kW-hr per mile, the calculated CH_4 emissions would be 0.46 grams per mile. Actual THC data for the S-10 range around 0.5 grams per mile. NMHC, however, has been repeatedly speciated at about 0.01 grams per mile with this catalyst, with and without 15% hydrogen by volume in natural gas.

With NMHC at such low levels, NOx and CO become the most significant emissions criteria. Given a control system capable of holding the mixture at the optimum equivalence ratio, $\phi = 1.005$, Figure 4-19 indicates that NOx and CO emissions can be so low that measurement is difficult. Post-catalyst NOx emissions for $\phi \geq 1.015$ average 0.2 gram/kW-hr over all data. Post-catalyst CO emissions for $0.980 \leq \phi \leq 1.000$ average 0.85 gram/kW-hr over all data. A light duty vehicle that requires an average of 0.2 kW-hr per mile in a Federal urban driving cycle would emit about 0.2 grams per mile of CO and 0.04 grams per mile of NOx at the steady state levels.

Figure 4-20 shows "Hot 505"[4] test results for the S-10 with this same catalyst. The NOx emissions drop to 0.04 grams per mile in the rich range to the right of the figure. CO emissions fall to 0.3 grams per mile toward the left of the figure. Running slightly leaner at the California Air Resources Board, this vehicle and catalyst ran the full Federal test repeatedly with 0.14 grams per mile of CO and 0.2 grams per mile of NOx. The fact that the S-10 cannot give simultaneous CO and NOx emissions comparable to the steady state tests is attributable to imperfections of the control system. The steady state engine tests in the present study were manually set at the optimum equivalence ratio, $\phi = 1.005$, within ± 0.002.

From Figure 4-19, it is apparent that the deviations of a control system around the optimum equivalence ratio can have major effects on NOx and CO emissions. The consequences of a $\pm 1\%$ deviation from the optimum equivalence ratio, $\phi = 1.005$, are shown in Figure 4-21.

[3] See Appendix A

[4] A "Hot 505" test is the last 505 seconds of a Federal urban driving cycle, performed with a thoroughly warmed up engine and catalyst.

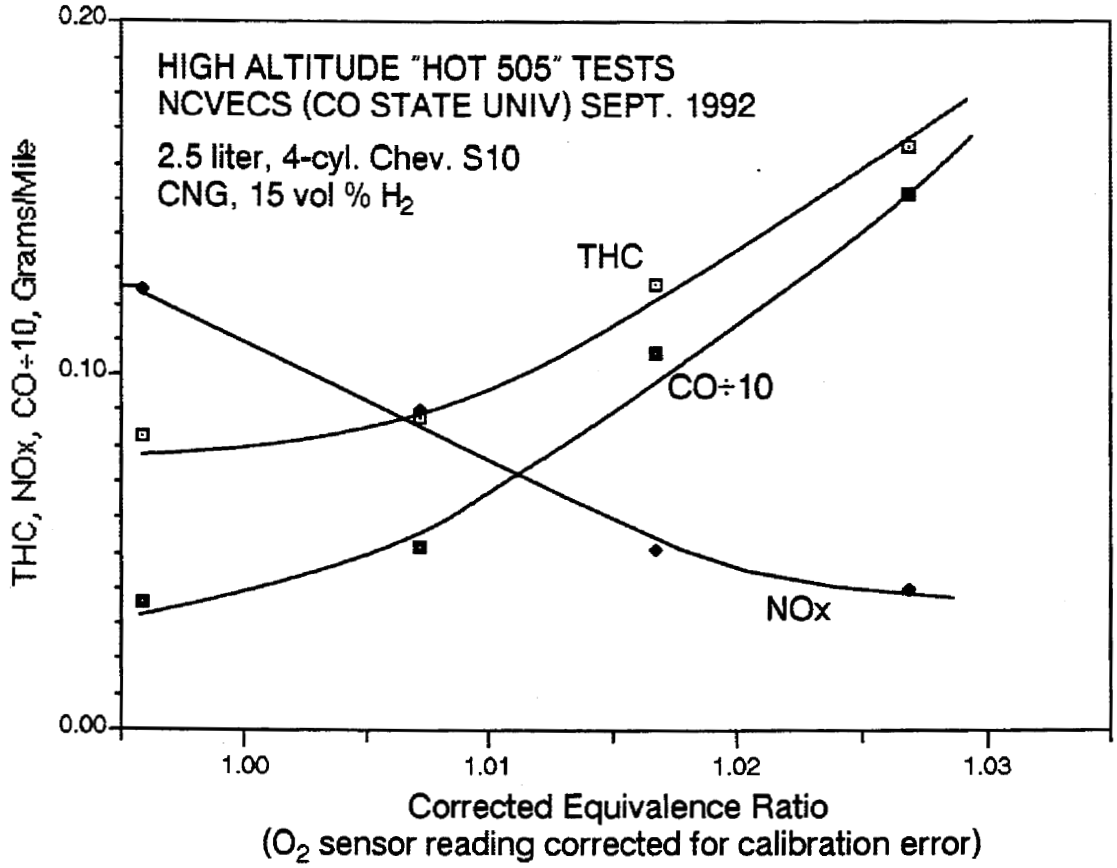

Figure 4-20. Transient vehicle tests with the same catalyst used in the present study have demonstrated NOx emissions, running slightly rich, and CO emissions, running slightly lean, that agree well with the steady state engine tests reported above. The vehicle is unable to demonstrate minimum NOx and CO at the same settings because the control system cannot maintain optimum mixture.

The transient vehicle emissions test data in Appendix A show strong hydrogen effects that are not apparent in the stoichiometric steady state state tests reported above. The vehicle tests show repeatable trends with 4 different test vehicles at 4 different EPA-approved laboratories.

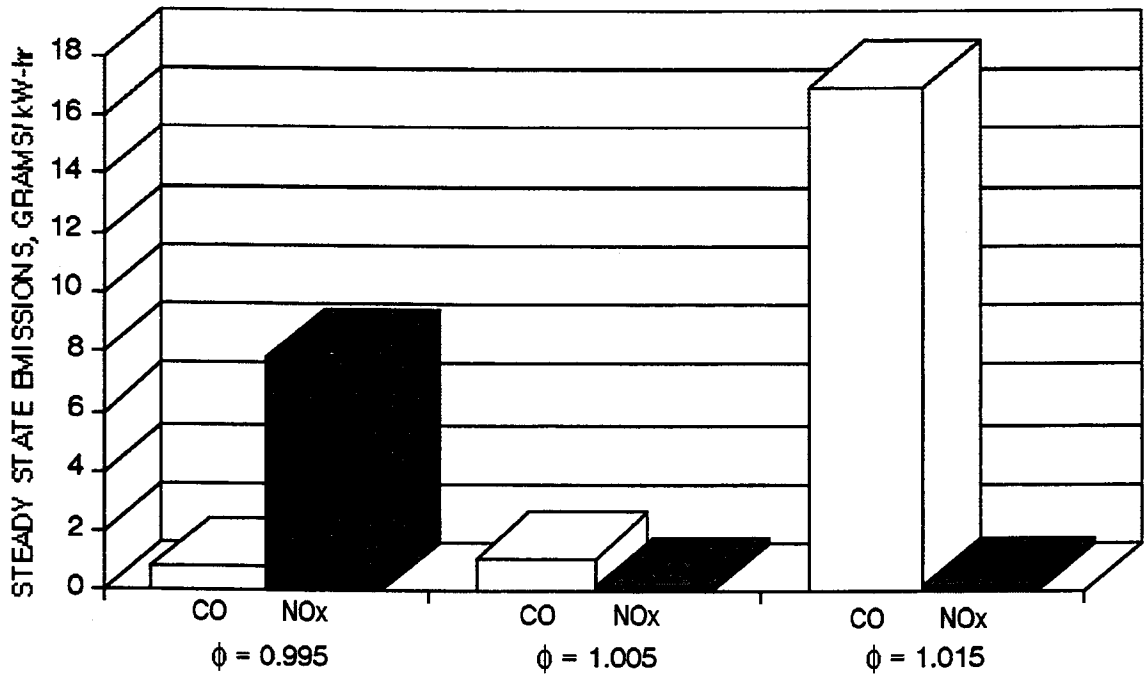

Figure 4-21. Emissions consequences of ±1% error from optimum equivalence ratio for the three-way catalyst (steady state data from the present study).

5.0 Engine Performance

The effects of altitude on the engine performance data presented here are significant. The altitude of Colorado State University, Ft. Collins, Colorado is 1539 m (5050 ft). Atmospheric pressure, less pressure drop through the intake air system including a laminar air flow element, air ducts, elbows, gas mixer and static mixer (see Section 2.7), gives a typical manifold air pressure (MAP) of 80 kPa at wide-open throttle. At low altitude without the instrumentation, the MAP would be 20-25% greater and engine torque and power would increase significantly. This should be taken into account in interpreting the performance data reported below.

Figure 5-1 is the BMEP vs. rpm curve for the engine operating on natural gas in closed loop control at an equivalence ratio, $\phi = 1$ with best torque spark advance.

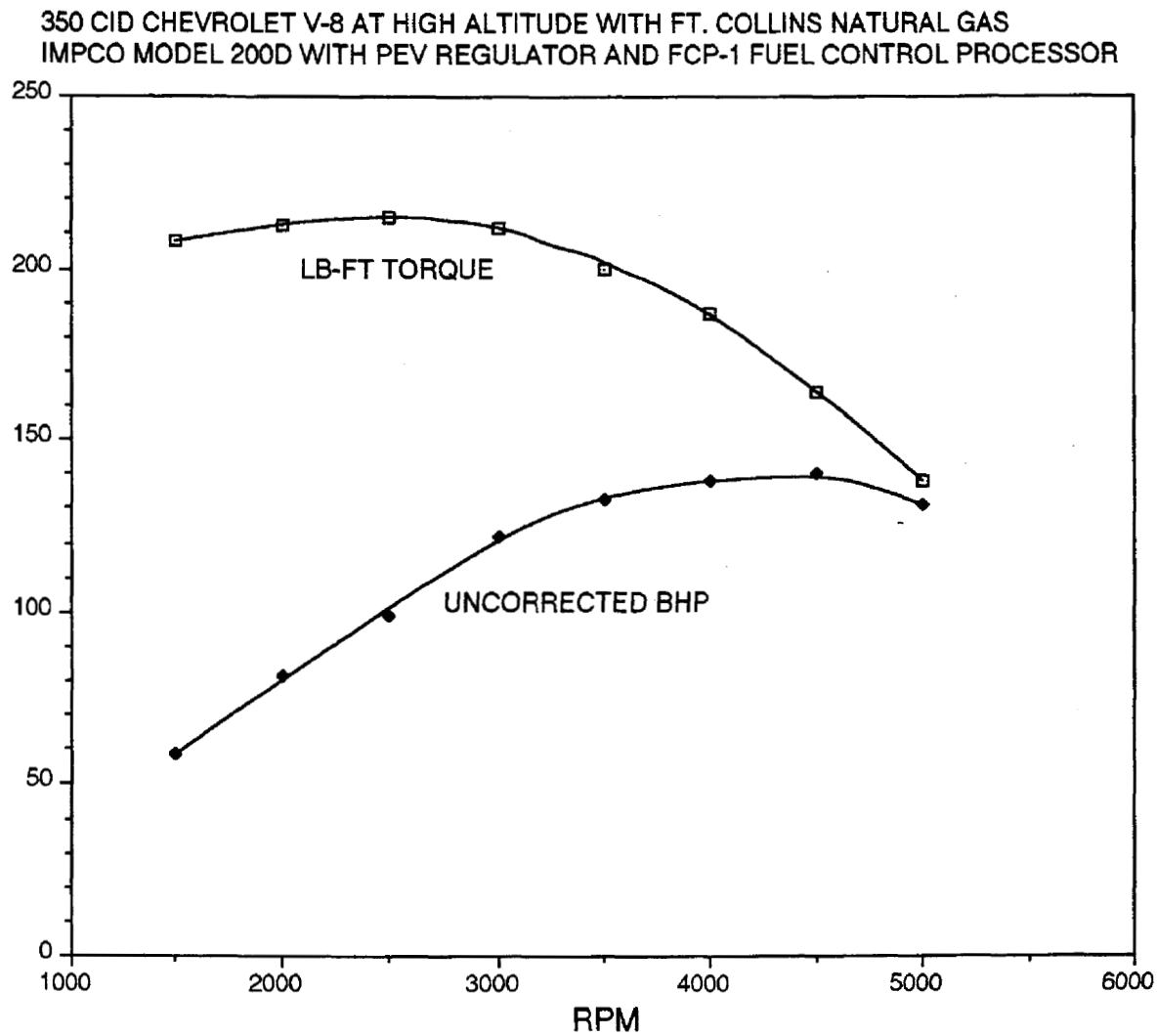

Figure 5-1. Baseline power and torque curves for the test engine on local natural gas before beginning the test program with pure methane and hydrogen.

5.1 Effects of H_2 on Brake Mean Effective Pressure

Figure 5-2 shows that the influence of H_2 on BMEP is negligible for $\phi \geq 0.75$. The apparent upward slope with increasing H_2 content at ϕ =1.00 is within limits of error. It may be the result of an interesting effect that H_2 has on throttled flow. At constant rpm and throttle angle, a slight increase in MAP with H_2 content was observed. Since the speed of sound in hydrogen is much greater than in air or CH_4, an increase in flow under choked conditions (Mach 1 past the throttle) is to be expected as the speed of sound of the mixture increases. The effect is within limits of experimental error and, once discovered, the throttle angle was adjusted to maintain exactly 35 kPa at each test point.

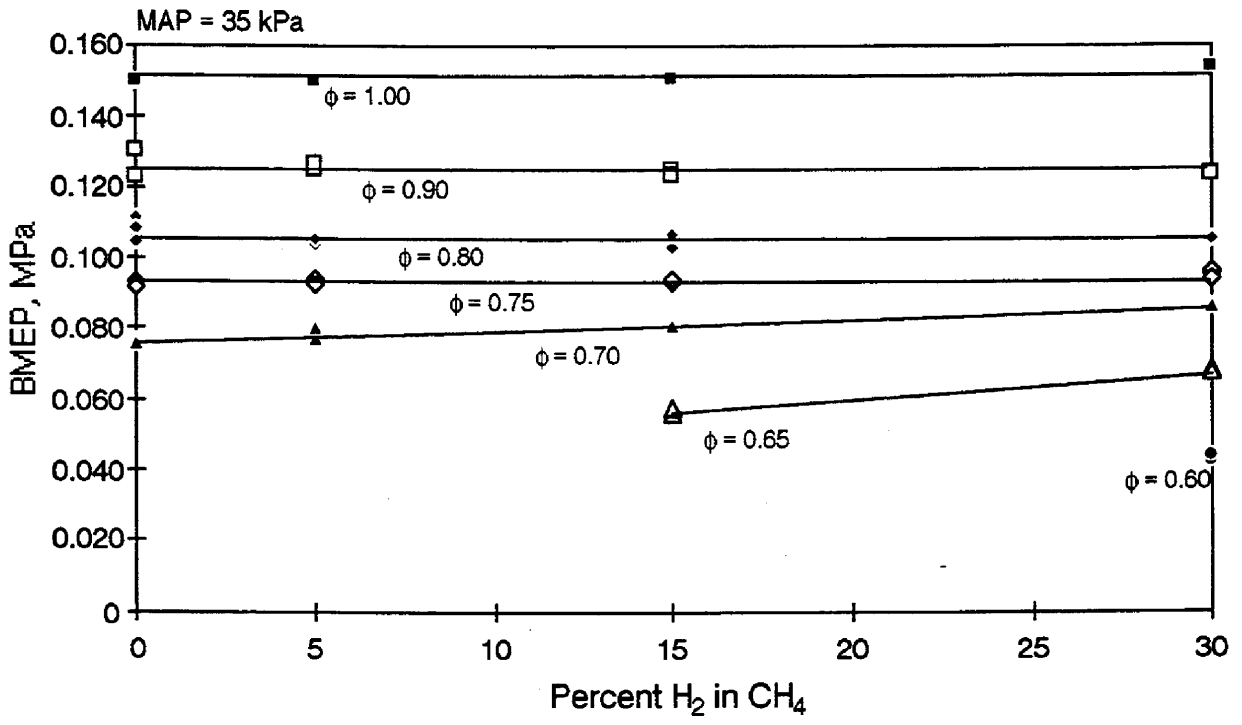

Figure 5-2. Effect of H_2 on BMEP at 35 kPa MAP at various constant equivalence ratios.

The area of greatest interest for lean burn NOx control is $\phi \leq 0.7$. Lean burn NOx data at 35 kPa show a strong downward trend with decreasing ϕ in the range of ϕ = 0.7 but H_2 content, per se, has little effect. The BMEP advantage, indicated in Figure 5-2 with increasing H_2 content at $\phi \leq 0.7$, can be converted into lower NOx emissions at the same BMEP as pure methane.

In throttled modes of operation with pure CH_4, BMEP (torque) is a constant, set by operating circumstances. A balance is struck by the engine designer between MAP and ϕ to get the desired BMEP. Design trade-offs occur between emissions and fuel consumption, but not with respect to BMEP--constant by definition under part load

conditions. Therefore, if BMEP increases with H_2 content, there are several ways to decrease BSNOx while reducing BMEP to equal the CH_4 base case.

The excess BMEP may be sacrificed for lower NOx emissions by retarding the spark until Hythane BMEP = methane BMEP. Since NOx varies little with H_2 content at lean part load conditions and strongly with spark advance, this approach will succeed. Other possibilities are to reduce ϕ to a weaker mixture at the same MAP or to simply reduce MAP at the same ϕ. The former will be more effective because BSNOx falls faster with ϕ than with MAP.

Another possibility, not explored in this project, is exhaust gas recycle (EGR). Increasing H_2 content allows greater amounts of EGR for the same reason that H_2 permits leaner operation. "Dilution tolerance" increases with H_2 content. Diluting the air/fuel mixture with EGR at constant MAP will reduce BMEP and NOx.

Similar effects can be seen at wide-open throttle in Figure 5-3. The effect of H_2 is nil or negative with $\phi \geq 0.7$. In the range of greatest interest for lean burn NOx control, $\phi <$ 0.7, the effect of hydrogen is beneficial. As before, H_2 provides a BMEP (torque) advantage that can be parlayed into a NOx advantage.

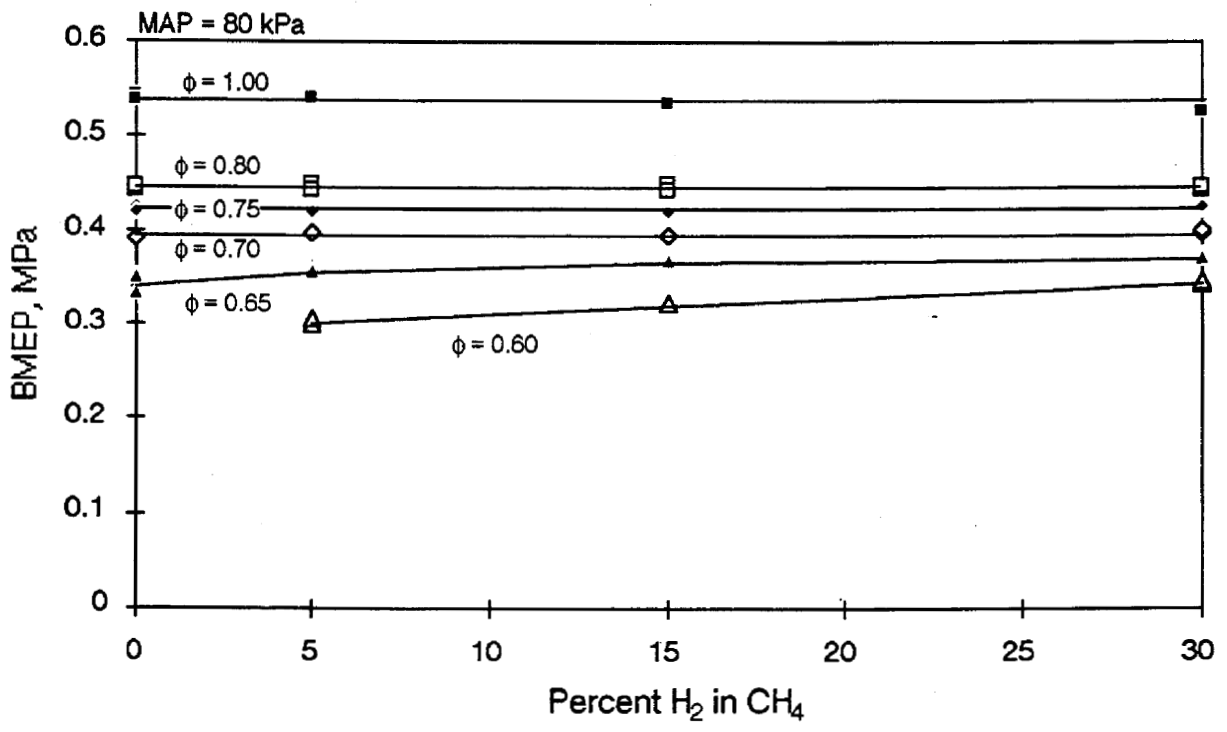

Figure 5-3. Effect of H_2 on BMEP at 80 kPa MAP at various constant equivalence ratios.

One explanation for a slight power loss with near stoichiometric mixtures is that H_2 has less energy per unit volume of stoichiometric air/fuel mixture than CH_4. The opposite is true near the lean limit. Figure 5-4 shows two counteracting effects that nullify one another at $\phi = 0.7$.

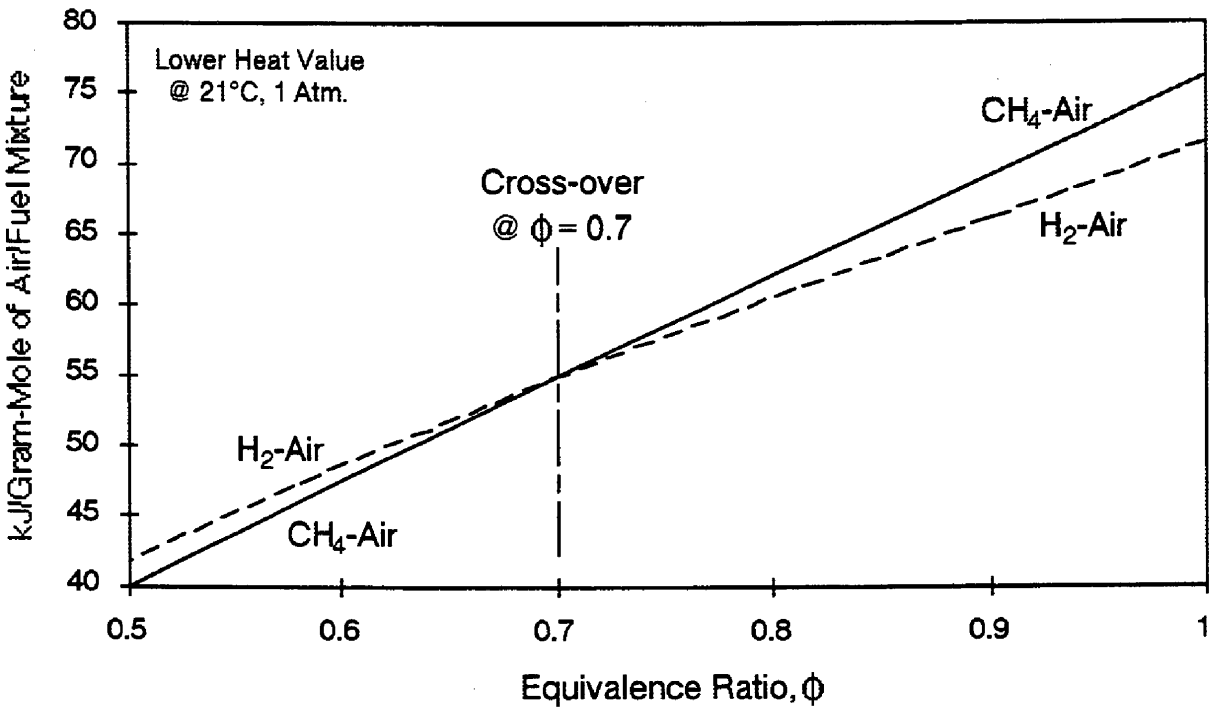

Figure 5-4. Molar energy densities for H_2-air vs. CH_4-air at varying ϕ.

The two effects that are responsible for the cross-over in Figure 5-4 are:

- H_2 delivers more lower heat value per unit of oxygen consumed than does CH_4.
- H_2 displaces more air than does CH_4.

Near stoichiometric, the latter effect dominates. At lean mixtures where the displacement of air by the fuel gases is less, the former effect dominates. In all cases the differences are small, especially for Hythane--at most 30% H_2 by volume in this project.

The actual increase in BMEP in the lean range is significantly greater than the increase indicated by Figure 5-4. Figure 5-5 compares the actual increase in BMEP with 30% H_2 as a percentage of the CH_4 baseline. The 7% improvement at ϕ =0.65 is attributed mainly to improved combustion stability.

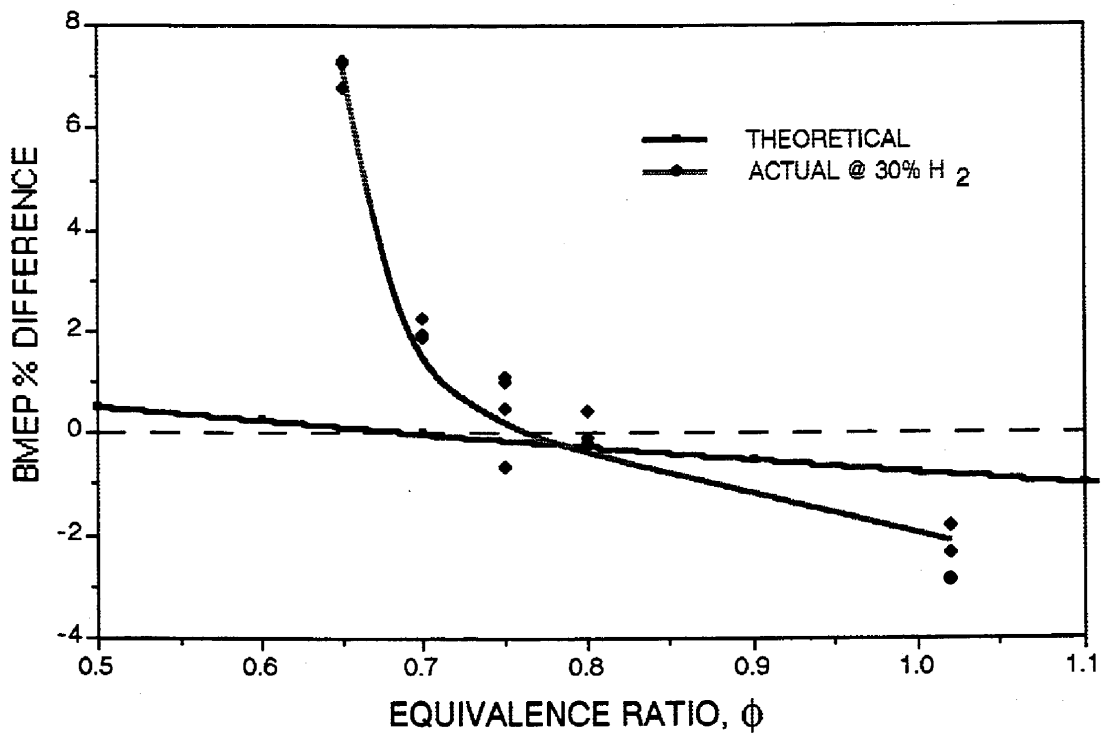

Figure 5-5. Comparison between theoretical and actual BMEP improvement with 30% H_2 in CH_4 at 80 kPa MAP.

5.2 Effects of H_2 on Brake Thermal Efficiency

The sacrifice of excess performance for emissions reduction is not an "all or nothing" proposition. It is possible to reduce emissions, to some extent, while maintaining some of the performance advantage of H_2. Assuming that the base case with CH_4 provides adequate BMEP under all circumstances, performance improvements with H_2 can be used to increase efficiency.

Just as with BMEP, BTE improvements with H_2 are only observed near the lean limit. Figures 5-6 and 5-7 show zero or slightly negative changes in BTE with H_2 additions for $\phi > 0.7$. However, with $\phi = 0.65$ and 0.60, there is a significant improvement in BTE with increasing H_2 content. At 35 kPa the engine could not be operated below $\phi = 0.7$ without adding hydrogen. At wide open throttle, $\phi = 0.65$ was accessible with pure CH_4. However, the BSHC emissions were reduced by 60% with as little as 5% hydrogen by energy content (15% by volume).

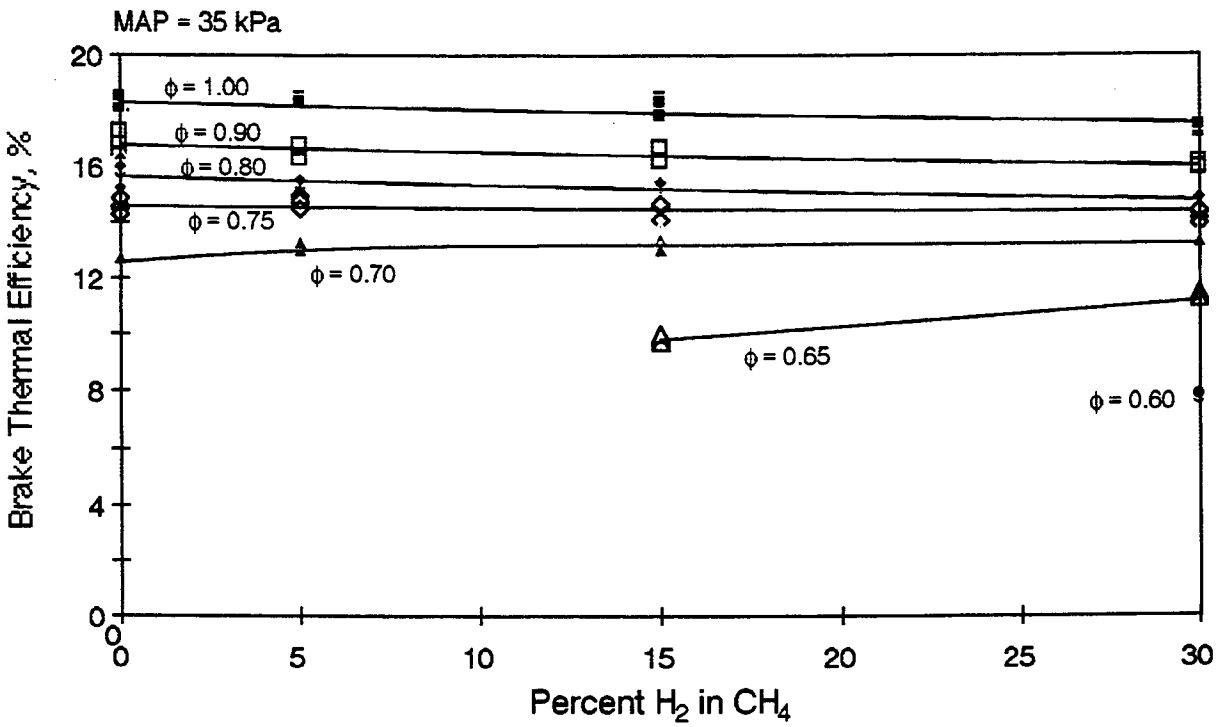

Figure 5-6. Effect of H_2 on BTE at 35 kPa MAP at various constant equivalence ratios.

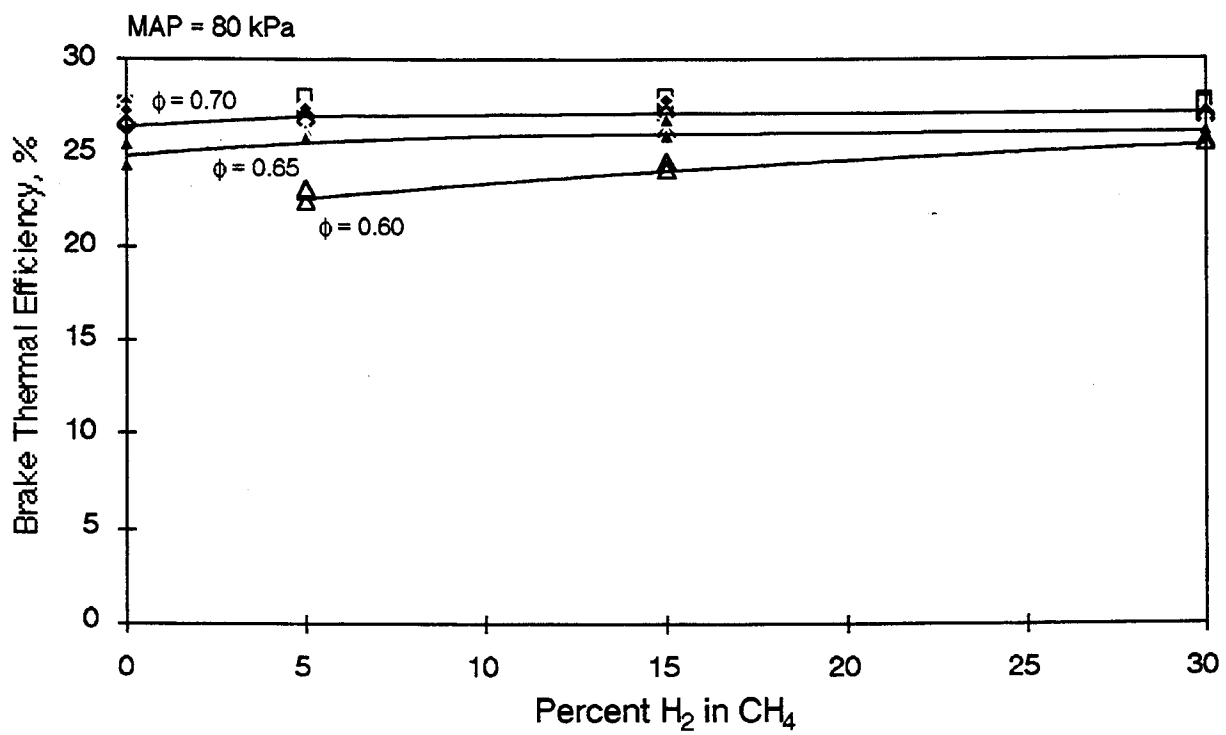

Figure 5-7. Effect of H_2 on BTE at 80 kPa MAP at various constant equivalence ratios.

5.3 Performance Conclusions

The addition of H_2 to CH_4 with $\phi \leq 0.7$ improves BMEP and BTE. The improvement in BMEP is, to a small extent, attributable to greater charge energy density with $\phi < 0.7$. A more potent effect results from improved combustion stability. These improvements come with significant reductions in BSHC and pre-catalyst CO but little change in NOx. The performance improvements may be sacrificed to reduce NOx by retarding spark, operating leaner or perhaps with EGR.

6.0 Project Conclusions

Conclusions about emissions and performance are presented in greater detail in Sections 4.6, 4.11 and 5.3. Strongly "leveraged" benefits were observed in terms of emissions reductions and performance improvements relative to percent hydrogen energy substitution in methane.

6.1 Lean Burn Emissions

- H_2 enables leaner operation.
- NOx decreases rapidly with equivalence ratio.
- H_2 enables NOx reduction via leaner operation at part load conditions.
- H_2 increases NOx and torque at wide open throttle near the lean limit.
- H_2 enables NOx reduction at equal full load conditions via leaner operation, spark retard, or exhaust gas recycle (the later not tested).
- H_2 decreases HC and CO emissions.
- Post-catalyst CO emissions are negligible, with or without H_2.

6.2 Stoichiometric Emissions

- Emissions are extremely sensitive to equivalence ratio, ϕ: Optimum $\phi = 1.005$, with or without H_2.
- $\pm$ 1% deviation from $\phi = 1.005$ causes 10-fold changes in CO and NOx.
- At $\phi = 1.005$, post-catalyst CO and NOx were so low that $\pm$ 50% change was below instrument resolution.
- H_2 effects, if any, were within the range of scatter for CO at 1.1 grams/kW-hr and NOx at 0.2 grams per kW-hr
- 1.5% lean error is caused by zirconia-based oxygen sensors with CH_4 or Hythane: This contributes to the popular misconception that natural gas engines are high NOx emitters--its just a calibration problem.
- THC averaged about 2.3 grams per kW-h with this catalyst.
- NMHC, with or without H_2, is negligible with this catalyst in FTP tests.

6.3 Performance

- H_2 improves torque with $\phi \leq 0.7$
- The above is mainly due to greater thermal efficiency with H_2
- A small torque improvement is due to greater charge energy density with H_2

6.4 Exploitation of Hydrogen Advantages

There are two fundamental advantages of adding 15 to 30 volume % hydrogen to natural gas in the lean burn range;

1) at any part load condition, Hythane will provide the same performance and fuel economy with a leaner mixture and a higher manifold air pressure, hence less NOx (up to a limit imposed by incomplete combustion).

2) at wide-open throttle, Hythane provides efficiency and torque advantages near the lean limit that may be sacrificed to get a NOx reduction at equal performance and fuel consumption.

Advantage 1) may be exploited by burning the leanest mixture and highest manifold pressure possible at all part load conditions without exceeding the natural gas baseline fuel consumption or HC emissions.

Advantage 2) may be exploited at any wide-open condition by a) leaning the mixture until either HC or fuel consumption rises or torque falls to equal the natural gas baseline (whichever occurs first) and by b) retarding the spark until either HC or fuel consumption rises or torque falls to equal the natural gas baseline (whichever occurs first). A combination of a) and b) may also be effective.

6.5 Recommendations for Future R&D

For the same reasons that hydrogen extends the lean limit of methane combustion, it should extend the tolerance for exhaust gas recycle (EGR). It is common knowledge that EGR has strong effects on NOx emissions. A future study to explore the synergistic effects of hydrogen and EGR on natural gas engine performance and emissions is warranted.

The ultralow emissions levels that were observed when the test engine was held precisely on the optimum air/fuel ratio for three-way catalysis are truly remarkable. Highly precise mixture control systems and advanced oxygen sensors should be high priority objectives for future development.

7.0 Relevant Literature

The effects of hydrogen on the combustion of hydrocarbons has been studied in laboratory experiments and engines since the dawn of combustion science[1]. The literature[2] provides summaries of contributions toward understanding how hydrogen affects combustion of other fuels. Several publications during the last 20 years are applicable to this study[3, 4, 5, 6, 7, 8, 9, 10, 11, 12]. Recent publications in this area include references [13, 14, 15, 16, 17, 18, 19, 20].

[1] Burstall, A. F., "Experiments on the Behavior of Various Fuels in a High Speed Internal Combustion Engine", Institution of Automobile Engineers, Vol. 22, (1927). This work included methane, hydrogen and mixtures of the two in "town gas".

[2] Lewis, B. and von Elbe, *Combustion, Flames and Explosions of Gases*, 2nd ed. Academic Press, New York (1961).

[3] D.B. Eccleston and R.D. Fleming, CLEAN AUTOMOTIVE FUEL , Bureau of Mines Automotive Exhaust Emissions Program, Technical Progress Report 48, Feb. 1972

[4] The Aerospace Corp., Lean Combustion in Automotive Engines, ERDA CONS/1101-1 (1976)

[5] Parks, F.B., "A Single Cylinder Study of Hydrogen Rich Fuels", SAE 760099, (1976)

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[7] Finegold, J.G., "Reformed Methanol Vehicle System Considerations", Proc. 18th Intersociety Energy Conversion Engineering Conf., Orlando (1983).

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[11] A.A. Sheipak & V.N. Kabalkin, "Adaption of Truck to Gasoline-Hydrogen Fuel," Moscow Automobile Construction Institute, USSR.

[12] A.N. Podgorny & A.I. Mishchenko, "Hydrogen Application to Gasoline AutomotiveEngines," Institute for Problems in Machinery Academy of Sciences, USSR.

[13] Lynch, F.E. and Egan, G.J., "Near Term Introduction of Clean Hydrogen Vehicles via H_2-CNG Blends", Proc. 4th Canadian Hydrogen Workshop, Toronto (1989).

[14] A. Ando, as reproduced in *Present and Future Automotive Fuels*, ed. O. Hirau, R. Pefley, Wiley (1989).

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[17] Meyer, R. C. and Hedrick, J.C., "Advanced Gas Prime Mover Concepts", Final Report SwRI-1613, for Gas Research Inst., Cont. No. 5086-233-1442 (1990).

[18] J. Hacohen, G. Pinhasi, Y. Puterman & I. Sher, "DrivingCycle Simulation of a Vehicle Motored by a SI Engine Fueled with H_2- Enriched Gasoline," International Journal of Hydrogen Energy, Vol. 16, No. 10, 1991, pp. 695-702.

[19] Swain, M. R. et al., "The Effects of Hydrogen Addition on Natural Gas Engine Operation", SAE Paper No. 932775 (1993).

[20] Cattelan, A., et al, "Hythane and CNG Fueled Engine Exhaust Emission Comparison", Proc. 10th World Hydrogen Energy Conf., Miami (1994).

Appendix A:
Transient Vehicle Tests

A.1 Possible Effects of Hydrogen on Control System Stability

The steady state test results for stoichiometric operation with a three-way catalyst (see Section 4.7 through 4.11) were inconclusive regarding hydrogen effects. The post-catalyst emissions were so low that the emissions instruments were unable to measure them precisely. Figure 4-19 shows that natural gas engine emissions, with or without hydrogen, can be extremely low if the mixture is controlled precisely at the optimum value for a three-way catalyst. The correct equivalence ratio for optimum use of the Englehard three-way catalyst, with natural gas or Hythane is ϕ =1.005.

Any differences between methane and Hythane in Figure 4-19, duplicated below as Figure A-1, are below test sensitivity. This does not mean that there are no differences. For example, diluted sample NOx data past ϕ = 1.005 are typically 1 ppm ± 2-3 ppm. Some NOx readings are negative. Therefore, differences of the magnitude observed in the transient tests discussed below are "within scatter" of Figure A-1.

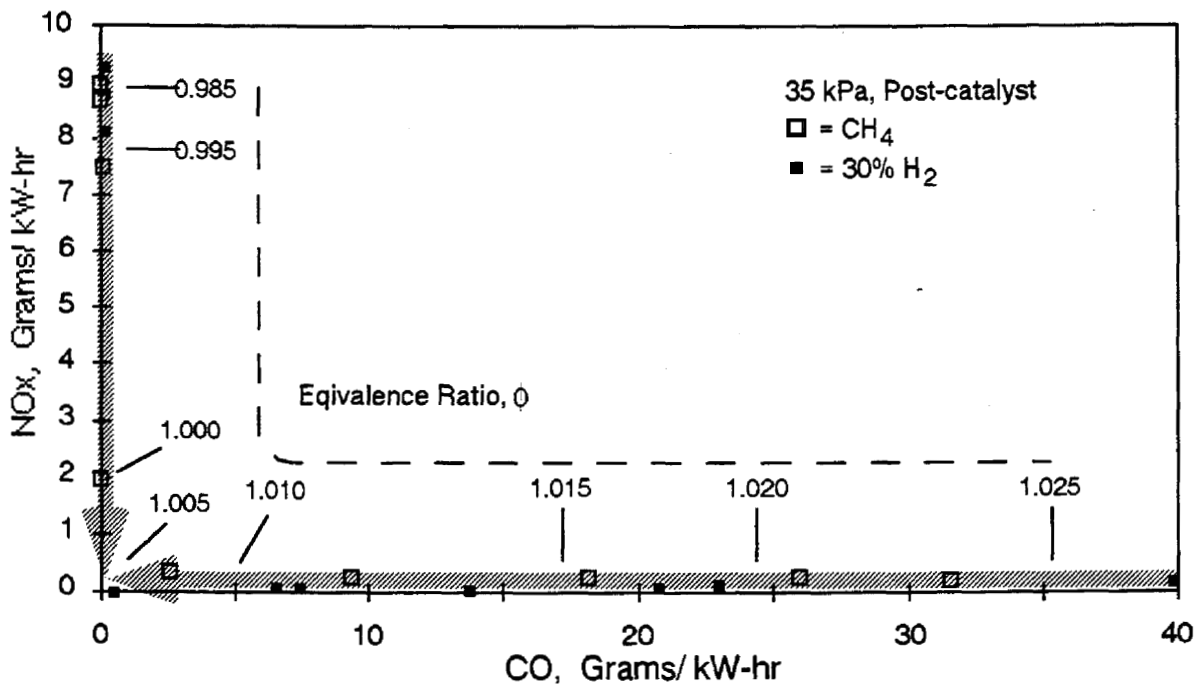

Figure A-1. NOx vs. CO characteristic of the three-way catalyst. The slightly lower NOx shown for Hythane is within the noise level of the instruments.

This emphasizes the importance of control system precision and response rates in transient tests. Virtually all of the pollution accumulated in a transient Federal emissions test (FTP) are the result of a cold catalyst early in the test and off-optimum transient operation. The present hypothesis for explaining the differences observed in

transient tests is that the stabilizing effect of hydrogen on natural gas combustion reduces misfiring. The response of the control system to misfires may result in less precise mixture control because of the resulting oxygen in the exhaust.

The control system of the S-10 Hythane prototype goes full rich during misfire circumstances like downhill or other modes of operation where the gasoline EGR schedule is excessive for natural gas operation. Combustion is supposed to go to completion on the catalytic surfaces of the oxygen sensor, even if the engine misfires. Apparently this is not quite true with common zirconia oxygen sensors. The sensor interprets exhaust oxygen due to misfires as a lean deviation. The control system goes full rich trying to compensate for the error. Hydrogen stabilizes the combustion of natural gas and reduces misfiring. This may reduce the number and duration of rich errors over the course of a Federal Emissions test (FTP).

A.2 FTP Test Results

Whether or not this hypothesis is correct, hydrogen clearly has strong effects on FTP emissions of a natural gas vehicle. The first FTP comparison of Hythane and natural gas was made by the California Air Resources Board (CARB) in 1991. Figure A-2 is a four-test average CO and NOx comparison. With or without the hydrogen additive, HCI's Chevrolet S-10 meets CARB's Ultralow Emission Vehicle (ULEV) criteria. Hydrocarbon emissions are not plotted in Figure A-2. The tests show a small THC improvement with Hythane but non-methane hydrocarbon (NMHC) is extremely low

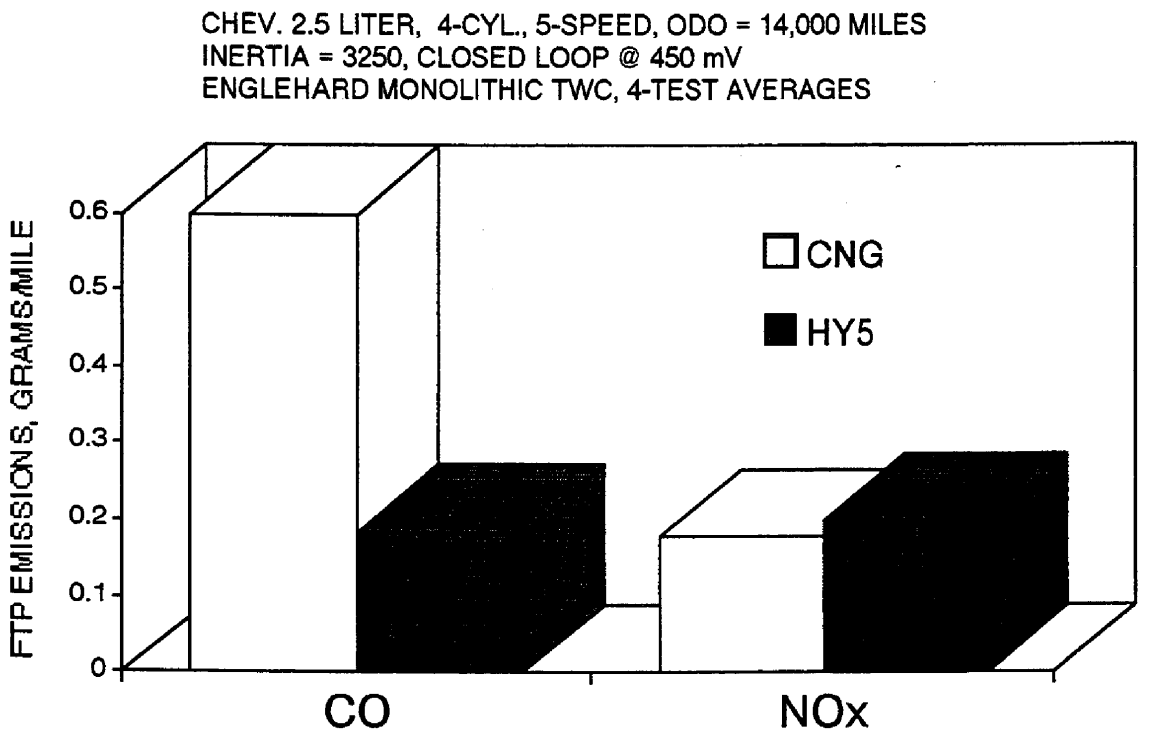

Figure A-2. "HY5", Hythane with 5% hydrogen by energy content, shows much lower CO and slightly higher NOx than natural gas in CARB tests of HCI's S-10 prototype.

(ca. 0.01 gram per mile) with or without hydrogen. The differences in CO and NOx emissions are therefore of greatest interest. A large reduction in CO emissions with Hythane is realized at the expense of a small increase in NOx, relative to pure natural gas.

The trend observed in the 1991 CARB tests has been confirmed with four different vehicles at four EPA-certified emissions laboratories, two at high altitude and two at low altitude. Table A-I is a description of Hythane projects to date. Figure A-3 shows data from the Denver Hythane Project, courtesy of the Colorado Dept. of Health (CDH) Emissions Tech Center. The vehicles are much heavier than HCI's S-10 and the emissions are higher, but two-test averages for each of two gaseous fueled trucks show the same trend as the CARB tests; Hythane produces lower CO and higher NOx.

Gasoline data from a third identical truck in the Denver Hythane Project are also shown in Figure A-3. The THC advantage shown for gasoline does not follow through in NMHC measurements. NMHC is consistently lower with the gaseous fuels.

This trend repeated itself in high altitude tests of the S-10 at CSU's National Center for Vehicle Emissions Control and Safety (NCVECS) and again at the Environmental Protection Agency (EPA) in Ann Arbor, MI. Figure A-4 shows EPA's "preliminary"[1] test results for a van from the Pennsylvania Energy Office (PEO) Hythane Project. The test vehicle is a National Fuel Gas service van from Erie, PA. The only similarity between this van and HCI's S-10 or the Denver Hythane Project's heavy-duty pick-ups is a GM label and an HCI-modified IMPCO fuel control system. All test data from the projects listed in Table I indicate that, when hydrogen is added to natural gas in a test vehicle with no other changes, CO emissions go down by a significant margin and NOx goes up by a smaller margin.

[1] The EPA report is not yet available. The data in Figure 8 are from notes taken by F. Lynch during tests in July 1993.

Table I. Hythane Vehicle Test Projects to Date.

HCI/American Lung:	(1989)
Vehicle:	1979 Dodge D-50 Pickup, 2.6 liter 4-Cylinder, Turbo Intercooled, HCI Parallel Induction, Open Loop
Funding:	HCI Internal R&D
Participants:	HCI (lead) American Lung Assn. (Riverside, CA), Tren Fuels, Nat'l. Ctr. Vehic. Emissions Cont. & Safety
HCI Hythane Prototype:	(1990 - present)
Vehicle:	1991 Chevrolet S-10 Pickup, 2.5 liter 4-Cylinder Impco CA125 mixer, FCP1 Controller, HCI Interface
Funding:	HCI Internal R&D
Participants:	HCI (lead) California Air Resources Board, City and County of Denver, Colorado Dept. of Health, Impco, Englehard, Nat'l. Ctr. Vehic. Emissions Cont. & Safety, Tren Fuels.
Denver Hythane Project:	(1991 - 1993)
Vehicles:	Three 1991 Chevrolet Cheyenne Pickups, 5.7 liter V-8 Impco CA300 mixer, FCP1 Controller, HCI Interface
Funding:	Urban Consortium (DOE), Air Products & Chemicals, Public Service Co. of Colorado
Participants:	City and County of Denver (lead), Air Products & Chemicals, Colorado Dept. of Health, Public Service Co. of Colorado, HCI
PEO Hythane Project:	(1992 - 1993)
Vehicles:	1992 Chevrolet Van, 4.3 liter V-6 Impco CA300 mixer, FCP1 Controller, HCI Interface
Funding:	Pennsylvania Energy Office, Cost Sharing; National Fuel Gas (Erie, PA) Air Products & Chemicals, Bruderly Engineering, HCI
Participants:	Bruderly Engineering (lead), Air Products & Chemicals National Fuel Gas, U.S. EPA (Ann Arbor), HCI

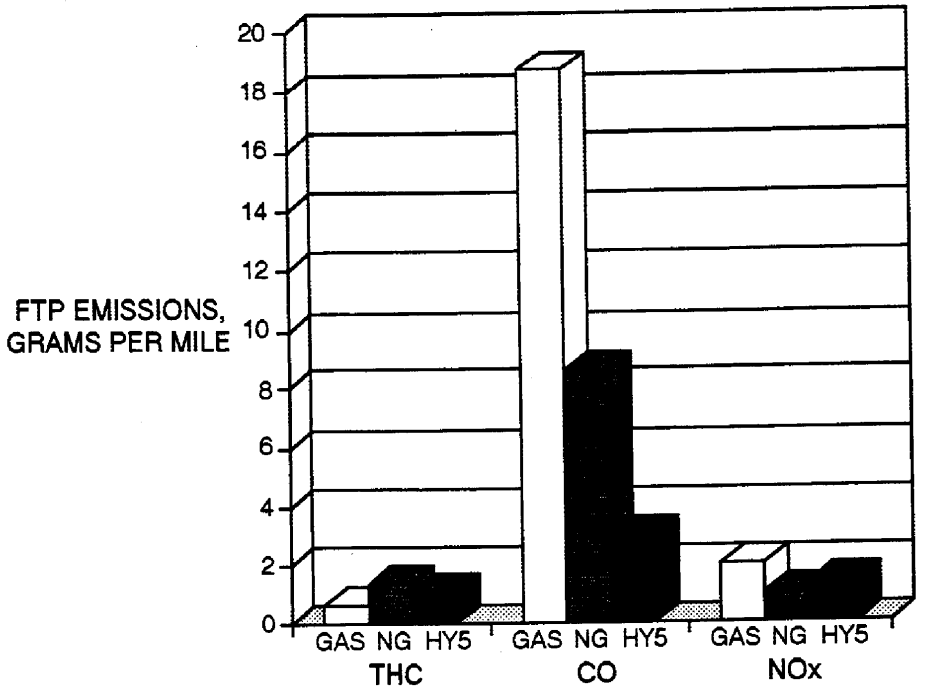

Figure A-3. CDH emissions comparison during Round 2 of the Denver Hythane Project show the same trend as Figure A-2.

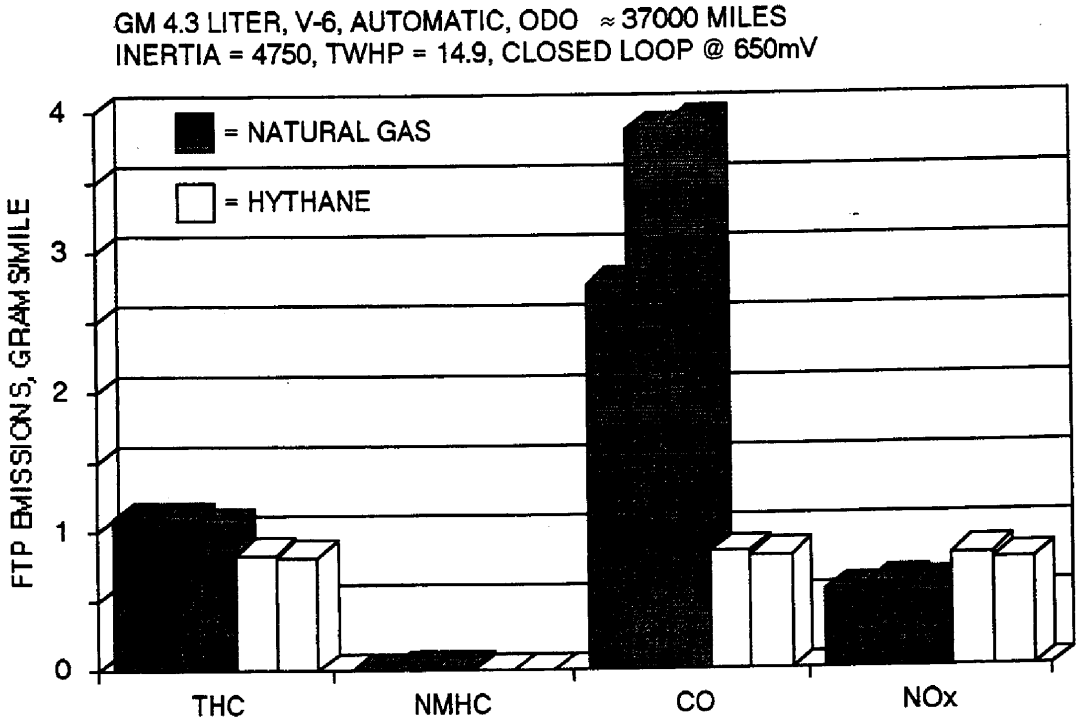

Figure A-4. Preliminary FTP emissions test results from EPA during the PEO Hythane Project. As before, CO is lower and NOx is higher with Hythane.

A.3 "Hot 505" Test Results with Mixture Enrichment

It is common knowledge that CO emissions go down as NOx emissions go up during rich-to-lean calibration changes with hydrocarbon fuels. The question then becomes, "are the CO reductions observed with Hythane the result of a control system calibration shift caused by hydrogen?" This was explored during the Denver Hythane Project.

Figure A-5 shows "Hot 505"[2] test results taken at the conclusion of the Denver Hythane Project. The calibration of the control system was shifted from an oxygen sensor control voltage of 440 mV to 762 mV (slightly richer). As expected, this caused CO to increase and NOx to decrease. If the natural gas and Hythane emissions had become equal at any particular control voltage, the usefulness of the hydrogen additive would be questionable. That is not what happened. Based on the results shown in Figure A-5, it appears possible to get a leverage factor of about 10 on NOx and CO, i.e.; 5% hydrogen by energy content makes 50% reduction in emissions. The THC leverage factor is about 6.

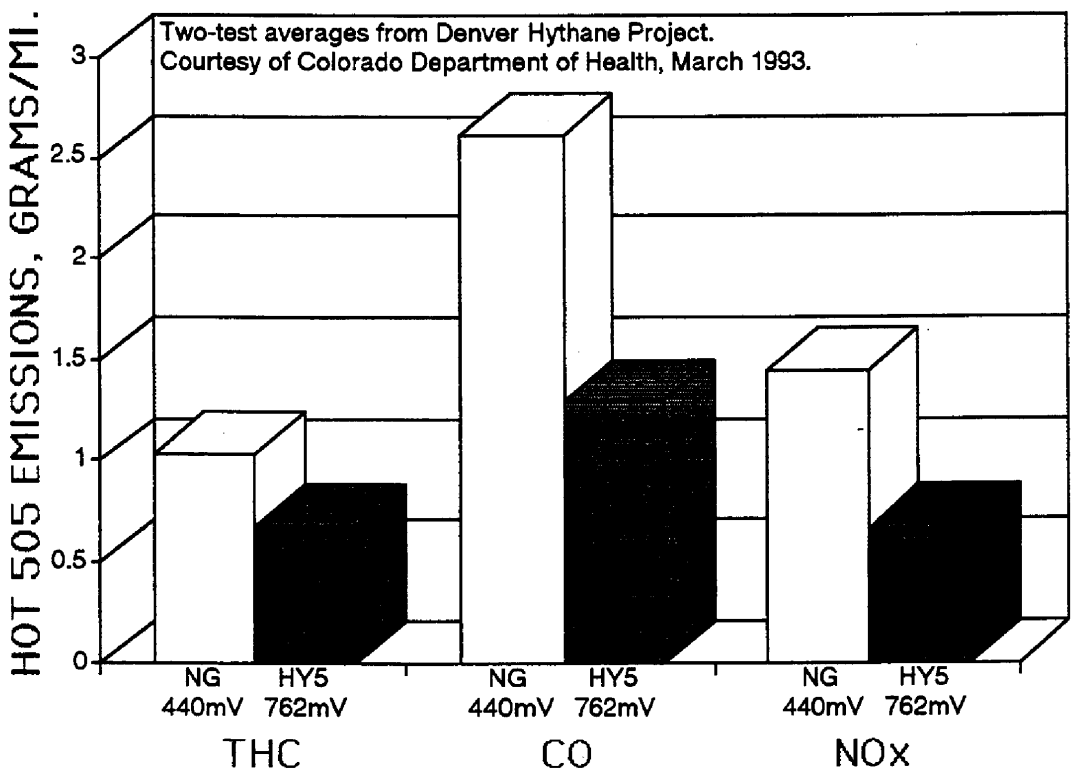

Figure A-5. Hot 505 emissions with natural gas and HY5 at different oxygen sensor control voltages.

A.4 Transient Vehicle Test Conclusions

The advantages of Hythane for operation with near stoichiometric mixtures and a three-way catalyst are not completely understood. Strong effects, consistently

[2] A "hot 505" test is a subset of the Federal test commonly used for research purposes.

observed in transient tests of four vehicles by four different laboratories, were not apparent in the steady state engine tests conducted during this project. Further work is needed to understand and fully exploit the effects observed in transient tests.

A.5 Acknowledgements

HCI gratefully acknowledges the contribution of the following individuals and their organizations in conducting the projects and obtaining the data reported in this appendix:

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Bill Howell

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Dr. Steve Foute, Deborah Kielian, Terry Henry, Mike Merino

National Center for Vehicle Emissions Control & Safety;
Dr. Joe Beebe, Dr. Birgit Wolff

National Fuel Gas;
John Groth, Ronald Gray

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16. Abstract (Limit: 200 words)
The overall objective of the work was to seek homogeneous blend ratios of hydrogen:methane that provide "leverage" with respect to exhaust emissions or engine performance. The leverage sought was a reduction in exhaust emissions or improved efficiency in proportions greater than the percentage of hydrogen energy in the blended fuel gas mixture. The scope of the study included the range of air/fuel mixtures from the lean limit to slightly richer than stoichiometric. This encompasses two important modes of engine operation for emissions control; lean burn pre-catalyst (some natural gas engines have no catalyst) and post-catalyst; and stoichiometric with three-way catalyst. The report includes a brief discussion of each of these modes.

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