EVALUATION OF CATALYST AND ALCOHOL FUEL EMISSIONS CONTROL FOR A SMALL FOUR CYCLE UTILITY ENGINE

by

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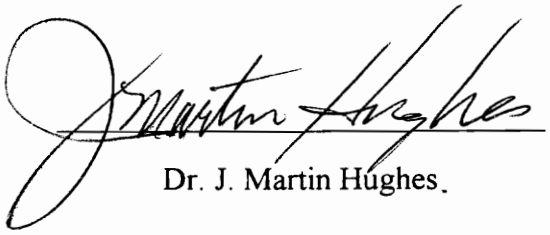

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ABSTRACT

This research investigated emissions of formaldehyde, acetaldehyde, carbon monoxide, and hydrocarbons from a small utility engine fueled with mixtures of gasoline, ethanol, and methanol. Measurements made for each fuel mixture, with and without a catalyst, allowed a qualitative evaluation of the catalyst effect on the aforementioned pollutants. California Air Resources Board small utility engine regulations motivated this research.

The engine was loaded by an electrical generator with output of approximately 1000 watts to simulate actual operating conditions. Operation occurred at steady state conditions with a fixed air/fuel ratio.

Alcohol addition reduced emissions of carbon monoxide (CO) and total hydrocarbons (THC) from gasoline only levels. Adding a 50% volume of ethanol to the fuel, CO and THC emissions decreased 75% and 50% respectively. Adding 50% methanol reduced CO and THC 95% and 60% respectively.

Qualitatively, no catalytic control of CO or THC was demonstrated with any of the fuels used. However, a lack of replicates prevented quantification of catalyst results.

Both formaldehyde and acetaldehyde emissions increased with the addition of ethanol. Addition of 50% ethanol resulted in an increase of at least 600% in acetaldehyde emissions. Methanol addition increased formaldehyde emissions, but correlation of emissions with alcohol content was not possible. Acetaldehyde emissions appeared to decrease with increasing methanol content after an initial increase from the gasoline only values.

No catalytic oxidation of formaldehyde was demonstrated, but acetaldehyde emissions may have been decreased by the catalyst when employing 50% ethanol fuel.

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I. INTRODUCTION

The establishment in California, of new emissions standards for small utility engines, motivated this research. The California Air Resources Board (CARB) promulgated regulations to reduce the exhaust emissions of small utility engines. The class of small utility engines includes engines on hand held and non-hand held devices, not intended for on road vehicle use. These devices include, but are not limited to, lawn mowers and other lawn and garden equipment, chain saws, portable generators, and other two and four-cycle internal combustion (IC) engine powered products. Not included are off road motorcycles and recreational vehicles, that are covered by other regulations. The regulations deal with emissions of carbon monoxide (CO), oxides of nitrogen (NO_X), and total hydrocarbons (THC), and take effect in two phases. The less stringent emissions standards of 1994 may be met by engines using current small engine technology and mixture enleanment. Mixture enleanment is the term used for operating engines with high air/fuel ratios to provide additional oxygen which allows more complete combustion. The more stringent 1999 emissions standards may, and probably will, require the use of catalytic converters and other emission control techniques. (CARB, 1990) Table I presents CARB emission standards applicable to the engine under study. The 1999 standards do not apply to specific size engines, but whether or not the devices they operate are handheld. Handheld for the purposes of these regulations means that the operator of the device fully supports the weight of the device.

Table I - CARB Utility Engine Emission Standards for Total Hydrocarbons, Oxides of Nitrogen, and Carbon Monoxide

Engine Displacement/Class	Year Effective	THC + NO_X (g/kW-hr)	CO (g/kW-hr)
<225 cc	1994	16.1	402
≥ 225 cc	1994	13.4	335
Non-hand held equip't	1999	4.3	134

Total Hydrocarbons (THC), Oxides of Nitrogen (NO_X), and Carbon Monoxide(CO) Specific Emissions Based on Engine Brake Horsepower (BHP) Using SAE J1088 Procedure

Adapted from California Air Resources Board "California Exhaust Emission Standards and Test Procedures for 1991 and Subsequent Model Year Utility and Lawn and Garden Equipment Engines"

Pollutant emissions from small, gasoline powered utility engines contribute greatly to total air pollution in California as well as other areas of the country. It was estimated that utility engine emissions of hydrocarbons and carbon monoxide were equivalent to five percent and four percent respectively of mobile source emissions of these pollutants statewide (CARB, 1990). This was roughly equivalent to an additional 3.5 million 1991 automobiles driven 16,000 miles each. Catalytic control of pollutants from these engines has been suggested, and previous use of catalysts demonstrated success in reducing carbon monoxide and hydrocarbon emissions. This thesis evaluated the usefulness of gasoline/alcohol fuel mixtures and catalytic control on such engines to reduce emissions of formaldehyde, acetaldehyde, total hydrocarbons and carbon monoxide.

Previous studies determined emissions from small utility engines, and investigated the effects of gasoline/alcohol fuel mixtures on aldehyde emissions. This thesis focuses, for what appears to be the first time, on emissions and control of aldehydes from a small utility engine, and the effects of gasoline/alcohol fuel blends on catalytic control efficiency.

Alcohol fuel additives were used for fuel oxygenation in the past, and continue to be used in the present. Fuel oxygenation is the process of adding oxygen containing compounds to a fuel to improve combustion characteristics. Alcohols such as ethanol and methanol are renewable fuels which are readily available, and reasonably inexpensive. These factors make the general use of alcohol fuel additives for emissions control attractive to anyone operating small utility engines.

Gasoline/alcohol fuel mixtures are commonly designated by the volume percentage of alcohol in the mixture. As an example, a common gasoline/methanol fuel blend made up of 85% methanol and 15% gasoline is designated M85. This research evaluated emissions generated from the combustion of the fuel mixtures listed below:

1. Gasoline with no added alcohol

2. Methanol mixtures from 10 to 50%: M10, M25, and M50
3. Ethanol mixtures from 10 to 50%: E10, E25, and E50

Fuel methanol can be used in higher concentration than those evaluated here. However, because of methanol's corrosive tendencies, engines using those fuels must be specially prepared. Therefore, this study was limited to the concentrations listed above.

Exhaust constituents characterized before and after the catalytic converter, for each fuel mixture, were carbon monoxide (CO), carbon dioxide (CO_2), oxygen (O_2), total hydrocarbons (THC) as carbon, formaldehyde, and acetaldehyde. Although specific emissions from utility engines are typically expressed in terms of engine brake horsepower (BHP), the use of generator power output is conservative, in that this power will be about 5% less than BHP. Emissions were measured at a power rating expected under normal operating conditions, and while operating at a fixed air/fuel ratio.

The objectives of this research were to determine:

- the effect of ethanol and methanol fuel addition on the emissions of carbon monoxide and total hydrocarbons from a small utility engine,
- the effect of ethanol and methanol fuel addition on the emissions of formaldehyde and acetaldehyde from a small utility engine,
- the effectiveness of a catalytic converter on control of carbon monoxide, total hydrocarbons, formaldehyde, and acetaldehyde, and
- the correlation between fuel alcohol content and catalytic converter efficiency.

Although it was desirable to determine whether the emission control techniques investigated in this research would generate compliance with the 1999 CARB standards, differences in testing methods did not allow this comparison. These differences are pointed out in the discussion of testing methods.

II. LITERATURE REVIEW

Basic Engine Measurements

Measurement of basic engine operating parameters was used to determine whether the engine operated as expected, based on manufacturer specifications and accepted parameters for gasoline engine operation. Measurement of air and fuel rates into the engine allowed calculation of the air/fuel ratio, an important combustion parameter. These measurements also allowed the exhaust flow rate to be estimated. In order to measure air flow into a small engine such as the one under study, flow pulsations at the intake had to be damped out. Taylor (Taylor, 1968) described the use of dampening chambers to reduce these flow pulsations and discussed the sizing of these chambers. Other small engine test facilities found in the literature (Donohue *et al.*, 1972, Hare and White, 1991) also employed dampening chambers. Three researchers (Donohue *et al.*, 1972, Hare *et al.*, 1973, Taylor, 1968) presented various methods of measuring the intake air flow rate. Donohue *et al.* and Hare *et al.* referred to the use of laminar flow meters, while Taylor recommended the use of a calibrated orifice. Pitot tubes can also be used. Although sophisticated electronic flow meters can be used to measure fuel rates, Taylor and Hare *et al.* presented a less expensive burette and timer method for making this measurement. A method for estimating engine air/fuel ratios from exhaust gas analyses (Spindt, 1965) was consulted for use in this research.

Standard Emissions Measurements

Common pollutants emitted from IC engines included carbon monoxide and hydrocarbons. As carbon monoxide is considered a priority pollutant with specific ambient standards, control of this pollutant is important. Hydrocarbons emitted into the atmosphere react with oxides of nitrogen in the presence of sunlight to form photochemical smog or ozone pollution. As this pollutant is prevalent in California and

other highly urbanized areas, control of hydrocarbon emissions is also important. Table II below presents typical values for CO and THC emissions from gasoline fueled, single cylinder, four-cycle small engines found in the literature. Also presented are EPA emission factors developed from studies of many different classes of stationary, industrial, gasoline powered IC engines.

The SAE Modal Testing Method J1088 can be used to collect and analyze emissions from small engines (Donohue *et al.*, 1972, Hare *et al.*, 1973). With J1088, modal testing is performed wherein the engine is operated at various loads while the air/fuel ratio is varied. Donohue *et al.* performed a version of modal testing in which the engines were run at three power levels with three air/fuel ratios: fuel lean, manufacturer recommended, and fuel rich. Collected samples included combined emissions from all these modes. Donohue *et al.* recommended that future testing be performed at the manufacturer recommended carburetor setting. Other researchers (Hare *et al.*, 1973, Hare and White, 1991) justified alternative testing methods for small engines as well.

Determination of CO and CO_2 in combustion exhaust using non-dispersive infrared (NDIR) methods dated back to 1965 (Donohue *et al.*, 1972, Hare *et al.*, 1973, Spindt, 1965). The polarograph (Donohue *et al.*, 1972), electrochemical methods (Hare *et al.*, 1973), and a paramagnetic analyzer (Spindt, 1965) determined oxygen concentration. The same researchers (Donohue *et al.*, 1972, Hare *et al.*, 1973, Spindt, 1965) used a flame ionization detector (FID) to measure total hydrocarbons.

Table II - Specific CO and THC Emissions from Gasoline Fueled, Single Cylinder, Four-Cycle Small Utility Engines

Source	Min. CO (g/kW-hr)	Mean CO (g/kW-hr)	Max. CO (g/kW-hr)	Min. THC (g/kW-hr)	Mean THC (g/kW-hr)	Max. THC (g/kW-hr)
Donohue *et al.*, 1972[a]	107.5	185.4	255.3	2.7	7.7	16.1
Hare and White, 1991[b]	471	480	491	23.7	24.1	24.9
EPA AP-42 Emission Factors (US EPA, 1992)[c]		267			8.96	

[a]Donohue *et al.* reported the results of a Bureau of Mines test of 29 four-cycle engines ranging from 2 to 20 horsepower (HP). The Bureau of Mines employed a form of modal testing wherein the engines under study were run at full, intermediate, and low power settings while varying the air/fuel ratio through rich, lean best power, and lean settings. Results reported here are for the full load, condition and lean best power setting, which best represents the operating conditions used in this research.

[b]Hare and White tested a Tecumseh Model OVRM40, 3.5 HP four-cycle , overhead valve engine operated at 3,200 RPM. The testing method employed a modified SAE J1088, 6-Mode procedure. The results reported are those for the aggregate sample from the six testing modes.

[c]Aggregate emission factors from the EPA AP-42 were developed by testing a wide variety of utility engines up to 250 HP. It was recommended that these emission factors be applied to a population of engines rather than to individual powerplants.

Due to the oxygen content of alcohols, decreased emissions of CO are expected with increasing alcohol content. Automobiles operating with methanol fuel blends demonstrated this behavior (Williams *et al.*, 1990). Although his results varied, Williams demonstrated a decrease in CO emissions up to 50% using gasoline fuel with 85% methanol added. The same research showed that hydrocarbon emission rates also decreased with increasing fuel methanol content for automobiles (Williams *et al.*, 1990). Hydrocarbon emissions decreased 78% with the addition of 85% methanol to the fuel. Likewise, small engines operating with ethanol added to the fuel emit less CO and hydrocarbons (Hare and White, 1991). Although the fuel concentration of ethanol was not specified, this reference used a "reformulated" gasoline containing ethanol for one study. Most ethanol enhanced gasoline mixtures include 10% ethanol. Carbon monoxide emissions decreased approximately 10% (from 480 g/kW-hr to 433 g/kW-hr), while non-methane hydrocarbon emissions decreased 20% (from 21.5 g/kW-hr to 17.2 g/kW-hr).

Aldehyde Emissions Measurements

When alcohol is combusted as a fuel, aldehyde byproducts result. These aldehydes can be ozone formers, irritants, or carcinogens. Although chronic exposure studies of aldehyde effects on humans is lacking, exposure to formaldehyde at levels less than 1 ppm were shown to cause irritation to the eyes, throat, and respiratory system (National Research Council, 1976). The American Conference of Governmental Industrial Hygienists has listed formaldehyde as a known or suspected human carcinogen (ACGIH, 1991). Acetaldehyde produced irritation similar to formaldehyde when concentrations exceeded 200 ppm (National Research Council, 1976). For gasoline combustion formaldehyde and acetaldehyde constitute 75 - 80% of all aldehyde emissions (National Research Council, 1976). These factors make investigation of formaldehyde and acetaldehyde emissions important.

It was expected that alcohol combustion would result in an increase of emissions of the aldehyde oxidation product of the alcohol being combusted. Ethanol combustion would produce acetaldehyde while methanol combustion would result in increased formaldehyde emissions. The literature results bore these ideas out. Table III shows small engine aldehyde emissions from one reference and EPA emission factors. Formaldehyde emissions increased four fold when 85% methanol fuel was used in automobile studies (Williams *et al.*, 1990). This phenomenon was accompanied by a 19% decrease in acetaldehyde emissions to almost zero for 100% methanol fuel. Small engines using ethanol enhanced fuel showed increased acetaldehyde emissions (Hare and White, 1991). Acetaldehyde emissions increased slightly over 200% with the ethanol enhanced, reformulated gasoline. Again, no fuel fraction was supplied for the added ethanol.

Although one reference mentioned the use of wet chemical methods for the quantification of aldehydes (Hare *et al.*, 1973), most of the reviewed literature indicated the use of some variation of EPA Method TO-5 for aldehydes in ambient air (Hare and White, 1991, Williams *et al.*, 1990). This research used a newer method, EPA Method IP-6A, for evaluation of aldehyde emissions (US EPA, 1989). Both EPA methods use dinitrophenylhydrazine (DNPH) in some form to react with the aldehydes for later quantification through high performance liquid chromatography (HPLC). These methods would be expected to be more accurate than the wet chemical method. Additionally, EPA method IP-6A should be somewhat more robust as it uses laboratory prepared DNPH cartridges rather than DNPH solution filled impingers like TO-5. The use of these cartridges makes sampling and subsequent analyses simpler, quicker, and less error prone.

Table III - Aldehyde Emissions from Single Cylinder, Four-Cycle Small Utility Engines Fueled with Gasoline Only

Source	Minimum Formaldehyde (mg/kW-hr)	Maximum Formaldehyde (mg/kW-hr)	Acetaldehyde (mg/kW-hr)
Hare and White, 1991[a]	145		25
EPA Emission Factors (US EPA, 1992)[b]	60	210	

[a]Hare and White presented a single determination for formaldehyde and acetaldehyde emissions from the 3.5 HP Tecumseh engine.

[b]EPA Emission Factors only presented data for formaldehyde emissions.

Catalytic Converter Utilization

A catalytic converter is a device used to control emissions from combustion and process sources. A catalyst material (usually a combination of noble metals such as platinum, palladium, and rhodium) is plated onto a substrate material for support in the exhaust stream. Platinum and palladium are used for control of carbon monoxide (CO) and hydrocarbons (HC) while rhodium is used in so called three-way catalysts for control of oxides of nitrogen (NO_X). Control of these pollutants is accomplished through chemical oxidation in the case of CO and HC and chemical reduction in the case of NO_X. Precise control of combustion air/fuel ratios is required for NO_X control. Converter substrates are typically of honeycomb or pellet type. Honeycomb substrates are preferred for use for internal combustion engines due to their reliability and performance characteristics (Kummer, 1981). These substrates can be made of metal or ceramic material with metal substrates producing lower pressure drops, 65% less for flows of 250 m^3/hr (Swiatek *et al.*, 1989).

Although the catalyst material is not consumed in the reactions it promotes, the thinly deposited material is eventually eroded from the substrate and the catalyst assembly must be replaced. In addition, certain components of fuels (lead for instance) can "poison" or deactivate the catalyst material. This severely shortens the life of the catalytic converter which results in the need for premature replacement. Overheating caused by unburned air/fuel mixtures in the catalyst can also cause damage (Kummer, 1981).

Production of secondary pollutants such as sulfuric acid or hydrogen sulfide can be a result of catalyst usage. Sulfuric acid is produced when sulfur dioxide from fuel sulfur is oxidized to sulfur trioxide (SO_3) in the oxidation catalyst. The SO_3 then reacts with water at ambient temperatures to form sulfuric acid aerosols. Hydrogen sulfide is

three-way catalysts. This occurs when sulfur dioxide from fuel sulfur is reduced in the catalyst to form hydrogen sulfide.

A reference discussing catalyst effects on speciated hydrocarbons (McCabe *et al.*, 1992) indicated various catalytic converter efficiencies for different types of hydrocarbons. Efficiencies of from 57 - 79% were reported for saturated hydrocarbons while higher efficiencies, 84 - 92%, were reported for unsaturated and aromatic compounds. Oxygenates and aldehydes were oxidized with efficiencies ranging from 77 - 100%. These efficiencies were observed from combustion of single component fuels (e.g. isooctane and n-heptane) in a pulse flame combustor.

One reference (Swiatek, *et al.*, 1989) demonstrated that catalytic converters were effective in controlling CO, THC, and NO_X emissions from small engines. Swiatek studied the effect of catalytic conversion on a single cylinder, 242cc, 4-cycle engine connected to a 3.0kW Honda generator. Catalyst efficiencies exceeded 90% for hydrocarbons and carbon monoxide. However, this effectiveness depended on high secondary air flow rates (up to 5000 L/hr) introduced into the catalyst. This study found some increase in THC emissions with the catalyst installed and no secondary air flow. Increased back pressure on the exhaust system, and a subsequent change in the engine air/fuel ratio served as a possible explanation for this result.

Kummer discussed pollutant formation (Kummer, 1981), and also discussed temperatures and residence times required for catalytic oxidation. He pointed out that catalytic oxidation of CO and hydrocarbons can take place at temperatures as low as 250^{o}C. This oxidation requires sufficient excess oxygen from secondary air, or engine operation at lean air/fuel ratios. Space velocities of 20,000 - 100,000/hr appear in Kummer's work. The catalyst space velocity is a measure of the gas residence time in the catalyst, and plays an important role in the amount of pollutant oxidized in the catalyst.

Most automotive oxidation catalysts use platinum and palladium mixtures. These mixtures allow more effective pollutant control, as palladium is more active in the oxidation of CO, olefins (alkenes), and methane, while platinum more actively promotes the oxidation of paraffins (alkanes) with three or more carbons. The two noble metals exhibit similar activity with respect to aromatic oxidation. Kummer presented an expression for the CO oxidation rate which showed CO and olefin oxidation inhibition at high CO and olefin partial pressures. Although no specification of "high" partial pressures was made, Kummer points out that the CO oxidation rate is a maximum for 0.05% CO at 400°C. Additionally, these oxidation rates showed inhibition in the presence of NO in the 0-1000 ppm range. The paraffin oxidation rate "...varies with the first power of the hydrocarbon partial pressure, is inhibited by CO, olefins, and NO, and increases as the O_2 partial pressure is decreased to near stoichiometric values." (Kummer, 1981)

III. METHODS AND MATERIALS

Experimental Design

Since this research sought to quantify emissions of formaldehyde, acetaldehyde, carbon monoxide, and total hydrocarbons, methods of sampling and analyzing for these pollutants were important. Additionally, as the evaluation of the effects of alcohol fuel addition was also desired, a decision had to be made concerning the amount and types of alcohols added to the fuels. After reviewing the literature and evaluating available resources, a plan was established.

Three factors made the selection of ethanol and methanol fuel additives simple: (1) these alcohols are readily available for general fuel use, (2) these alcohols have been successfully used as fuel additives in the past, and are currently being used as fuel additives and primary fuels, and (3) literature relating to the use of these alcohols as fuels, and the emissions characteristics associated with their use was available. The previous section contains citations of much of this literature.

It is important in any research effort to insure that representative samples be obtained in sufficient quantity to allow credible conclusions to be drawn. This necessity must be balanced against available resources such as time, money, and the availability of analytical equipment. Difficulties arose in obtaining multiple samples for each operating condition, due to the large number of conditions under which the emissions from this small utility engine had to be evaluated, and the cost for some of the analyses.

For determination of typical pollutants such as carbon monoxide, and total hydrocarbons, two samples at each condition were collected in 12 liter (L) Tedlar® bags. Since sample collection took place over time periods approaching 20 min, these samples should be representative of the average engine operation. Additionally, the large sample size allowed multiple (up to 3) determinations of pollutant concentrations from each

sample. Non-dispersive infrared and paramagnetic analyzers, and a flame ionization detector belonging to the Mechanical Engineering department facilitated the analysis of these samples.

The sampling pump of a Teledyne Max 5 combustion analyzer (Teledyne Analytical Instruments, City of Industry, CA) allowed for sample collection. A rotameter attached to the analyzer allowed for measurement of the sampling rate, after the rotameter was calibrated with a GCA/Precision Scientific wet test meter. Only the pump and rotameter of this instrument were used in this project.

Some analytical methods for aldehydes in the exhaust gas might have proved difficult. The original method considered, EPA TO-5 (US EPA, 1984), involved the use of acidified DNPH in liquid filled impingers. This method could have been messy and unreliable, given the nature of the compounds involved and the sensitivity of the method to contamination. A newer method used cartridges of silica gel, coated with acidified DNPH, and was a vast improvement over the older method. In addition, the availability of professionally prepared cartridges made the decision to adopt EPA Method IP-6A an easy one. However, the cost of the Waters Sep-Pak® cartridges prohibited more than two aldehyde samples for each operating condition. These two samples allowed some idea of the range of results to be determined.

During experimentation, it was not always possible to measure all engine operating parameters simultaneously. Some experiments yielded certain results, other experiments others. In order to evaluate the results of particular experiments in the context in which they were conducted, Table D.I in Appendix D presents a listing of all experiments conducted, engine operating conditions, and measurements and samples taken. All experiments conducted utilized the high load setting, and sampling rates were recorded.

Engine Test Setup

Evaluated in this research was a Honda, 107 cc (cubic centimeter), four-cycle gasoline fueled engine. The engine had overhead valves and was attached to a 1400 W peak power electrical generator. Being previously used, the oil and spark plug were changed prior to this research. Figure 1 shows a schematic of the engine test system. Air entered the laminar flow meter which was mounted on the intake dampener. Air then entered the carburetor and was mixed with fuel from either the fuel tank or the burette. Measurements from a digital volt meter (DVM) and clamp on ammeter allowed calculation of power consumed by the load. The optional catalytic converter could be installed in the 3/4" exhaust system pipe as desired. The exhaust entered the exhaust dampener and exited through the muffler. The sampling probe of the Max 5 was inserted in the exhaust system downstream of the exhaust dampener. A Waters Sep-Pak® cartridge inserted between the sampling probe and the sampling pump captured aldehydes from the exhaust gas. The exhaust sample then flowed through the rotameter. When sampling for standard emissions (carbon monoxide and total hydrocarbons), the Sep-Pak® cartridge was omitted. A tube of indicating Drierite placed between the sampling probe and pump removed water from the sample stream. Finally, the exhaust sample was collected in the Tedlar® bag. These samples typically remained at room temperature overnight (several hours at most) before being analyzed.

A commercial Pilot Oil station supplied the gasoline for this research. The rated octane of the gasoline was 89 and no alcohol was added by the refiner. The Virginia Tech Chemistry Department stores provided the alcohols and acetonitrile used. The Fisher methanol was bulk, pumped, ACS reagent grade; the ethanol was Aaper 200 proof and the acetonitrile was Fisher HPLC grade.

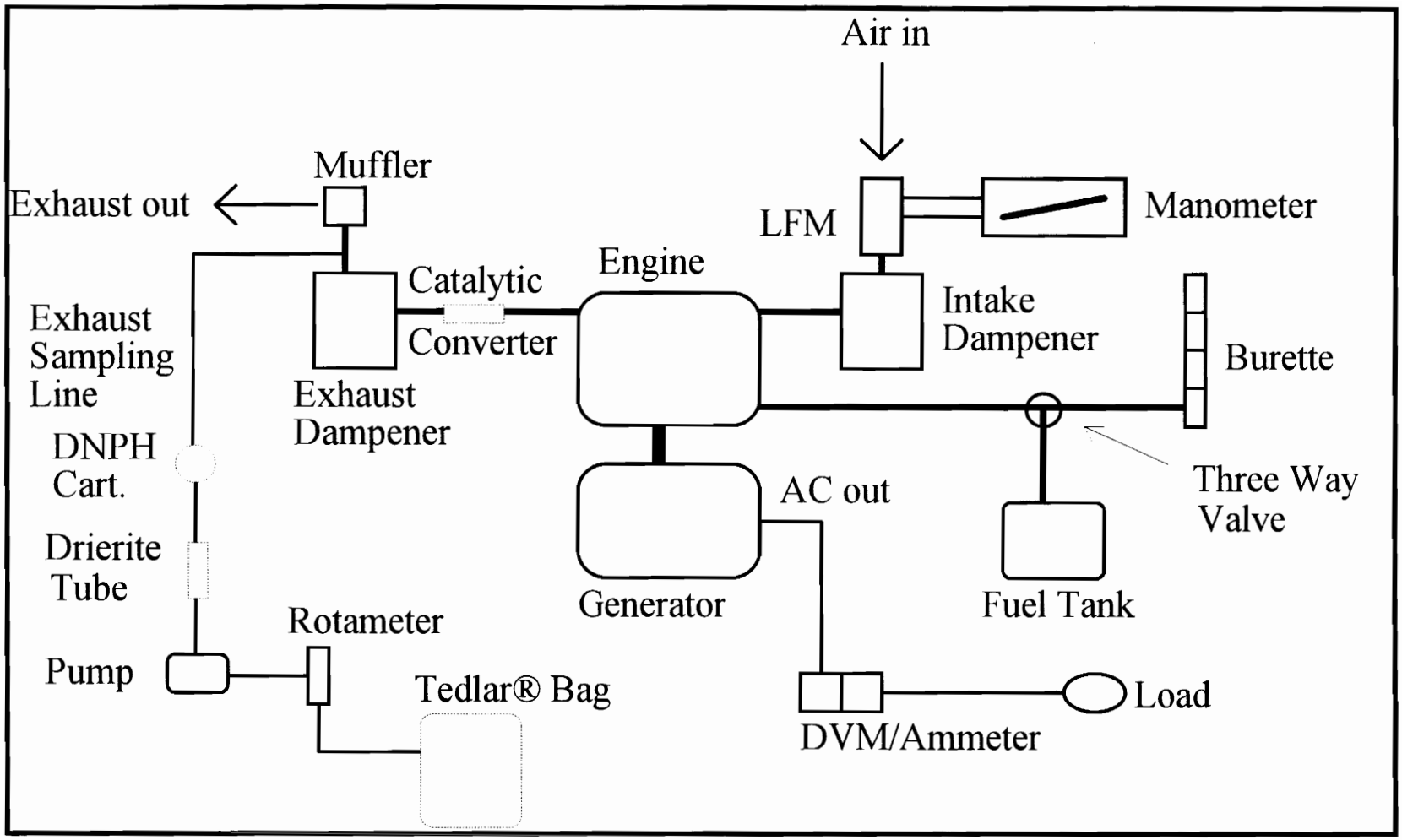

Figure 1 - Engine Test Setup Schematic

Basic Engine Measurements

A General Radio 1531-AB Strobotac® stroboscope provided means to measure the engine speed. Calibration employed the 60 Hz frequency from line power to calibrate a frequency of 3600 Hz on the stroboscope. The stroboscope flashes illuminated part of the rotating crankshaft, and the frequency was adjusted to determine the speed of the engine. The stroboscope was calibrated before each use.

Using pure gasoline, the fuel rate into the engine was measured using a burette. The initial measurement of the fuel in the burette was recorded before switching the fuel feed to the burette. The engine consumed the fuel from the burette for a measured time and the final burette measurement was recorded. The difference in burette readings and the measured time interval gave the volume rate of fuel into the engine. The volume rate and known density of the fuel allowed determination of the fuel mass rate. The fuel density was determined by weighing a known volume of the fuel. It was not possible to measure volumetric rate of the gasoline/alcohol mixtures, as the fuel caused the plastic burette to become brittle and crumble. Some other types of plastics may be resistant to these fuel mixtures, but were unavailable. Additionally, a glass burette was not used for this purpose, out of concern for possible injury in the event of fuel exploding in the burette. As a result, it was assumed that the volume rate for each fuel was the same, and the mass rate was computed from the fuel density. The volume proportions and densities of the fuel components allowed calculation of the densities of the fuel mixtures. The fuel consumption rate was controlled by a governor attached to the generator, keeping the rate constant for a given power setting.

The laminar flow meter designed for this study measured the volume rate of the engine intake air. Figure 2 shows a schematic of the laminar flow meter.

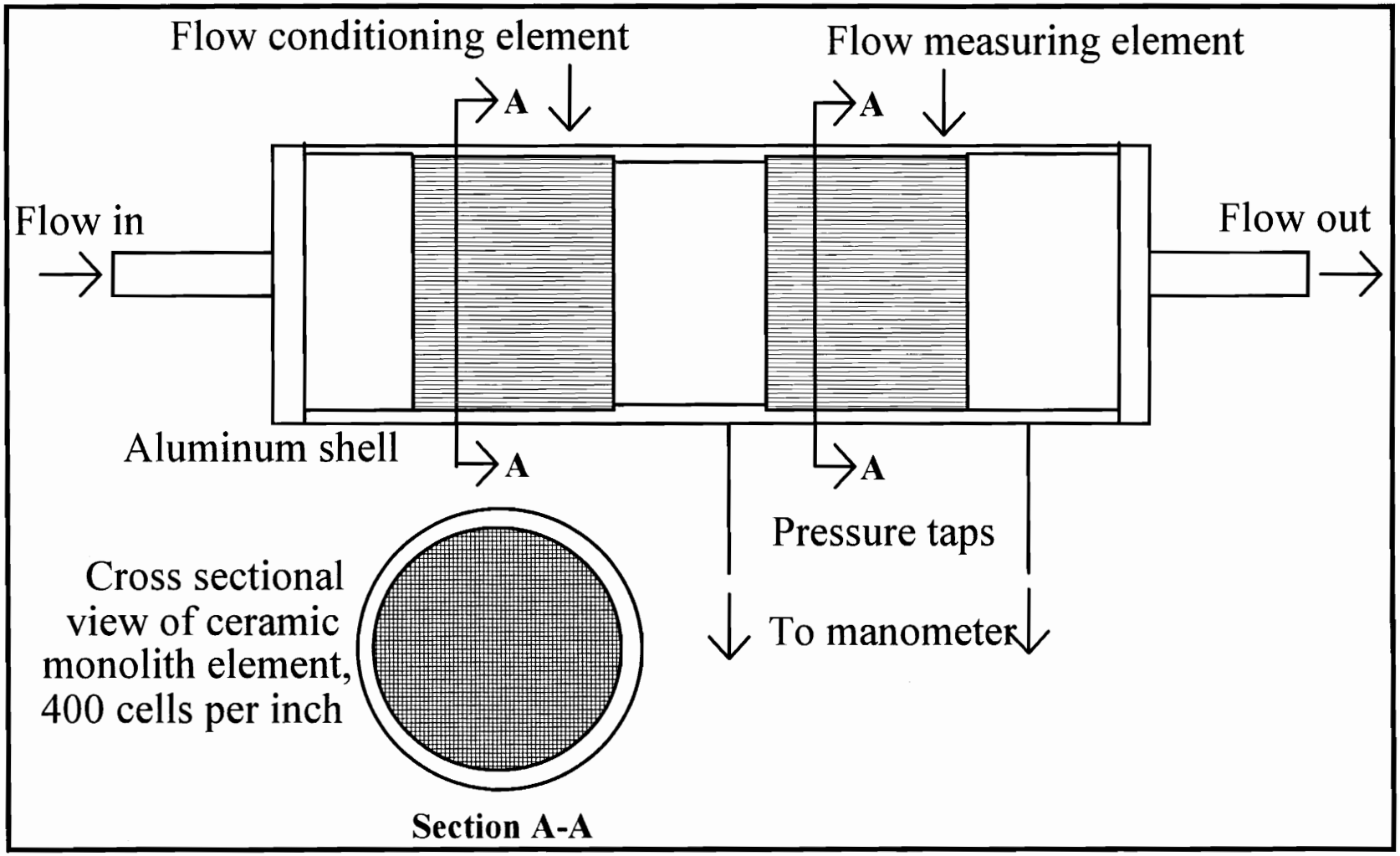

Figure 2 - Laminar Flow Meter Schematic

The laminar flow meter was made from a large hollow aluminum cylinder and uncoated, ceramic, catalytic converter elements. The flow through the element was laminar due to the small size of the honeycomb, and as a result, the pressure drop across the element is proportional to the volume flow rate through the element. This type of flow regime is known as Poiseuille flow. The laminar flow meter calibration occurred using a vendor calibrated, Meriam laminar flow meter with a pressure drop of eight inches of water (in H_2O) per 100 cubic feet per minute (cfm). The laminar flow meter was installed in series with the Meriam meter and pressure drops for several flow rates were recorded. Table A-I in Appendix A contains the data plotted on the calibration curve shown in Figure 3.

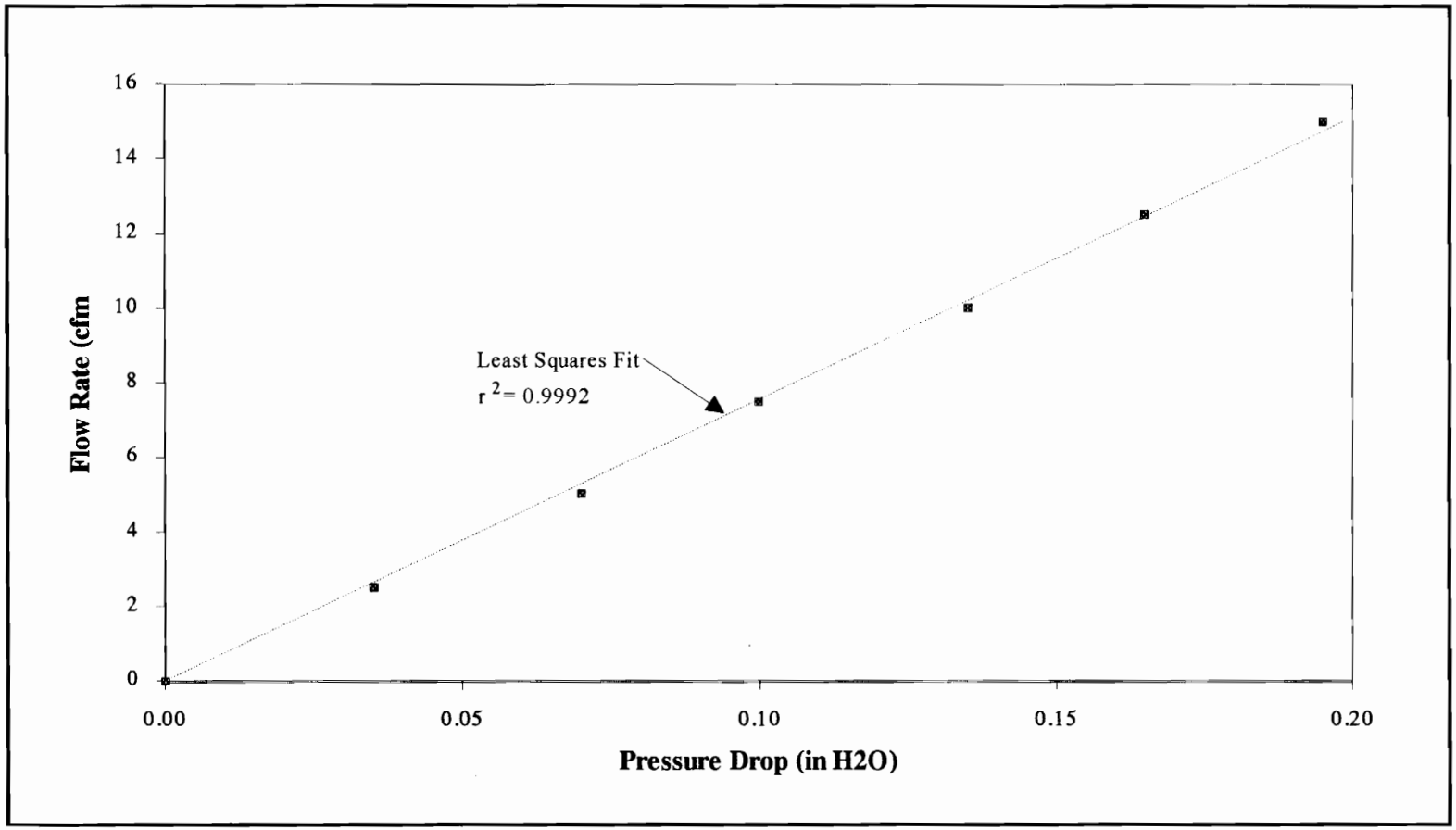

Figure 3 - Laminar Flow Meter Calibration Curve Generated Using Custom Built Meriam Laminar Flow Meter

Meriam Laminar Flow Meter Exhibited 8 in H_2O Pressure Drop per 100 Cubic Feet per Minute (cfm) Flow

Measurement of the intake flow rate required the installation of flow dampening chambers on the intake and exhaust of the engine, due to the pulsating flow present at these ports. Taylor stated that the minimum size for these dampening chambers should fifty times the cylinder displacement (Taylor 1968). Thus for this 107 cc engine, the required dampening chamber volume was 5.4 L. An 18.9 L plastic carboy served as the intake dampening chamber. The exhaust dampening chamber was made from a sealed, metal desiccator of approximately 6.3 L.

The load applied to the generator consisted of a small portable hair dryer with high and low power settings. The high power setting simulated an actual operating load level. A Micronta digital multimeter and clamp-on ammeter measured generator output voltage and load current respectively. These electronic meters did not require calibration, however the ammeter was manually zeroed before measurement. The power factor of the load was not known, so treating the load as purely resistive, with a power factor of 1.0, the generator power was calculated as the product of the measured voltage and current.

Fuel mixtures were prepared by measuring appropriate volumes of gasoline and alcohol using a graduated cylinder. Mixing of the fuel components occurred just before their introduction into the fuel tank.

Allied-Signal supplied a platinum catalyst which was installed in the engine exhaust system. The catalyst measured 2.5 in. long by 1.5 in. in diameter, with 400 cells per square inch. This catalyst was similar to prototype catalysts supplied to the small engine industry and was chosen because of its availability and characteristics representative of small engine catalysts. Additional specific information was not available due to the proprietary nature of this product. Figure 4 shows the catalyst element mounted in a 2.5 in. long x 1.5 in. diameter pipe. The pipe required machining to allow the installation of a 3M insulating material called Interam™. The Interam™ served to hold the catalyst in

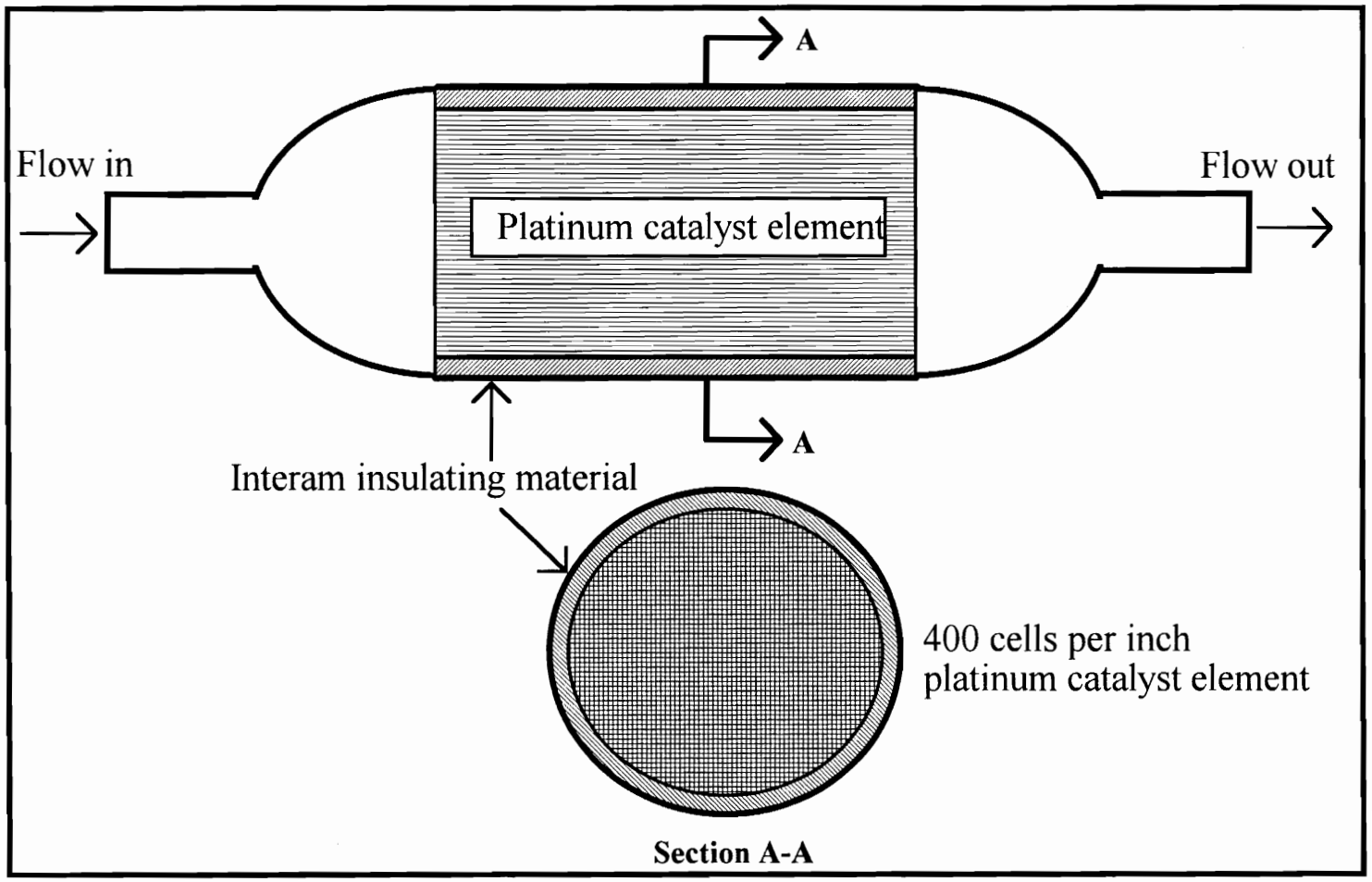

Figure 4 - Catalytic Converter Schematic

place. Transition pipe fittings allowed connection of the catalytic converter to the 3/4 in. exhaust system.

Standard Emissions Measurements

Standard emissions measurements included quantification of carbon monoxide and total hydrocarbon specific emissions, as well as determination of exhaust carbon dioxide and oxygen concentrations. As mentioned previously, the SAE Modal Method J1088 describes collection and analysis of engine emissions while operating the engine at different power output levels, while varying the intake air/fuel ratio. While this method may be applicable to automobile testing, it was not necessarily applicable to the small engine studied in this research. This engine operated at a fixed air/fuel ratio, governed by the generator power output. As a result, no attempt was made to fully conform to the J1088 method.

The Max 5 pump provided for extraction of samples of exhaust gas. A rotameter installed on the Max 5 measured the sample flow rate which was controlled by a valve on the rotameter. A GCA/Precision Scientific wet test meter served as the standard for calibrating the rotameter. Calibration of the rotameter was performed twice during the research, once using the wet test meter and once using a direct displacement method. Figure 5 shows the calibration curve for the rotameter, generated by the data in Table A.II in Appendix A. The least squares fit of these data is also shown in the figure. The wet test meter data agreed well with those obtained by the direct displacement method. Table A.III in Appendix A contains the direct displacement calibration data.

A tube containing indicating Drierite removed water from the exhaust gas samples before collection in the 12 L Tedlar® bags. The change in the weight of the Drierite tube was used to determine the amount of water removed during sampling. Some sample collection resulted in water condensing in the sampling train prior to the Drierite tube or Sep-Pak® cartridge. This caused the measured amount of water to be less than the amount actually in the sample.

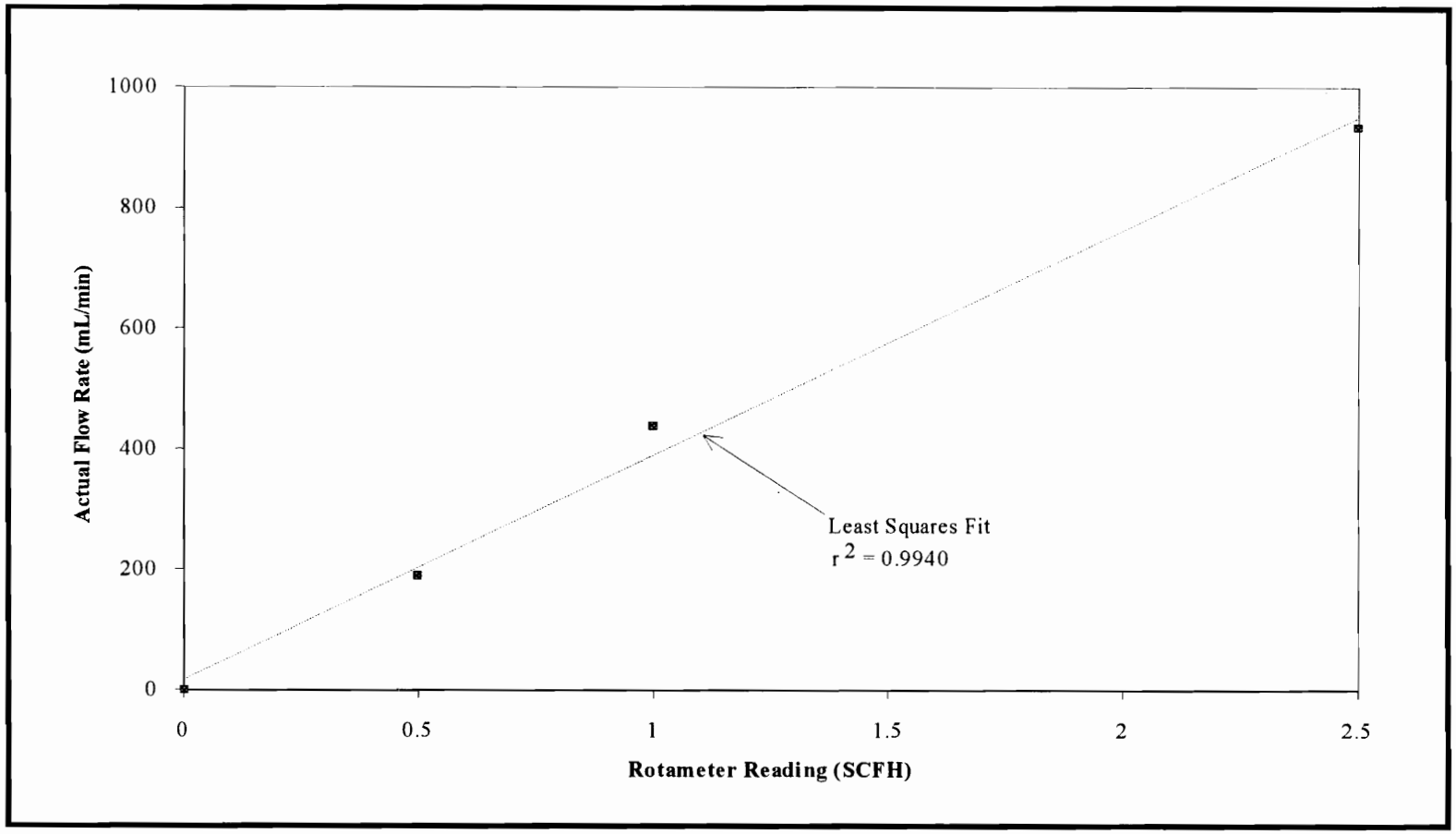

Figure 5 - Rotameter Calibration Curve Generated Using GCA/Precision Scientific Wet Test Meter

Rotameter Reading in Standard Cubic Feet per Hour (SCFH)

A Horiba (Irvine, CA) Model FIA 22A flame ionization detector (FID) provided the means for determining the total hydrocarbons in the bagged gas samples. The FID output was connected to a digital multimeter (DMM) and a strip chart recorder. The strip chart recorder continuously recorded the voltage response, while the DMM displayed a numerical value. During calibration, the output of the FID was adjusted to a specific voltage which was referenced when comparing samples to the standard. Prior to each set of analyses, the FID was zeroed using zero air, and calibrated using propane with a concentration of 3120 ppm in nitrogen. This calibration was equivalent to 9360 ppm as carbon (C) as per EPA Method 25B (Federal Register). The method reported by Donohue *et al.* also specified calibration of the FID using propane. No attempt was made to determine hydrocarbons which may have been sorbed to particulates caught in the Drierite tube, or dissolved in water condensed in the sampling train. Visual examination of the Drierite tube indicated minimal particulate matter collected.

Non-dispersive infrared absorption (NDIR) provided the means for determining CO and CO_2 concentrations. The Horiba Model PIR 2000 NDIR equipment was zeroed with nitrogen (N_2), and calibrated with span gases of the following concentrations: CO, 4.89%, ±0.02%; CO_2, 19.84%, ±0.02%. A Horiba Model OPE 325 paramagnetic analyzer allowed exhaust oxygen concentrations to be determined. The analyzer was zeroed with N_2 and calibrated at 21.0% with atmospheric oxygen. Calibration of the Horiba FID, NDIR, and paramagnetic analyzers was performed prior to each set of Tedlar® bag analyses.

The analytical equipment provided results for CO, CO_2, O_2 and THC as volume percentages on a dry basis. Once these pollutant concentrations were obtained, specific emission rates could be calculated. See Appendix B for formulae related to these calculations.

Aldehyde Emissions Measurements

EPA Method IP-6A (US EPA, 1989) provided the protocol for determining aldehyde concentrations in the exhaust gas. This method specified the use of silica gel cartridges coated with acidified 2,4-dinitrophenylhydrazine (DNPH) to capture carbonyl compounds from ambient air. This method became applicable to this research after adjusting sampling times based on estimated exhaust concentrations of the aldehydes of interest. The method specified subsequent high performance liquid chromatography (HPLC) analysis. Procedures for this method as well as those outlined by Millipore Corporation (Millipore, 1992) were employed in these analyses.

Waters Sep-Pak® DNPH-Silica cartridges allowed for easy sampling for exhaust aldehydes. These cartridges were the first element in the sampling train when sampling for aldehydes. Exhaust gas passed through the cartridges at various rates, measured by the rotameter. The rotameter installed in series with the sampling pump and sampling cartridge allowed determination of the sampling rate, which was held constant during sampling. Recorded sampling times permitted the total volume sampled to be determined. In some cases, two cartridges installed in series allowed a determination of breakthrough of the main sampling cartridge. After sampling, the cartridges were enclosed in the supplied foil pouches, placed in a capped Nalgene® bottle, and refrigerated before elution.

Elution of each cartridge required 5 mL of acetonitrile. As a 5 mL volumetric flask was not readily available (US EPA, 1989), sample vials were weighed before and after elution to determine the mass of acetonitrile in the eluate. Having previously determined the density of the acetonitrile by weighing a known volume, the volume of the eluate could be determined (Millipore, 1992).

Controls processed in this analysis included vendor blanks, lab blanks, and breakthrough cartridges. The vendor blank cartridges were opened just before elution and

analyzed for contamination that: (1) might have been present from the vendor, (2) might have occurred during storage, or (3) might have been present in the acetonitrile used to elute the cartridges. Lab blank cartridges were opened and exposed to laboratory air while the actual sampling cartridges were installed. Analysis of these blanks allowed a determination of any contamination of the sample cartridges which might have occurred during installation into the sampling system. A blank processed by drawing a sample through the exhaust system with no engine operation served as a sampling system blank.

The Waters manual (Millipore, 1992) described the preparation of HPLC standards. Concentrated hydrochloric acid (HCl) was dissolved in one liter of distilled, deionized water and split into two half liter portions for preparation of the DNPH-formaldehyde and DNPH-acetaldehyde derivatives. Approximately 5 grams (g) of DNPH solid, dissolved in each half liter of HCl solution and stirred for one hour, produced saturated solutions of acidified DNPH. Vacuum filtering subsequently removed any undissolved DNPH. Formaldehyde and acetaldehyde were added separately to the half liter DNPH solutions until additional precipitate failed to form. Stirring and filtering recovered the previously formed precipitate which was then dried in a 50^{o}C oven for several hours. Approximately 10 mg of each derivative dissolved in 100 mL of acetonitrile served as the base standards from which less concentrated standards were derived. These standards consisted of the following dilutions: 1:2, 1:5, 1:10, 1:20, and 1:50 of the original solution. Figure 6 shows standard curves generated by HPLC analyses while Table A.IV in Appendix A contains the calibration data.

The HPLC used for the aldehyde analyses was a Hewlett-Packard Model 1090 liquid chromatograph equipped with an ultraviolet (UV) detector. The UV detector employed a diode-array detector (DAD) to continuously scan from 210 nm to 400 nm. Sample separation was accomplished using a 4.6 mm x 250 mm Zorbax ODS column

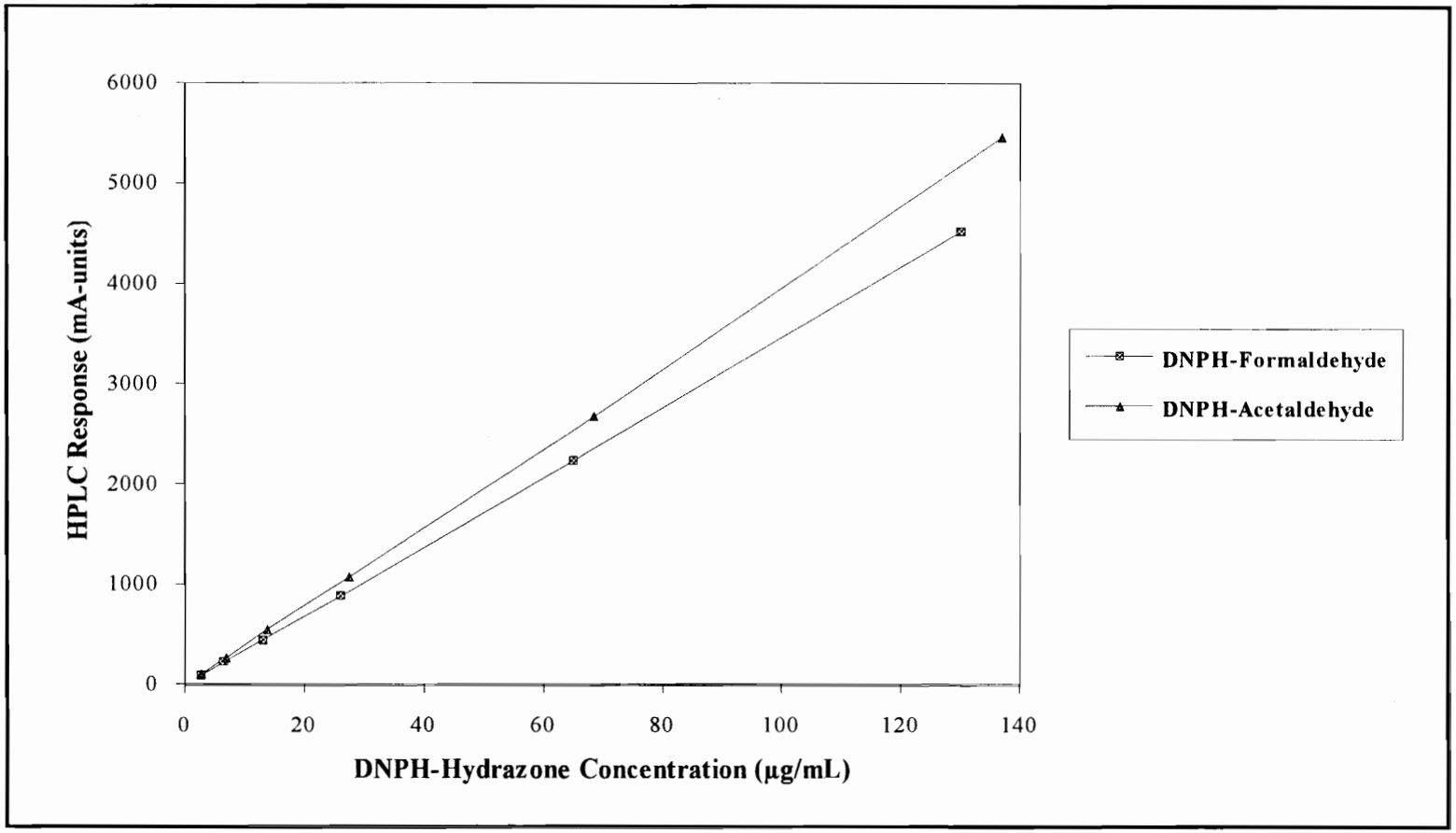

Figure 6 - High Performance Liquid Chromatograph (HPLC) Dinitrophenylhydrazine (DNPH) - Derivative Standards Curves
DNPH-Formaldehyde Standard Solutions of 2.6, 6.5, 13.0, 26.0, 65.0, and 130.0 µg/mL
DNPH-Acetaldehyde Standard Solutions of 2.7, 6.9, 13.7, 27.4, 68.5, and 137.0 µg/mL
HPLC Response in Milli-Area Units
Correlation Coefficients Reported in Table A.IV, Appendix A

(MAC-MOD Analytical Inc., Chadds Ford, PA). The HPLC program used is shown in Appendix C. A 40°C oven contained the column, onto which a 20 μL of sample or standard was injected. The HPLC pump maintained a 1.5 mL/min flow rate throughout the analysis. The mobile phase initially consisted of a 60/40 water/acetonitrile mix, pumped for 1.0 min. A gradient to 40/60 water/acetonitrile took place over a period of 10 min and the analysis continued to its conclusion, for a total time of 25 minutes. Analysis of all standards, blanks, and samples used this HPLC procedure.

IV. RESULTS

Basic Engine Measurements

Table IV shows typical ranges of values for engine operating parameters determined from measurements. As these parameters were not measured for every sampling run, the average values were sometimes used in calculations. The data from which these values were derived are presented in Appendix D.

Table D.II shows engine speeds measured on 25 occasions and fuel rates measured on five occasions. Engine speed varied approximately 7.5% from maximum to minimum while the fuel rate varied approximately 40%. Although no accuracy value was given for the stroboscope used to measure engine speed, the 7% deviation would seem to be within the range expected for experimental error. The deviation in the fuel rate is most likely attributable to fuel surges which occurred when the fuel valve was switched from the fuel tank to the burette. When the valve was switched, the fuel level in the burette would quickly drop 2 to 5 mL. As the burette contained 25 mL of fuel at most, the times over which these measurements were conducted were not sufficiently long to average out these surges. Table D.III shows load voltage and current measured on 21 occasions. The voltage varied approximately 5% while the current varied approximately 8.5%. Accuracy of the digital multimeter (DMM) used to measure voltage was ±1.2%. The accuracy of the analog ammeter was not given, but the type of meter, coupled with error inherent in reading such a meter would lead to lower accuracy than that of the DMM. These accuracies lead to the belief that the voltage and current variations are mostly due to experimental error. The remainder of the variations can be explained by actual load changes due to fluctuations in ambient temperature.

Table IV - Ranges of Engine Operating Parameters for Honda 107 cc Four Cycle Overhead Valve Engine

Parameter	Number of Measurements	Low	Average	High	Std. Dev	Mfr. Spec.
Engine Speed (RPM)[a]	25	2940	3161	3360	111	
Generator Voltage (V)[b]	21	109.9	112.7	115.3	1.58	
Load Current (A)	21	8.3	8.6	9.0	0.192	
Power Output (kW)	21	0.92	0.97	1.04	0.032	1.2
Fuel Volumetric Rate (mL/min)[c]	5	13.4	15.2	18.9	2.1	.73 L/hr
Intake Air Volume Rate (m^3/min)[d]	4	0.11	0.13	0.15	0.02	

[a]Engine speed measured using a General Radio stroboscope.

[b]Generator electrical outputs measured using Micronta digital multimeter (DMM) and clamp-on ammeter.

[c]Fuel volumetric rate measured using burette method from Taylor, 1968.

[d]Air intake rate measured using laminar flow meter constructed for this research.

Fuel and air rates measured using gasoline only fuel. All other measurements taken during the course of the research using gasoline and gasoline/alcohol fuel blends.

Measurement of the fuel rate and intake air rate provided the data used to calculate the air/fuel ratio. Table D.IV shows four values of the air intake rate obtained during high power operation. The air intake rate varied approximately 36% from maximum to minimum. Although some of this variation is attributable to error in the manometer used to measure the laminar flow meter pressure drop, most is probably attributable to variations in engine operation. The average fuel rate and average air intake rate give a value of the air/fuel ratio of 10.2. The air/fuel ratio calculated for engine operation on 2/10/93, when air and fuel rates were measured simultaneously, was 12.0. The air fuel ratio was also calculated to be 11.25 using the Spindt method (Spindt, 1965). This value agreed with the two measured values within 10.3% and 6.7% respectively. All the air/fuel ratios calculated indicated that the engine was operating with less than the required stoichiometric amount of air, or "fuel rich". The air/fuel ratio and the fuel rate allowed the exhaust flow rate to be determined by using a mass balance.

Standard Emissions Measurements

Exhaust concentrations of CO, CO_2, O_2, and THC were obtained from NDIR, paramagnetic, and FID analyses. These values were used along with the exhaust flow rate and generator power output to calculate specific emission rates (mass per unit power output) for the engine.

Gasoline

Using 100% gasoline fuel (G100), three samples of exhaust gas were collected in Tedlar® bags and analyzed for their composition. The first two samplings occurred with no catalyst installed, while the third included the catalyst. Table V shows sampling dates and times, CO, THC, CO_2, and O_2 concentrations for the three samples. Specific emission rates for CO for the two samples were 113.7 and 123.2 g/kW-hr. Specific emission rates for THC for the two samples were 1.73 and 2.08 g/kW-hr. These two samples showed variations of approximately 8% and 20% for CO and THC emissions respectively. The CO_2 and O_2 concentrations are typical for those expected from a small IC engine operating fuel rich.

With the platinum catalyst installed, specific emission rates of CO and THC were 128.3 g/kW-hr, and 1.95 g/kW-hr respectively. The specific CO emissions after the catalyst were approximately 4% higher than the higher non-catalyst value. The value for specific THC emissions after the catalyst fell between the two values without the catalyst. These results indicate that catalytic oxidation of CO and THC did not occur while using G100 fuel. The CO_2 concentration is unusually low in the catalyst sample (4.5%), while the oxygen concentration is about 14% higher than the higher non-catalyst concentration. This difference is probably not significant given the spread (>50%) in the two non-catalyst values.

Table V - Exhaust Gas Constituent Concentrations and Pollutant Specific Emission Rates from Gasoline Only Fuel Combustion

Sampling Time			CO[a†]		THC[b†]		CO_2[a]	O_2[c]
Date	(min)	Catalyst	(%)	(g/kW-hr)	(ppm)	(g/kW-hr)	(%)	(%)
2/10/93	20.0	No	6.7	113.7	4054	1.73	10.2	0.51
4/28/93	17.0	No	7.2	123.2	4871	2.08	9.6	0.78
4/28/93	17.5	Yes	7.2	128.3	4463	1.95	4.5	0.88

Dry gas samples were collected in Tedlar® bags prior to analysis.

[a]Exhaust carbon monoxide (CO) and carbon dioxide (CO_2) concentrations determined using Horiba non-dispersive infrared (NDIR) equipment. The Model PIR 2000 analyzers were zeroed using nitrogen (N_2) gas and calibrated with 4.89% CO and 19.84% CO_2.

[b]Exhaust total hydrocarbon concentration determined using a Horiba flame ionization detector (FID). The Model FIA 22A detector was zeroed using N_2 gas and calibrated with 3120 parts per million (ppm) propane.

[c]Exhaust oxygen concentration determined using Horiba paramagnetic analyzer. The Model OPE 325 analyzer was zeroed using N_2 gas and calibrated using atmospheric oxygen.

†CO and THC concentrations (% and ppm respectively) were reported from the analyses while specific emissions (g/kW-hr) were calculated based on generator power output as outlined in Appendix B.

Ethanol

Table VI shows dates, times, and emissions for exhaust gas samples collected while using ethanol enhanced fuels. Throughout the presentation of these results, reductions in emissions and converter efficiencies were referenced to base emissions from G100 fuel with no catalyst. All statistical results and related data are shown in Tables D. V, D.VI, and D.VII in Appendix D. Statistical results were generated using linear statistical methods (Neter and Wasserman, 1974).

Figure 7 shows carbon monoxide data collected with ethanol addition to the fuel, with and without the catalyst. The regression lines for these data are also shown. For operation without the catalyst, although no CO reduction was demonstrated with the addition of 10% ethanol (E10), addition of 25% (E25) and 50% (E50) ethanol to the fuel resulted in decreased CO emissions of approximately 33% and 75% respectively. A t-test with a 95% confidence interval showed that the slope of the non-catalyst regression line was non-zero, indicating that the CO emissions were dependent on fuel ethanol content. With the catalyst installed, only one sample was taken at each ethanol level. As a result, these results should only be considered qualitatively. The results of a statistical test to determine the relationship between the two regression lines indicated a p-value of 0.54. The p-value indicates the level of significance at which the statistical conclusion concerning the regression lines indicates that the lines differ. Thus a p-value of 0.54 is equivalent to a confidence interval of 46%. These results seem to indicate that no catalytic control of CO was achieved at any level of ethanol addition.

Table VI - Exhaust Gas Constituent Concentrations and Pollutant Specific Emission Rates from Ethanol Enhanced Fuel Combustion

Fuel[a]	Alcohol by Volume (%)	Date	Sampling Time (min)	Catalyst	CO[b] (%)	CO (g/kW-hr)	THC[c] (ppm)	THC (g/kW-hr)	CO_2[b] (%)	O_2[d] (%)
E10	10	4/1/93	18.0	No	6.3	109.6	4620	2.01	10.5	0.60
E25	25	4/2/93	14.75	No	4.0	115.8	3385	1.89	11.9	0.79
E50	50	4/2/93	18.0	No	1.0	70.3	2320	1.48	13.3	1.52
E10	10	4/28/93	17.0	No	6.8	63.1	4422	1.26	10.2	0.89
E25	25	4/28/93	17.0	No	3.7	17.4	2986	1.02	12.6	0.74
E50	50	4/28/93	17.0	No	0.6	10.2	1589	0.66	13.5	2.11
E10	10	4/29/93	17.5	Yes	5.9	103.2	4096	1.79	11.3	0.52
E25	25	4/29/93	17.5	Yes	4.7	81.5	3627	1.58	10.9	2.10
E50	50	4/29/93	17.5	Yes	1.1	19.6	1397	0.65	14.0	1.04

[a]Gasoline alcohol fuel mixtures are commonly designated by the volume percentage of alcohol with the remaining fraction being made up of gasoline. For example, the abbreviation E10 designates a fuel made up of 10% ethanol and 90% gasoline by volume.

[b]Non-dispersive infrared (NDIR) analysis determined carbon monoxide (CO) and carbon dioxide (CO_2) concentrations.

[c]Flame ionization analysis (FIA) determined total hydrocarbon (THC) concentrations.

[d]Paramagnetic analysis determined oxygen (O_2) concentrations.

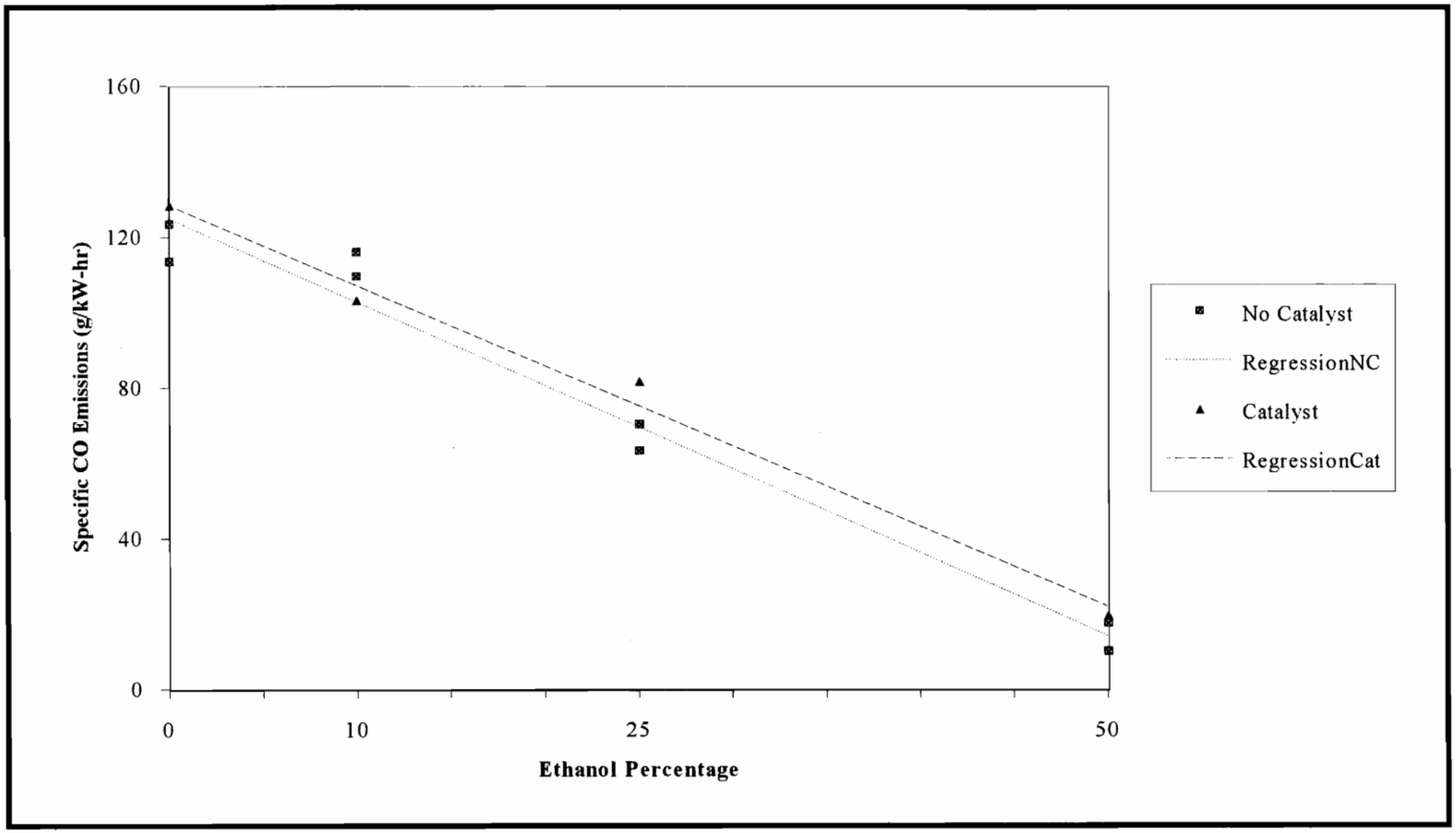

Figure 7 - Effect of Fuel Ethanol Content on Specific Carbon Monoxide Emissions

The line labeled "RegressionNC" is the least squares line fitting the carbon monoxide (CO) data collected without the platinum catalyst installed.

The line labeled "RegressionCat" is the least squares line for the CO data with the catalyst.

Regression parameters listed in Table D.V

Figure 8 shows total hydrocarbon data collected with ethanol addition, with and without the catalyst. Regression lines are also shown. Again, a trend in THC emissions with respect to ethanol content is seen at the 95% confidence level. With no catalyst installed, no reduction in specific THC emissions is observed with the E10 fuel, but reductions of approximately 25% and 50% were seen with E25 and E50 fuels respectively. The p-value for the catalyst vs non-catalyst results was 0.89, indicating practically no significant difference between the data with the catalyst and that without the catalyst.

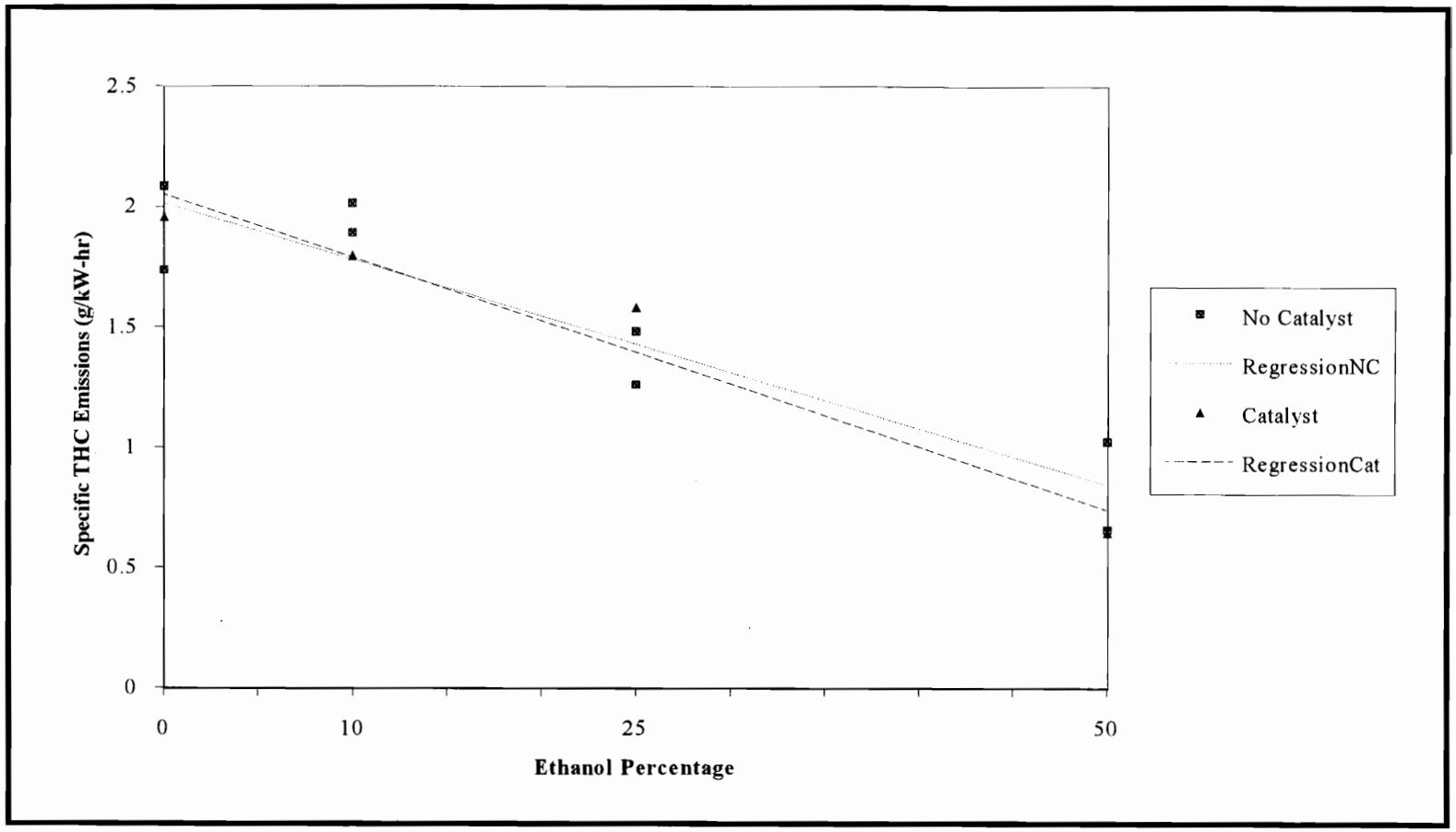

Figure 8 - Effect of Fuel Ethanol Content on Specific Total Hydrocarbon Emissions

The line labeled "RegressionNC" is the least squares line fitting the total hydrocarbon (THC) data collected without the platinum catalyst installed.

The line labeled "RegressionCat" is the least squares line for the THC data with the catalyst.

Regression parameters listed in Table D.V

Figure 9 shows the effect of ethanol addition on the exhaust concentrations of oxygen with and without the catalyst. With no catalyst, O_2 concentrations remained basically unchanged until an increase of about 40% occurred with E50 fuel. An analysis of the regression line indicated a non-zero slope at the 95% confidence level. With the catalyst installed, a p-value of 0.61 was generated. This indicates that installation of the catalyst had essentially no effect on the exhaust oxygen content. This served as confirmation that catalytic oxidation of CO and THC did not take place in the catalyst, as the oxygen level would have decreased had this occurred.

Figure 10 shows the effect of ethanol addition on the exhaust concentration of carbon dioxide. With no catalyst, there is a trend toward increasing CO_2 with increasing ethanol content, as a t-test showed the regression line to have a non-zero slope for a 95% confidence interval. This is expected as additional hydrocarbons are oxidized at higher ethanol levels. Considering catalyst versus non-catalyst emissions, a fairly high p-value of 0.89 was obtained. However, this was not considered to be due to catalytic activity, but rather an unusually low value of CO_2 concentration for the G100 results with the catalyst installed.

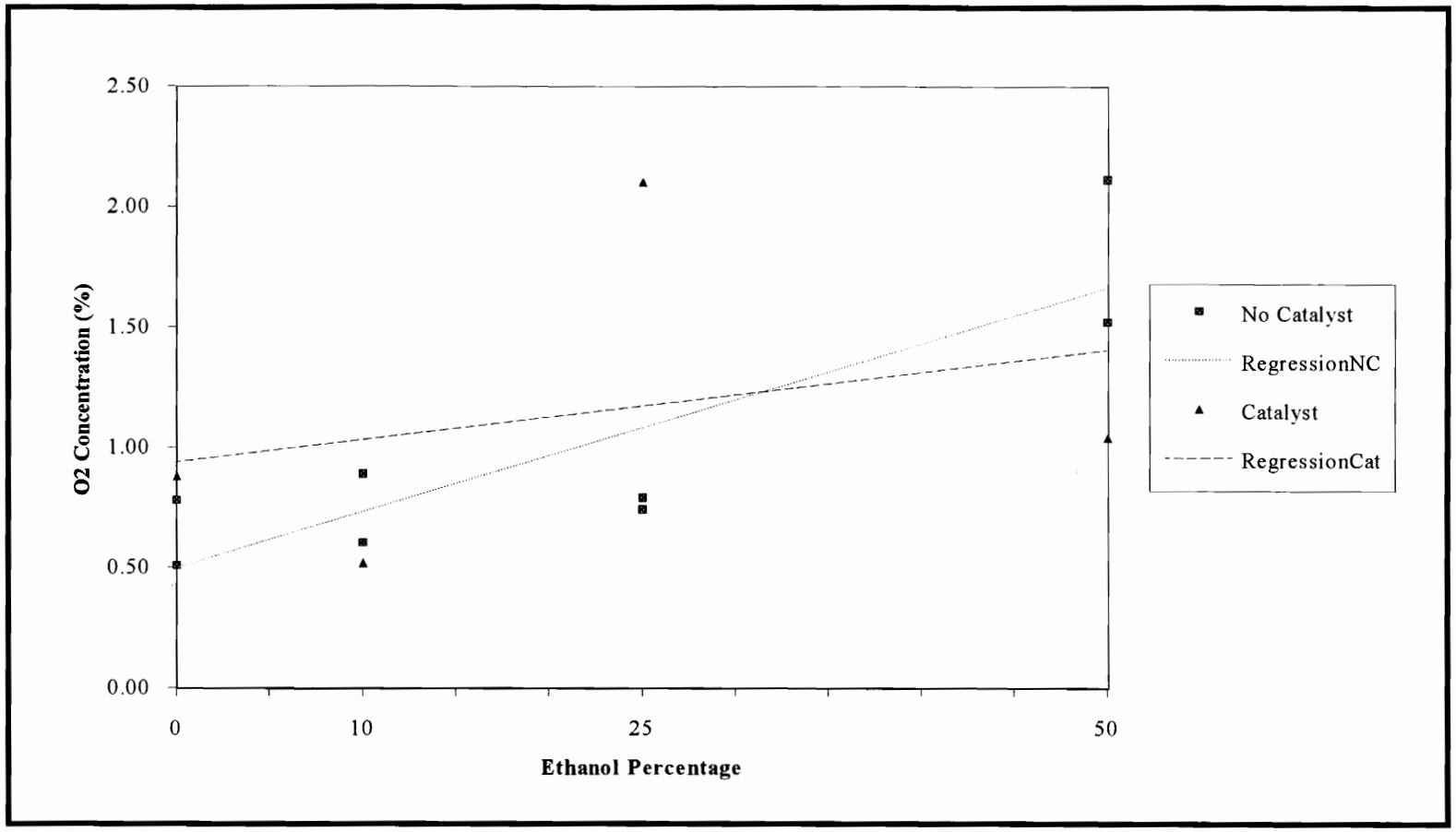

Figure 9 - Effect of Fuel Ethanol Content on Exhaust Oxygen Concentration

The line labeled "RegressionNC" is the least squares line fitting the oxygen (O2) data collected without the platinum catalyst installed.

The line labeled "RegressionCat" is the least squares line for the O2 data with the catalyst.

Regression parameters listed in Table D.V

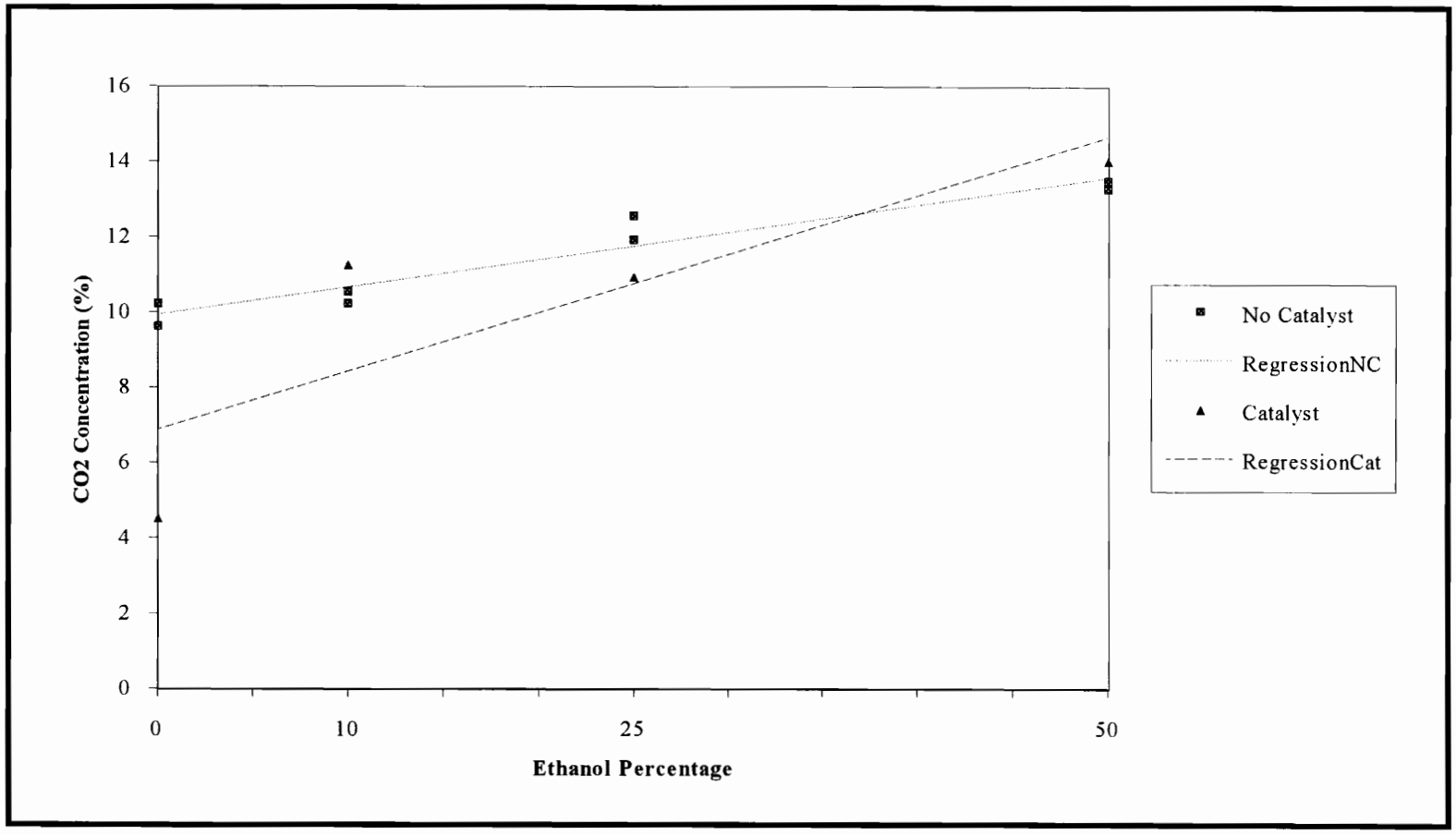

Figure 10 - Effect of Fuel Ethanol Content on Exhaust Carbon Dioxide Concentration

The line labeled "RegressionNC" is the least squares line fitting the carbon dioxide (CO2) data collected without the platinum catalyst installed.

The line labeled "RegressionCat" is the least squares line for the CO2 data with the catalyst.

Regression parameters listed in Table D.V

Methanol

Table VII shows dates, times, and emissions for exhaust gas samples collected while using methanol enhanced fuels. Figure 11 shows the effect of methanol addition on carbon monoxide emissions, with and without the catalyst. Regression lines are included. With no catalyst, CO reduction was seen at all levels of methanol addition. The value of specific CO decrease with M10 fuel is not certain due to the spread of the two M10 values. The data demonstrated decreases in specific CO emissions of almost 90% and 95% using M25 and M50 fuel respectively. A t-test again verified this trend for the 95% confidence level. With the catalyst, a trend of decreasing CO emissions with increasing methanol fuel content was demonstrated, but no catalytic control of CO was seen as indicated by a p-value of 0.44.

Figure 12 shows total hydrocarbon data collected with methanol addition, with and without the catalyst. With no catalyst, reduction in specific THC emissions was observed with all methanol fuel mixtures. Again, the decrease attributable to the M10 fuel was difficult to evaluate. Reductions of about 45% and 60% were seen with M25 and M50 fuels respectively. This trend was confirmed with a 95% confidence interval. With the catalyst installed, the trend of decreasing THC with increasing methanol fuel content was observed, but a p-value of 0.46 denied that any catalytic control of THC had occurred.

Table VII - Standard Emissions Samples for Methanol Fuel Mixtures

Fuel[a]	Alcohol (%)	Date	Sampling Time (min)	Catalyst	CO[b] (%)	CO (g/kW-hr)	THC[c] (%)	THC (g/kW-hr)	CO_2[b] (%)	O_2[d] (%)
M10	10	4/1/93	18.0	No	5.6	97.0	4110	1.79	11.2	.55
M25	25	4/1/93	25.0	No	0.8	14.6	2680	1.19	13.7	1.1
M50	50	4/1/93	18.0	No	0.5	8.5	1890	0.83	13.3	1.8
M10	10	4/29/93	19.0	No	1.4	23.3	2469	1.01	13.5	1.5
M25	25	4/29/93	14.25	No	0.9	15.3	2144	0.95	13.3	2.1
M50	50	4/29/93	17.0	No	0.2	4.4	1675	0.75	12.7	3.1
M10	10	4/29/93	19.0	Yes	5.7	98.3	3311	1.42	10.7	1.1
M25	25	4/29/93	17.0	Yes	3.5	58.7	2632	1.09	11.9	1.4
M50	50	4/29/93	17.0	Yes	0.07	1.2	708	0.31	13.5	2.6

[a]Gasoline alcohol fuel mixtures are commonly designated by the volume percentage of alcohol with the remaining fraction being made up of gasoline. For example, the abbreviation M10 designates a fuel made up of 10% methanol and 90% gasoline by volume.

[b]Non-dispersive infrared (NDIR) analysis determined carbon monoxide (CO) and carbon dioxide (CO_2) concentrations.

[c]Flame ionization analysis (FIA) determined total hydrocarbon (THC) concentrations.

[d]Paramagnetic analysis determined oxygen (O_2) concentrations.

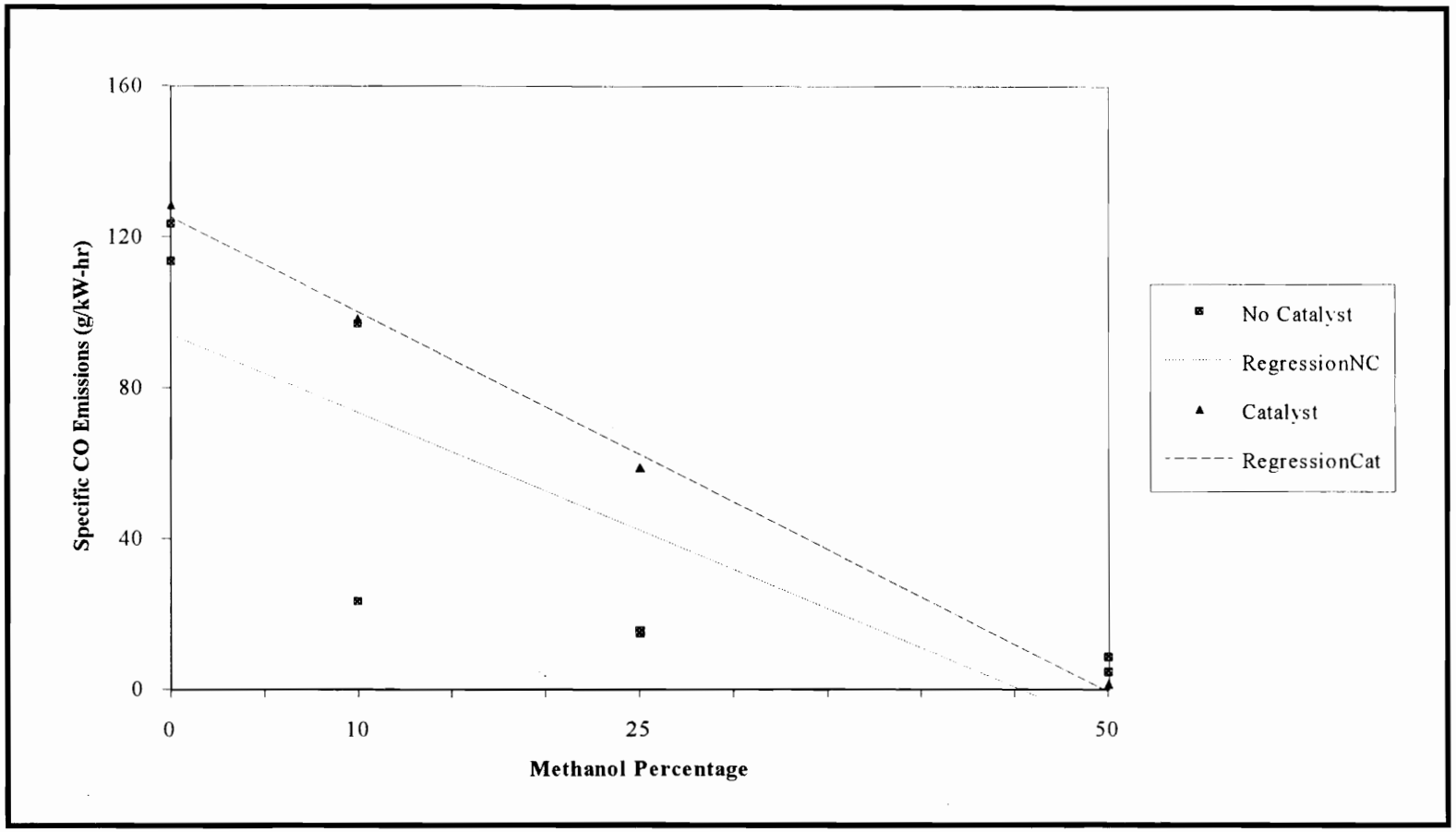

Figure 11 - Effect of Fuel Methanol Content on Specific Carbon Monoxide Emissions

The line labeled "RegressionNC" is the least squares line fitting the carbon monoxide (CO) data collected without the platinum catalyst installed.

The line labeled "RegressionCat" is the least squares line for the CO data with the catalyst.

Regression parameters listed in Table D.V

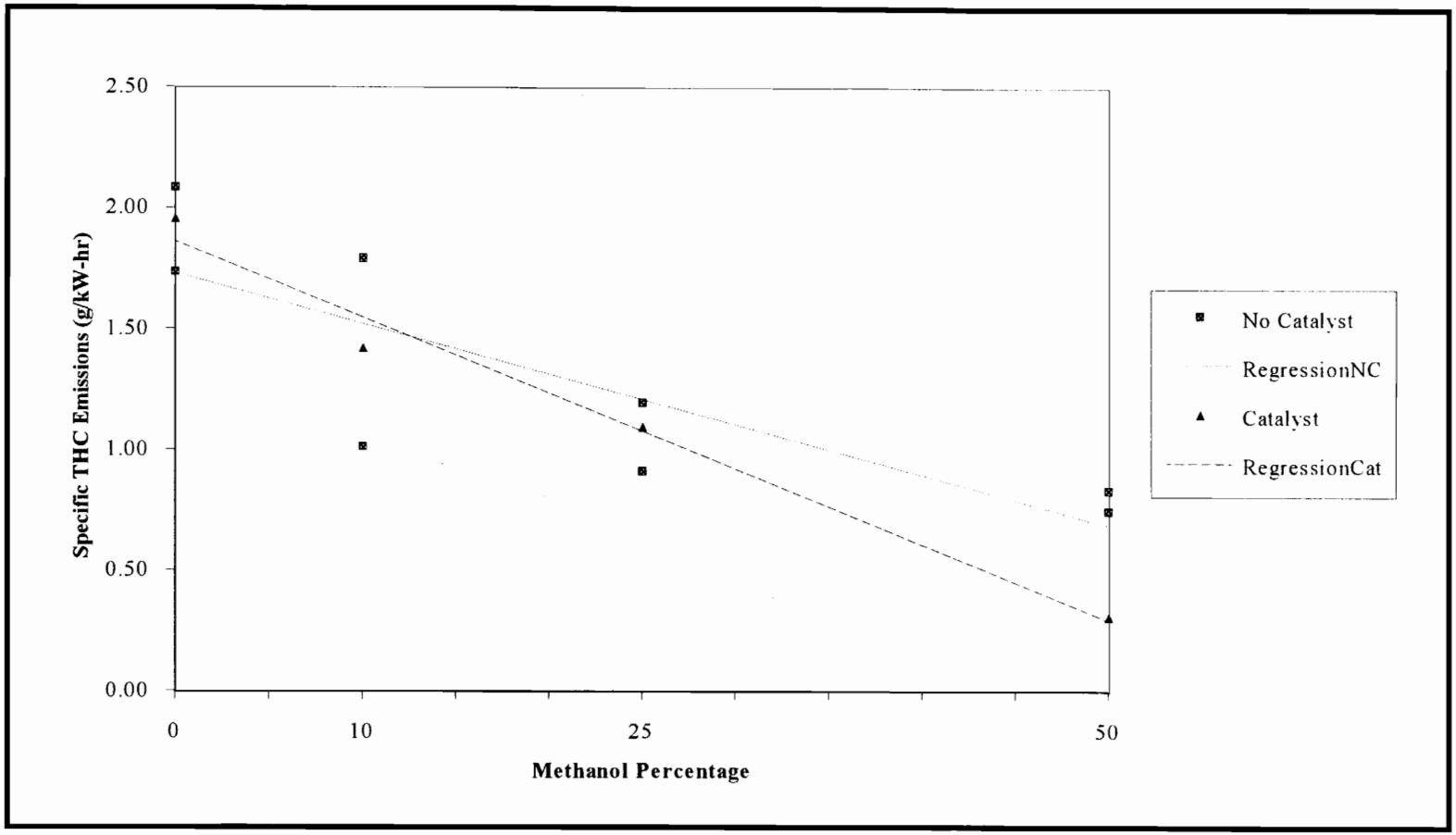

Figure 12 - Effect of Fuel Methanol Content on Specific Total Hydrocarbon Emissions

The line labeled "RegressionNC" is the least squares line fitting the total hydrocarbon (THC) data collected without the platinum catalyst installed.

The line labeled "RegressionCat" is the least squares line for the THC data with the catalyst.

Regression parameters listed in Table D.V

Figure 13 shows the effect of methanol addition on the exhaust oxygen concentration, with and without the catalyst. With no catalyst, O_2 concentrations increased with increasing methanol content. The variability between the samples taken at each methanol level did not allow a determination of quantitative increases, however, a t-test on the regression line confirmed the trend. With the catalyst installed, the same trend of increasing oxygen concentration was seen, with the catalyst values falling between the two non-catalyst values for each of the methanol enhanced fuels. The p-value for these data was 0.96, indicating that the two regression lines were virtually identical.

Figure 14 shows the effect of methanol addition on the exhaust concentration of carbon dioxide. With no catalyst installed, there was a small initial increase in CO_2 concentration with M10 fuel. The concentration then remained essentially constant for the other methanol enhanced fuels. This was borne out statistically, as an analysis of the regression line did not allow a conclusion of a non-zero slope. With the catalyst installed, a slight trend of increasing CO_2 with increasing methanol fuel content was observed. A very low p-value of 0.08 would seem to indicate some difference between the catalyst and non-catalyst CO_2 concentrations, but for the outlier with the G100 fuel.

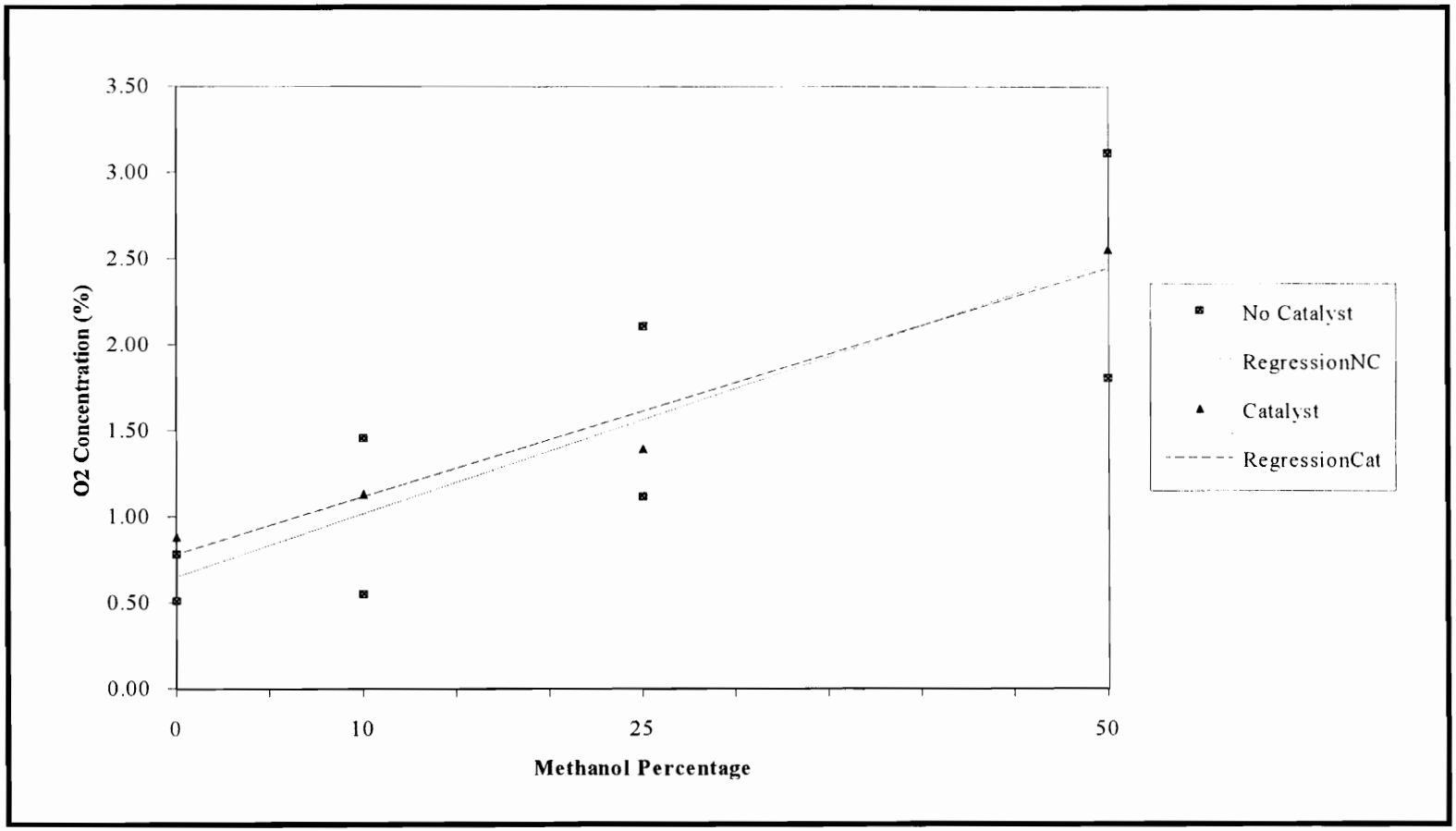

Figure 13 - Effect of Fuel Methanol Content on Exhaust Oxygen Concentration

The line labeled "RegressionNC" is the least squares line fitting the oxygen (O2) data collected without the platinum catalyst installed.

The line labeled "RegressionCat" is the least squares line for the O2 data with the catalyst.

Regression parameters listed in Table D.V

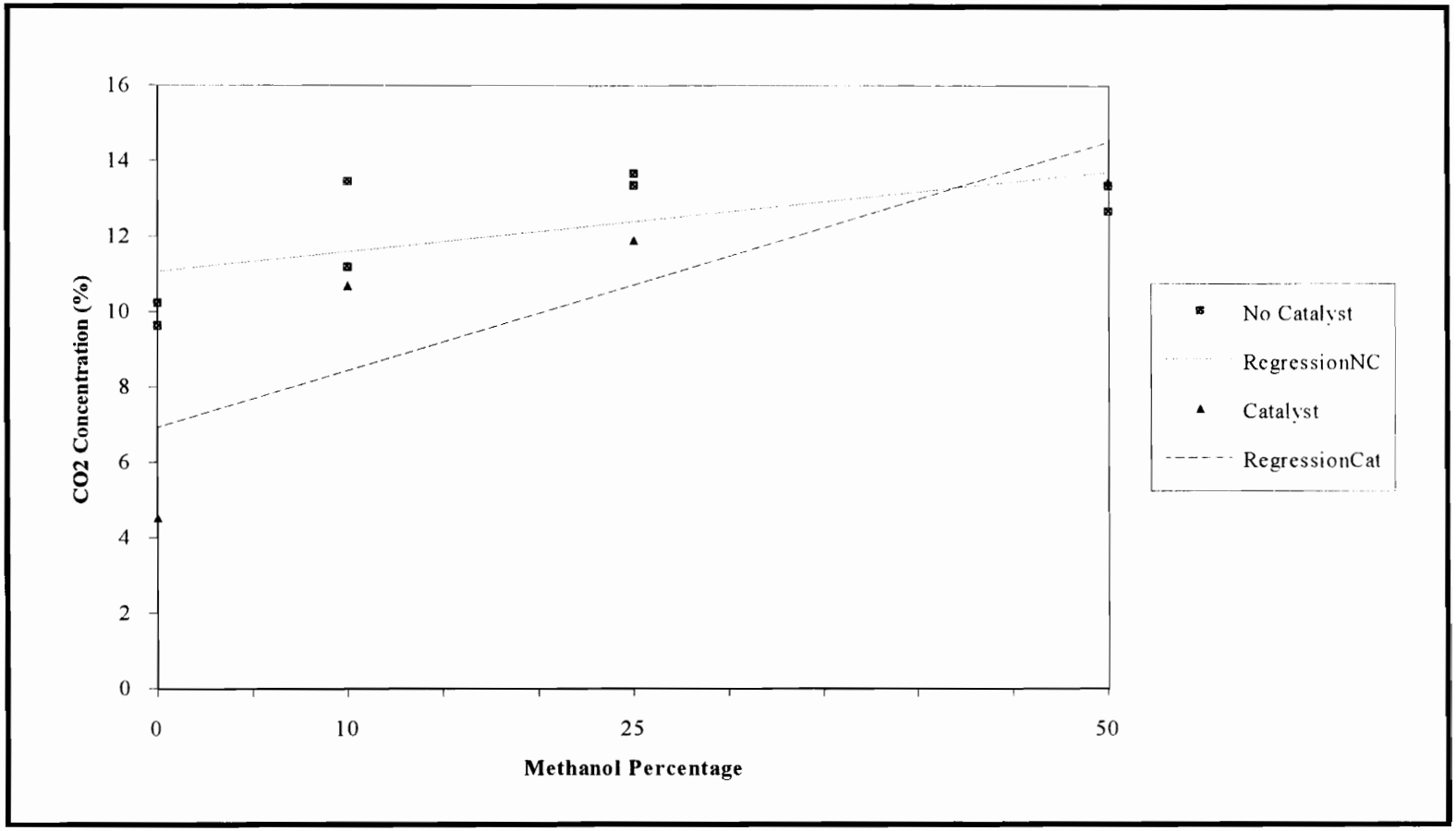

Figure 14 - Effect of Fuel Methanol Content on Exhaust Carbon Dioxide Concentration

The line labeled "RegressionNC" is the least squares line fitting the carbon dioxide (CO2) data collected without the platinum catalyst installed.

The line labeled "RegressionCat" is the least squares line for the CO2 data with the catalyst.

Regression parameters listed in Table D.V

Aldehyde Emissions Measurements

HPLC analyses permitted quantitative determination of the exhaust gas concentrations of formaldehyde and acetaldehyde. These values were then converted to specific values for presentation. See Appendix B for formulae relating to this procedure.

Table VIII presents results of the QA/QC analyses. None of the blanks analyzed, except the sampling system blank, contained formaldehyde or acetaldehyde above analytical detection limits. Significant amounts of both formaldehyde and acetaldehyde appeared in the sampling system blank. It was likely that the aldehydes detected came from the ambient air rather than the sampling system. This was believed to be the case as concentrations of both aldehydes in some exhaust gas samples were lower than those in the sampling system blank. However, formaldehyde concentrations in the exhaust were frequently similar to those found in the sampling system blank. Consequently, although results for formaldehyde will be presented and analyzed, the background levels found in the sampling system blank should be kept in mind when considering these results.

Gasoline

Table IX shows sampling dates, times and aldehyde concentrations for G100 fuel with and without the catalyst. For operation without the catalyst, the specific emission rates of formaldehyde ranged from a low of 71 mg/kW-hr to a high of 453 mg/kW-hr. The specific emission rates of acetaldehyde ranged from 18 mg/kW-hr to 880 mg/kW-hr.

With the platinum catalyst installed, the specific emission rates of formaldehyde were 239 mg/kW-hr and 460 mg/kW-hr, while the specific emission rates of acetaldehyde were 675 mg/kW-hr and 1550 mg/kW-hr. Considering the range of values for the uncontrolled aldehydes, changes in aldehyde emissions across the catalyst were difficult to predict.

Table VIII - Quality Assurance/Quality Control Results for Aldehyde Analyses

Control Type	Date	Sample Volume (mL)	Formaldehyde Concentration (µg/mL)	Acetaldehyde Concentration (µg/mL)
Vendor Blank	2/10/93	N/A	nd[a]	nd
Vendor Blank	2/10/93	N/A	nd	nd
Vendor Blank	3/4/93	N/A	nd	nd
Vendor Blank	3/25/93	N/A	nd	nd
Vendor Blank	4/28/93	N/A	nd	nd
Vendor Blank	4/28/93	N/A	nd	nd
Lab Blank	2/10/93	N/A	nd	nd
Lab Blank	4/28/93	N/A	nd	nd
Sampling System Blank	4/28/93	8105	0.045[b]	0.029[b]

[a]A designation of nd indicates that no peak was detected during the high performance liquid chromatography (HPLC) analysis discussed in the Methods and Materials section.

[b]The concentrations shown are those of the particular aldehyde in the air sampled to create the sampling system blank.

Table IX - Aldehyde Emissions from Gasoline Only Fuel Combustion

Date	Sampling Time (min)	Sample Volume[a] (mL)	Catalyst	Exhaust Formaldehyde Concentration[b] (µg/mL)	Formaldehyde Specific Emissions[c] (mg/kW-hr)	Exhaust Acetaldehyde Concentration[b] (µg/mL)	Acetaldehyde Specific Emissions[c] (mg/kW-hr)
2/10/93	12.5	2077	No	0.005	114	0.001	18
2/24/93	30.0	4986	No	0.003	71	0.024	567
4/28/93	5.0	1390	No	0.020	453	0.038	880
4/28/93	3.0	1309	Yes	0.019	460	0.028	675
4/28/93	3.0	1309	Yes	0.010	239	0.064	1550

[a]Sampling rate was measured using a rotameter which was previously calibrated using a wet test meter. The sampling rate and time allowed the sample volume to be calculated.

[b]Exhaust aldehyde concentrations were determined from the results of high performance liquid chromatography (HPLC) analyses and known sample volume.

[c]Aldehyde specific emissions were determined from the exhaust concentration, exhaust flow rate, and generator power output as outlined in Appendix B.

Ethanol

Table X shows sampling dates, times, aldehyde concentrations and specific emission rates for ethanol enhanced fuel exhausts. Figure 15 demonstrates the effect of ethanol addition on specific formaldehyde emissions. With no catalyst installed, formaldehyde may have increased about four times from the G100 level and remained fairly constant at all levels of alcohol addition. This would be the case if the high data point for G100 was an outlier. A t-test indicated that the slope of the regression line was non-zero for a p-value of 0.09. This 91% confidence level would seem to indicate that the addition of ethanol increases formaldehyde emissions, although the mechanism which caused this was unknown. A similar trend was detected at the 86% confidence level for formaldehyde emissions with the catalyst installed. A p-value of 0.62 generated when comparing the regression lines indicated that catalytic control of formaldehyde probably did not occur. Again, these data without replicates should be viewed qualitatively.

Without the platinum catalyst, acetaldehyde emissions were observed to increase with increasing ethanol fuel content as demonstrated by the t-test. This was expected as the same result was observed in the literature cited earlier. However, due to the variability in these data, the amount of increase could not be reliably quantified. The same trend was observed with the catalyst installed. A comparison of the catalyst and non-catalyst regression lines revealed a p-value of 0.14. Although this 86% confidence level might indicate possible catalytic control of acetaldehyde, visual inspection of Figure 16 shows that this control might only have occurred at the 50% ethanol level.

Table X - Aldehyde Emissions from Ethanol Enhanced Fuel Combustion

Fuel	Alcohol (%)	Date	Sampling Time (min)	Sample Volume[a] (mL)	Catalyst	Exhaust[b] Formaldehyde Concentration (µg/mL)	Specific[c] Formaldehyde Emissions (mg/kW-hr)	Exhaust[b] Acetaldehyde Concentration (µg/mL)	Specific[c] Acetaldehyde Emissions (mg/kW-hr)
E10	10	3/25/93	3.00	1309	No	0.015	349	0.203	4717
E25	25	3/25/93	1.37	428	No	0.020	472	0.449	10429
E50	50	3/25/93	3.00	722	No	0.017	396	0.515	11988
E10	10	4/28/93	2.00	873	No	0.016	375	0.056	1290
E25	25	4/28/93	2.00	873	No	0.017	398	0.097	2225
E50	50	4/28/93	2.00	873	No	0.022	489	0.266	5943
E10	10	4/28/93	2.25	982	Yes	0.016	355	0.042	949
E25	25	4/28/93	2.00	873	Yes	0.013	301	0.108	2513
E50	50	4/28/93	2.00	873	Yes	0.020	469	0.213	5111
E50	50	4/28/93	2.00	873	Yes	0.032	793	0.200	5016

[a]Sampling rate was measured using a rotameter which was previously calibrated using a wet test meter. The sampling rate and time allowed the sample volume to be calculated.

[b]Exhaust aldehyde concentrations were determined from the results of high performance liquid chromatography (HPLC) analyses and known sample volume.

[c]Aldehyde specific emissions were determined from the exhaust concentration, exhaust flow rate, and generator power output as outlined in Appendix B.

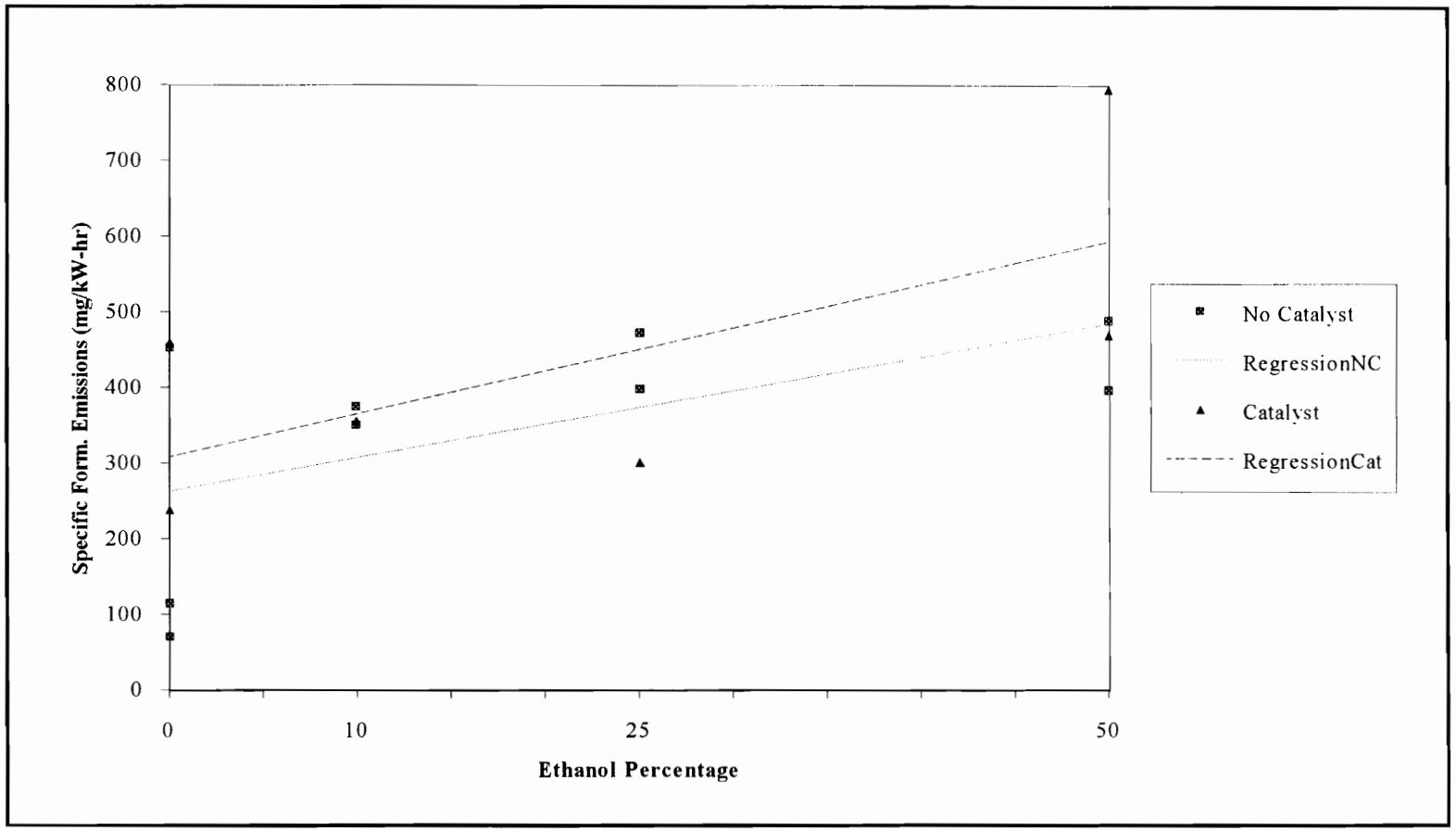

Figure 15 - Effect of Fuel Ethanol Content on Specific Formaldehyde Emissions

The line labeled "Regression NC "is the least squares line fitting the formaldehyde (Form.) data collected without the platinum catalyst installed.

The line labeled "Regression Cat" is the least squares line for the Form. data with the catalyst.

Regression parameters listed in Table D.V

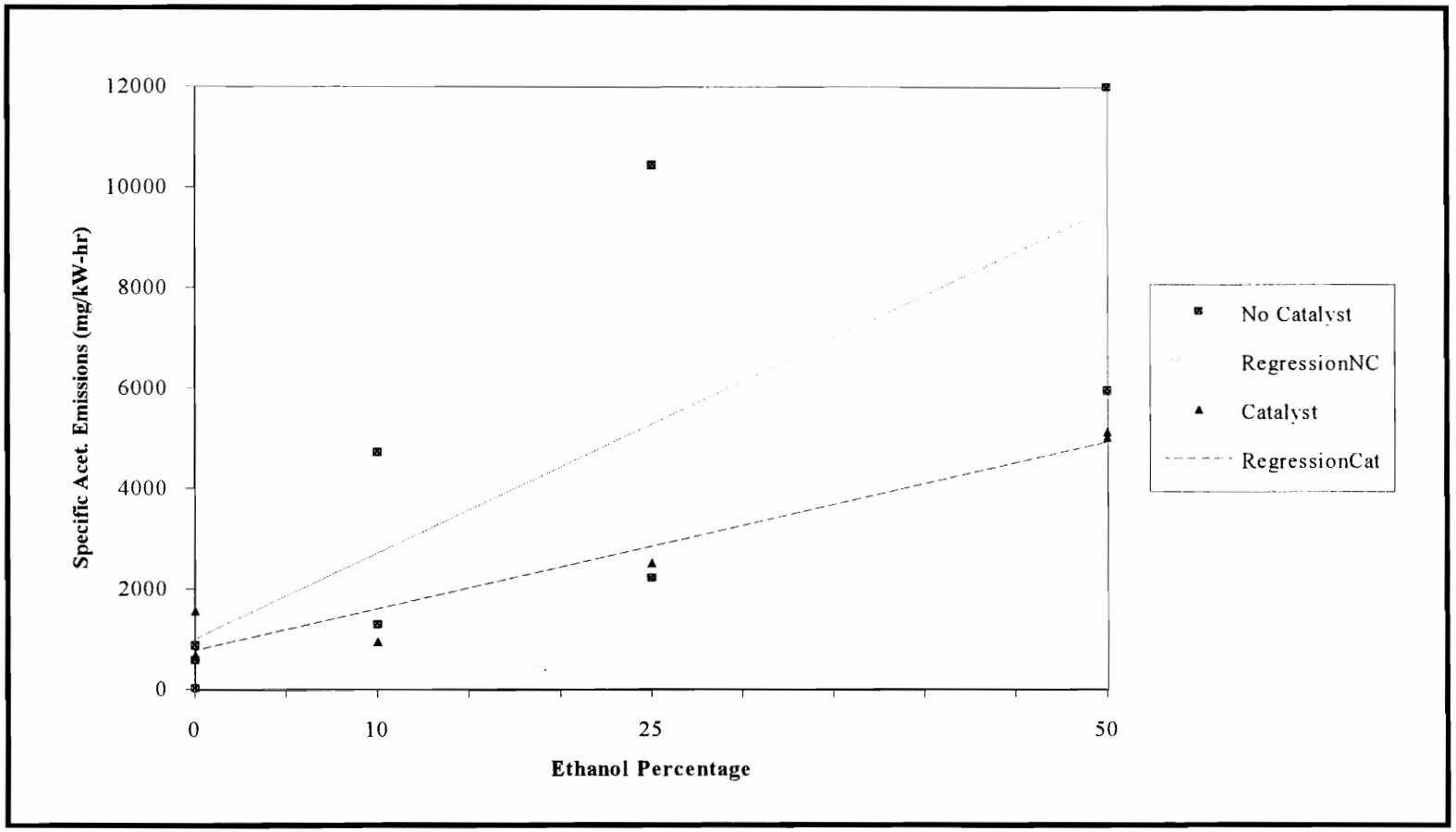

Figure 16 - Effect of Fuel Ethanol Content on Specific Acetaldehyde Emissions

The line labeled "Regression NC "is the least squares line fitting the acetaldehyde (Acet.) data collected without the platinum catalyst installed.

The line labeled "Regression Cat" is the least squares line for the Form. data with the catalyst.

Regression parameters listed in Table D.V

Methanol

Table XI shows sampling dates, times, aldehyde concentrations and specific emission rates for methanol enhanced fuel exhausts. Figure 17 demonstrates the effect of methanol addition on specific formaldehyde emissions. A t-test of the regression line for data collected with no catalyst installed indicated that emissions of formaldehyde were independent of fuel methanol content down to the 18% confidence level. With the catalyst installed, fairly consistent replicate samples showed the same result down to 23%. No catalytic removal of formaldehyde occurred as evidenced by the 0.87 p-value generated by a comparison of the regression lines.

Acetaldehyde emissions showed increases over G100 values while using M10, M25, and M50 fuels, but no trend in the emissions was observed based on a p-value of 0.77. With the catalyst installed, a slight trend of decreasing emissions with increasing methanol content was indicated at the 92% confidence level. Although the actual decrease in acetaldehyde emissions from 0% to 50% methanol was small (see Figure 18), the consistency of the replicates for these results probably influenced the statistical results. A p-value of 0.59 when comparing regression lines indicated a lack of any significant catalytic control of acetaldehyde.

Table XI - Aldehyde Emissions from Methanol Enhanced Fuel Combustion

Fuel	Alcohol Volume (%)	Date	Sampling Time (min)	Sample Volume (mL)	Catalyst	Exhaust Formaldehyde Concentration (µg/mL)	Formaldehyde Specific Emissions (mg/kW-hr)	Exhaust Acetaldehyde Concentration (µg/mL)	Acetaldehyde Specific Emissions (mg/kW-hr)
M10	10	3/25/93	3.00	1309	No	0.013	296	0.137	3174
M25	25	4/1/93	2.00	873	No	0.000	0	0.038	917
M50	50	4/1/93	2.00	705	No	0.012	281	0.072	1713
M10	10	4/28/93	3.00	1309	No	0.021	474	0.471	10454
M25	25	4/28/93	3.00	1309	No	0.027	615	0.157	3606
M50	50	4/28/93	5.00	1483	No	0.012	301	0.010	230
M10	10	4/28/93	3.00	1309	Yes	0.013	291	0.066	1535
M10	10	4/28/93	3.00	1309	Yes	0.011	259	0.056	1295
M25	25	4/28/93	3.00	1309	Yes	0.014	309	0.059	1337
M25	25	4/28/93	3.00	1309	Yes	0.019	420	0.048	1076
M50	50	4/28/93	3.00	1309	Yes	0.015	358	0.019	451
M50	50	4/28/93	3.00	1309	Yes	0.014	338	0.024	560

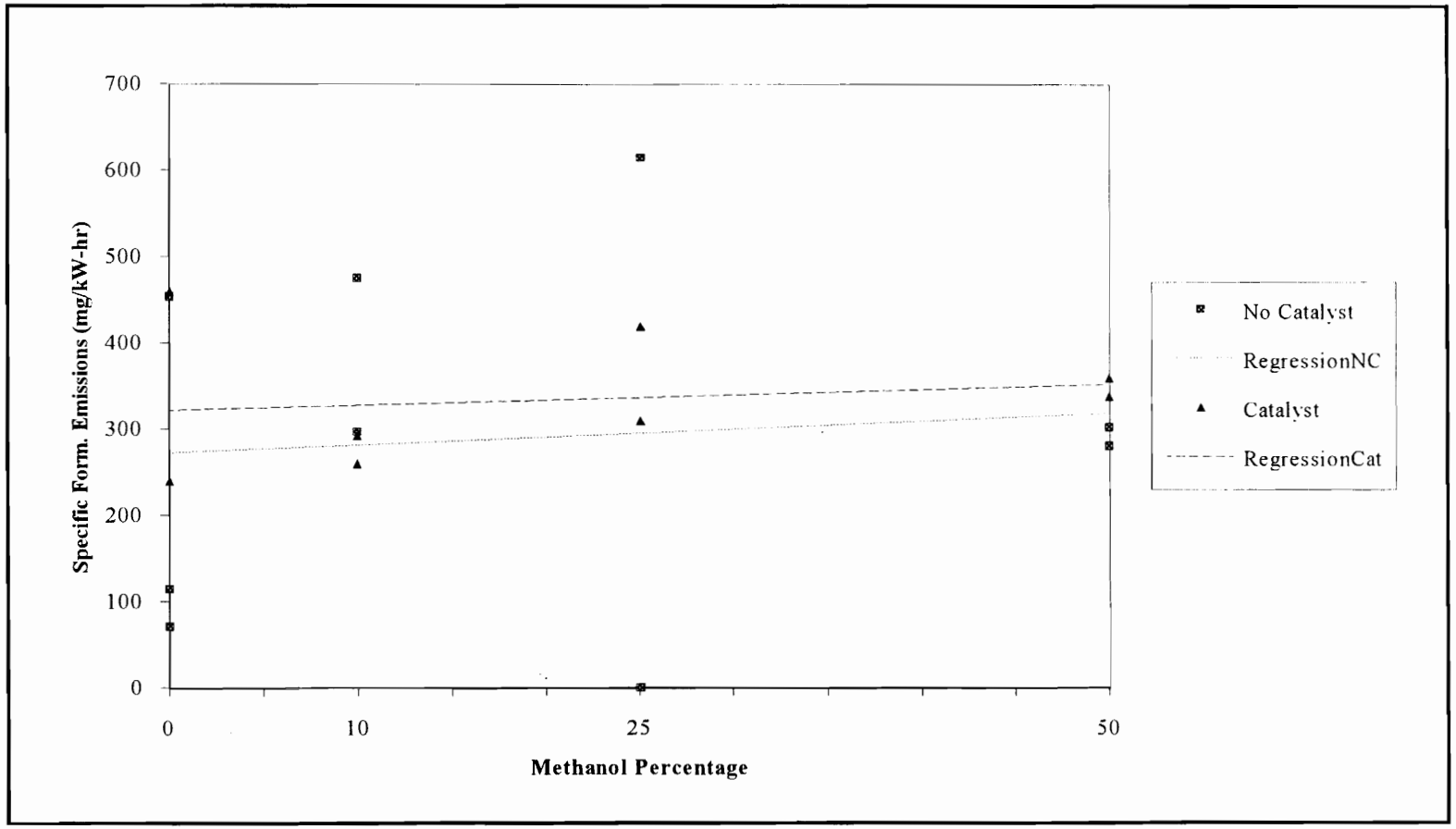

Figure 17 - Effect of Fuel Methanol Content on Specific Formaldehyde Emissions

The line labeled "RegressionNC" is the least squares line fitting the formaldehyde (Form.) data collected without the platinum catalyst installed.

The line labeled "RegressionCat" is the least squares line for the Form. data with the catalyst.

Regression parameters listed in Table D.V

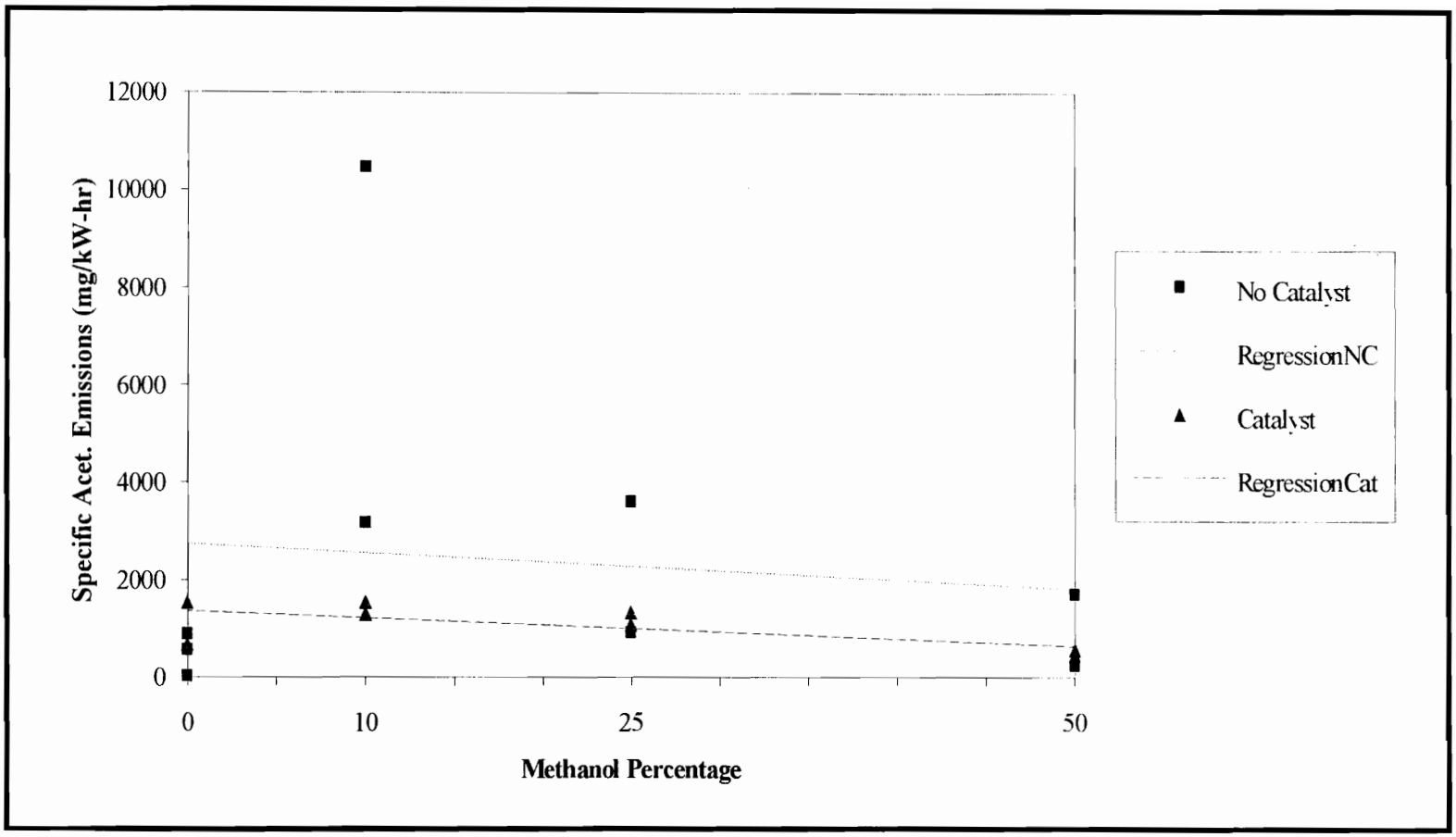

Figure 18 - Effect of Fuel Methanol Content on Specific Acetaldehyde Emissions

The line labeled "RegressionNC" is the least squares line fitting the acetaldehyde (Acet.) data collected without the platinum catalyst installed.

The line labeled "RegressionCat" is the least squares line for the Form. data with the catalyst.

Regression parameters listed in Table D.V

V. DISCUSSION

Basic Engine Measurements

The measured engine fuel rate was slightly higher than that reported by the engine manufacturer. The average measured rate was 15.2 mL/min (0.91 L/hr) while Honda rated fuel consumption at 0.73 L/hr. Measured air/fuel ratios were typical of those expected of gasoline fuel operation and agreed well with the average value calculated from the exhaust gas constituents. The stoichiometric air/fuel ratio for gasoline is approximately 15. Spindt reported values of air/fuel ratios from 10.5 to 18.0. Values determined in this research were from 10.2 to 12.0.

Standard Emissions Measurements

Carbon monoxide results using gasoline fuel were reasonable based on the results of Donohue *et al.*, but were much lower (one-quarter to one-half) than those reported by Hare and White and supplied in EPA AP-42 (EPA, 1992). These differences could be due to the testing methods used or the range of engine sizes tested in the case of the AP-42 results. Hydrocarbon emissions determined in this study were below those reported in the literature. This was probably because the Honda engine studied employed overhead valves designed to reduce emissions.

The catalytic converter did not effect a decrease in either CO or THC emissions when the engine was operated with G100 fuel. This was expected due to the low oxygen content (< 1%) of the exhaust. Although no replicate sample was taken with the catalyst, the 17.5 minute sample should be indicative of average engine operation. Conversely the carbon dioxide value for the catalyst sample is unusually low, 4.5%. Carbon dioxide concentrations from IC engines can range from about 6.3% to 15.3% for commercial fuels (Spindt, 1965). If no catalytic oxidation occurred, the CO_2 concentration should be

similar to those with no catalyst installed. If oxidation had occurred in the catalyst, the CO_2 concentration should have increased from the non-catalyst values. This low CO_2 concentration value could indicate sampling or analytical problems which a replicate could confirm or refute.

As expected, carbon monoxide and total hydrocarbon emissions generally decreased with increasing fuel alcohol content. Figure 19 compares the reduction of specific CO emissions due to ethanol and methanol fuel content. A statistical test of the regression lines indicates that the two alcohols had different effects on specific CO emissions at a p-value of 0.03 (97% confidence interval). It is evident than methanol decreased specific CO emissions more than ethanol with 25% alcohol fuel content. The spread in CO results for M10 make this observation somewhat more questionable, and it appears that the two alcohols had similar effects with 50% alcohol addition. Figure 20 shows THC reductions from ethanol and methanol addition. A significant difference between the regression lines exists with a 91% confidence interval. Variability of the results for the M10, E25, and M25 fuels made quantification of these differences difficult, and it is obvious that for the 50% alcohol level, there was no significant difference. None of the literature reviewed for this research compared the effects of ethanol and methanol on reduction of CO and THC. The literature did report reductions in these pollutants when using one alcohol or the other as a fuel additive. These results are cited in the literature review. It is not immediately apparent why methanol appeared to result in greater pollutant reduction than ethanol. One explanation may be that oxygen comprises a greater fraction of methanol's mass than ethanol's. Methanol is 50% oxygen by weight, whereas ethanol is only 36% oxygen by weight.

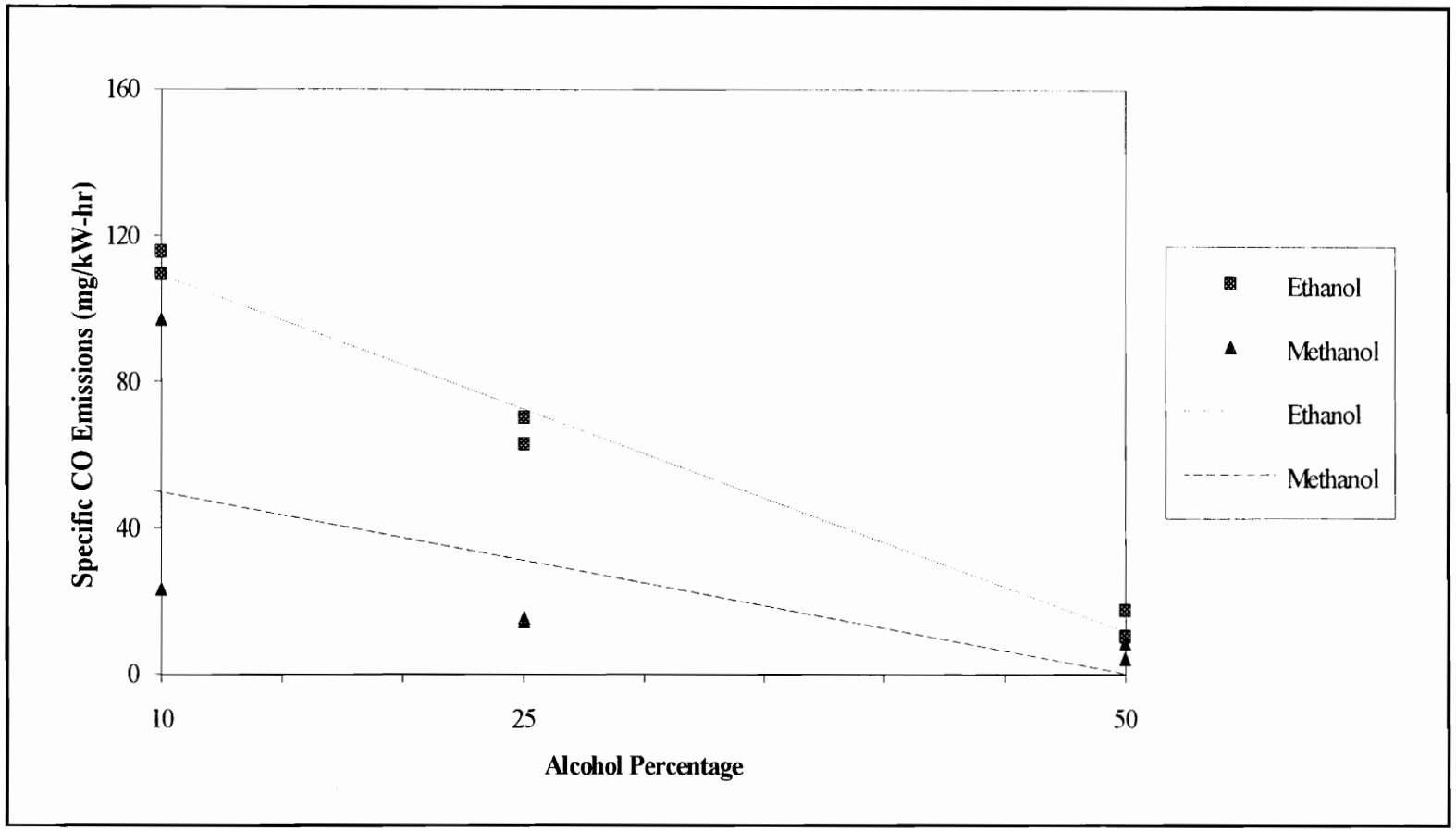

Figure 19 - Comparison of Specific Carbon Monoxide Emissions Reduction due to Ethanol and Methanol Fuel Content

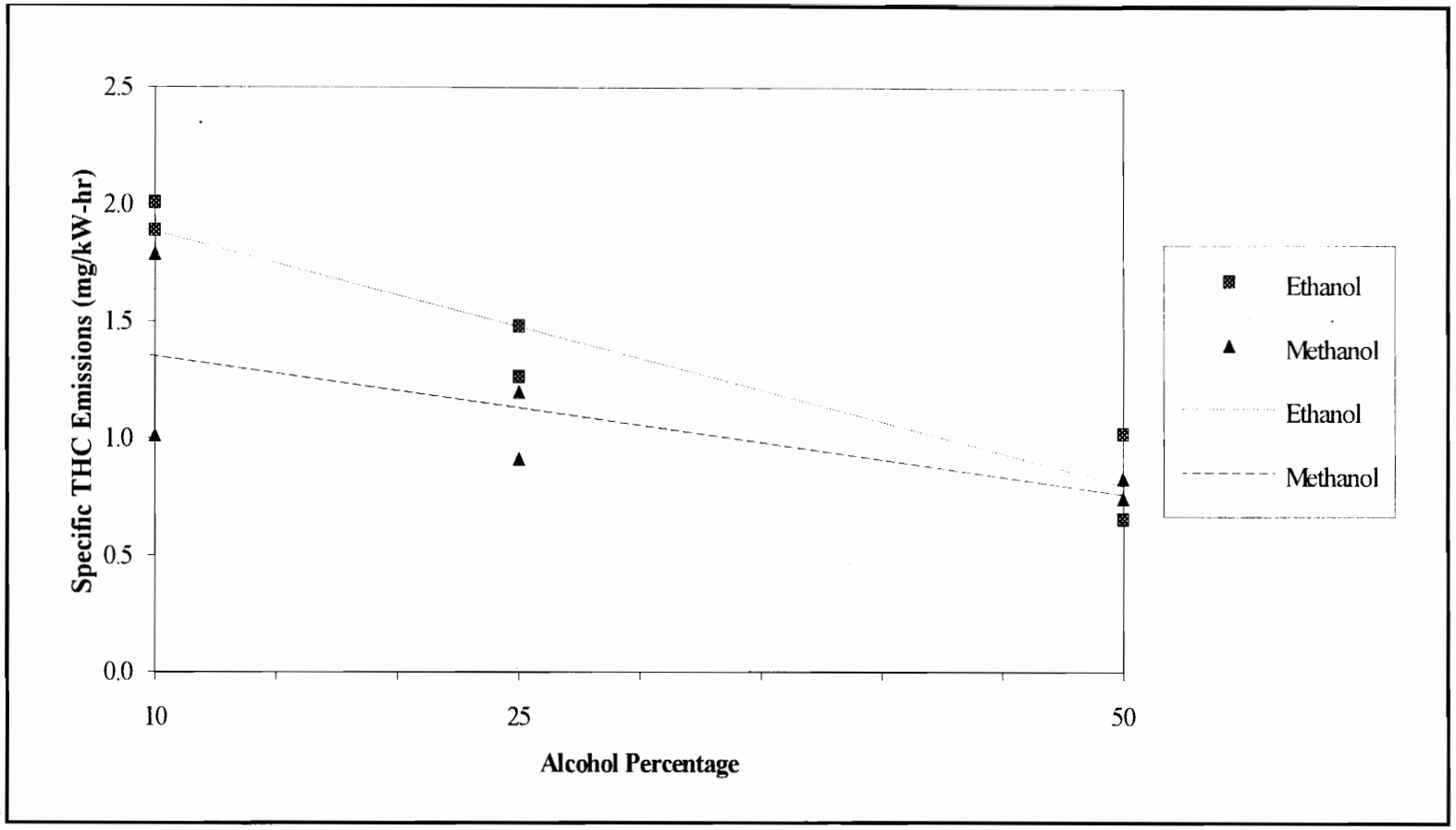

Figure 20 - Comparison of Specific Total Hydrocarbon Emissions Reduction due to Ethanol and Methanol Fuel Content

Most runs with the platinum catalyst installed resulted in only one sample being taken. As a result, quantitative results could not be determined. Qualitatively, however, no catalytic control of either CO or THC was observed. This conclusion was reached based on statistical analyses of the catalyst vs. non-catalyst pollutant emission rates as well as exhaust oxygen and carbon monoxide concentrations. Oxygen is consumed and carbon dioxide is formed in the oxidation reaction. No significant differences were detected between the catalyst and non-catalyst results near the 90% confidence level, except in the case of carbon dioxide. This result was likely due to the unusually low CO_2 concentration for G100 fuel with the catalyst.

Aldehyde Emissions Measurements

Gasoline

While operating with gasoline fuel, formaldehyde emissions were generally higher than those reported by Hare and White and the EPA emission factors. Two of the five measurements were within the reported range, however the large variability of the results made further analysis difficult. Acetaldehyde emissions were much higher than those reported by Hare and White. The reason for this was not known.

Ethanol

Ethanol addition caused an increase in emissions of both formaldehyde and acetaldehyde. Formaldehyde emissions increased above G100 values with ethanol addition but no correlation was evident between ethanol content and formaldehyde emissions. No catalytic control of formaldehyde was demonstrated, as shown by the results of the statistical test comparing the regression lines. Judging by the literature, aldehydes are readily oxidized in catalytic converters. Potential reasons for the lack of control in this care are discussed below. Again, it is important to keep the results of the QA/QC analyses in mind when considering these formaldehyde data.

Acetaldehyde emissions increased with increasing ethanol content, again with some variability among samples taken at given ethanol levels. This increase in acetaldehyde emissions was to be expected, as during combustion, the ethanol is oxidized to acetaldehyde, causing an increase in these emissions. Qualitatively, acetaldehyde emissions after the catalyst were near the lower end of the range of values measured without the catalyst. The 86% confidence level for a comparison of the catalyst vs. non-catalyst acetaldehyde results might indicate some control of this pollutant through the catalyst. A visible inspection of the data (Figure 16) indicated that this control could possibly have occurred with 50% ethanol. Indeed, the values of the E50 catalyst results compared to the non-catalyst results, coupled with the low variability of the E50 replicate samples with the catalyst reinforces the idea that catalytic control could have occurred with this fuel.

Methanol

Results similar to those from ethanol addition were observed with methanol addition. Increases in formaldehyde emissions were seen over the G100 values for any methanol addition. No dependence of formaldehyde emissions on methanol addition was apparent. Variability of non-catalyst results was great and any trend could have been lost in this variability. Operation with the catalyst installed resulted in no trend in formaldehyde emissions, although the variability between replicates was less than that with no catalyst. No control of formaldehyde was evident with the catalyst installed. Formaldehyde results may be suspect due to the high levels of formaldehyde found in the sampling system blank.

Methanol fuel addition was not be expected to increase acetaldehyde emissions, as no chemical mechanism for obtaining acetaldehyde from methanol exists. Appropriately, no trend of acetaldehyde emissions was apparent with increasing methanol fuel content.

Williams *et al.* reported decreasing acetaldehyde emissions with increasing methanol fuel content. This trend was seen with the catalyst installed. Acetaldehyde emissions with the catalyst installed were again near the lower values recorded without the catalyst, but no control of acetaldehyde was apparent.

Recommendations

A major difficulty with this research was the lack of a second sample acquisition system. With only one sampling system, it was necessary to complete all runs without the catalyst. The catalyst was then installed and new samples obtained. Any variation between the two engine runs could affect the emissions. As a result, any further research in this topic should be performed using simultaneous sampling before and after the catalyst.

One reason for the lack of catalytic oxidation may have been the placement of the catalytic converter in the exhaust system. In this experimental setup, the converter was installed several inches from the exhaust manifold. Spacing constraints necessitated this arrangement. In an engine equipped with a catalyst, the catalyst will likely be installed directly on the exhaust manifold to take advantage of the high temperature of the engine. Future research should be conducted with the catalyst installed directly on the exhaust manifold for the same reason.

In order to more accurately characterize the air fuel ratio and exhaust flow rate, the fuel rate into the engine should be measured. Perhaps a burette made of a plastic material which is resistant to the effects of the fuel mixtures could be used. Alternatively, an electronic flow meter could be used. This method would be more accurate, and would allow detection of continuous variations in the flow.

VI. CONCLUSIONS

The research results demonstrated the effective use of ethanol and methanol for reduction of carbon monoxide and total hydrocarbon emissions. However, the use of these fuel oxygenates increased emissions of formaldehyde and acetaldehyde. Ethanol fuel addition increased emissions of both aldehydes, while methanol addition increased formaldehyde emissions and possibly contributed to a decrease in acetaldehyde emissions. Since formaldehyde is a known or suspected carcinogen, and acetaldehyde an acute irritant, the use of high concentrations of alcohol fuel additives may be less than desirable from a toxic emissions standpoint.

Catalytic control of CO and THC was not effectively demonstrated for any of the fuel mixtures studied. Although increases in exhaust oxygen concentration were observed, other factors may have influenced this apparent lack of catalytic control.

Catalytic control of the aldehydes was not quantitatively demonstrated in this research. Qualitatively however, it appeared that some catalytic oxidation of acetaldehyde may have occurred when employing 50% ethanol fuel.

Analytical methods used in this research are considered proven and reliable. However, improvements in equipment setup and sampling techniques could result in improved reproducibility of results. Additionally, data collection for parameters such as fuel rates could be expanded to provide a greater basis for drawing conclusions.

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APPENDIX A - CALIBRATION DATA

Table A.I - Laminar Flow Meter Calibration Data

Meriam[a] dp[b] (in H2O)	ENE dp[b] (in H2O)	Flow Rate (cfm)	Slope (cfm/in H2O)	Intercept (cfm)	Correlation
0.0	0.000	0.0			
0.2	0.035	2.5			
0.4	0.070	5.0	71.4	0.0	
0.6	0.100	7.5	73.6	0.0	
0.8	0.135	10.0	73.9	0.0	
1.0	0.165	12.5	74.7	0.0	
1.2	0.195	15.0	75.6	0.0	0.9996
1.4	*0.215*	*17.5*	*77.4*	*0.0*	
1.6	*0.240*	*20.0*	*79.1*	*0.0*	
1.8	*0.250*	*22.5*	*81.6*	*0.0*	
2.0	*0.275*	*25.0*	*83.7*	*0.0*	
2.2	*0.300*	*27.5*	*85.4*	*0.0*	
2.4	*0.320*	*30.0*	*87.0*	*0.0*	
2.6	*0.330*	*32.5*	*88.9*	*0.0*	
2.8	*0.350*	*35.0*	*90.7*	*0.0*	
3.0	*0.370*	*37.5*	*92.3*	*0.0*	

Figures in italic indicate non-linear response of laminar flow meter.

[a]Laminar flow meter calibrated using custom built Meriam laminar flow meter with 8 in H_2O pressure drop per 100 cfm.

[b]dp indicates pressure drop across unit in in H_2O.

Table A.II - Rotameter Calibration Data from Wet Test Meter

Rot. Flow (SCFH)	V (ft^3)	Time (min)	Vol. Rate (cfm)	Vol. Rate (mL/min)	Correlation
0.0	0	0.00	0.0000	0.0	
0.5	0.339	10.00	0.0067	189.9	
1.0	0.1595	10.00	0.0154	436.4	
2.5	0.069	10.00	0.0329	932.3	0.997004

Teledyne Max 5 rotameter calibrated using GCA/Precision Scientific wet test meter.

Table A.III - Rotameter Calibration Data from Direct Displacement

Rotameter Flow (SCFH)	V1 (mL)	V2 (mL)	Time (min)	Vol. Rate (mL/min)
0.0	0	0	0.00	0
0.4	750	148	10.50	57
0.5	350	188	1.00	162
0.5	750	220	2.75	193
0.5	750	232	2.50	207
0.5	750	242	2.50	203
1.0	500	192	0.75	411
1.0	750	292	1.00	458
1.5	750	185	1.00	565
2.0	750	232	0.75	691

Teledyne Max 5 rotameter calibrated using a direct displacement method. Pump output was directed into water filled flask and run for a given time. The displaced water was determined using a graduated cylinder. Flow rate was determined using displaced water volume and pumping time.

Table A.IV - HPLC DNPH-Derivative Standards Calibration Data

	Ret. Time (min)	Conc. (µg/mL)	Area[a] (mA-units)	Slope (µg/mL·mA-units)	Intercept (µg/mL)	Correlation
DNPH - Acetaldehyde Derivative Standards						
	8.407	2.7	99			
	8.472	6.9	267			
	8.470	6.9	265	0.0246	0.308	
	8.336	13.7	544	0.0246	0.312	
	8.507	27.4	1073	0.0253	0.130	
	8.518	68.5	2668	0.0256	0.006	
	8.346	137.0	5459	0.0251	0.340	0.99994
Avg. Retention Time	8.437					
Standard Deviation	0.074					
Maximum Variation %	2.183					
DNPH - Formaldehyde Derivative Standards						
	6.621	2.6	86			
	6.623	6.5	221			
	6.627	6.5	220	0.0290	0.106	
	6.623	13.0	444	0.0291	0.100	
	6.672	26.0	878	0.0296	-0.008	
	6.642	65.0	2231	0.0291	0.135	
	6.616	130.0	4513	0.0288	0.305	0.99998
Avg. Retention Time	6.632					
Standard Deviation	0.019					
Maximum Variation %	0.846					

High performance liquid chromatography (HPLC) analysis performed on a Hewlett-Packard Model 1090 with an ultraviolet detector.

[a]HPLC response in milliarea units.

APPENDIX B - FORMULAE

Calculations for Estimating Exhaust Flow Rate

Knowing the fuel mass rate and the intake air rate, the mass rate of the exhaust can be estimated as the sum of the two mass rates. The mass rate of the intake air can be calculated from the volumetric flow rate.

$$m_{INT} = \frac{P_{AMB} V_{INT} MW}{R T_{AMB}}$$

m_{INT}= mass rate of intake air

P_{AMB}= ambient pressure

V_{INT}= volumetric flow rate of intake air

MW = molecular weight of air

R = universal gas constant

T_{AMB}= ambient temperature

$$m_{EXH} = m_{INT} + m_{FUEL}$$

m_{EXH}= mass rate of exhaust

m_{FUEL}= mass rate of fuel

The volume rate of the exhaust can then be calculated from the equation for intake air mass rate above, using the pressure, temperature, and molecular weight of the exhaust gas. The molecular weight of the exhaust gas can be determined from the volume (molar) fractions of species present in the exhaust gas and their respective molecular weights.

$$MW_{MIX} = \sum x_i MW_i$$

x_i= volume (molar) fraction of species i

MW_i= molecular weight of species i

Determination of Specific Emissions from Pollutant Concentrations

Given a volume fraction (or part per million) concentration of a pollutant, the mass concentration of the pollutant can be determined.

$$C_{MASS} = C_V \frac{P}{RT} MW$$

C_{MASS}= pollutant mass concentration, mass/volume

C_V= pollutant volume concentration, parts/part

P = gas pressure

R = universal gas constant

T = gas temperature

MW = pollutant molecular weight

For THC concentration given in parts per million (ppm), the volume concentration is:

$$C_V = C_{ppm}\ 10^6$$

Cppm= pollutant concentration, ppm

With the mass concentration and the exhaust flow rate, the mass rate of the pollutant can be calculated.

$$m = C_{MASS} V_{EXH}$$

m = pollutant mass rate, mass/time

V_{EXH} = exhaust volume rate, volume/time

The specific emission rate can then be calculated by:

$$E_{SP} = \frac{m}{P_{GEN}}$$

E_{SP} = specific emission rate, mass/power

P_{GEN} = generator power output

Determination of Specific Aldehyde Emissions

Given an HPLC response peak area, the concentration of aldehyde in the sample can be determined from the standard curves.

$$C_{SAMP} = A_{HPLC} \cdot m_{STD}$$

C_{SAMP}= aldehyde concentration in the sample, μg/mL

A_{HPLC}= HPLC peak area, mA units

m_{STD}= slope of the standard curve, μg/mL·mA units

This calculation was actually performed in Microsoft® Excel, using the TREND function, which simply evaluates the functional value of a least squares line for the supplied x-value. Given a known x-value, this function calculates a y-value from a set of known x and y-values. The known x and y-values are the values generated from the standard analyses.

Sample vials were weighed before and after eluting sample cartridges. The difference in mass was taken as the mass of the acetonitrile (MeCN). Knowing the mass of MeCN used to elute the Sep-Pak® DNPH cartridge, the volume of MeCN can be calculated from the density. The density was determined by weighing a known volume of MeCN.

$$\rho_{MeCN} = \frac{m_{MeCN}}{V_{MeCN}}$$

ρ_{MeCN}= acetonitrile density, g/mL

m_{MeCN}= mass of acetonitrile, g

V_{MeCN}= volume of acetonitrile, mL

The MeCN volume was measured using a 10mL volumetric flask. The flask was weighed before and after adding the MeCN, and the difference was taken as the mass of the MeCN.

From the aldehyde concentration and MeCN volume, the total mass of aldehyde collected can be calculated.

$$m_{ALD} = C_{SAMP} V_{MeCN}$$

m_{ALD} = total collected mass of aldehyde

Knowing the volume of exhaust sampled, the exhaust mass concentration of the aldehyde can be determined.

$$C_{MASS} = \frac{m_{ALD}}{V_{SAMP}}$$

C_{MASS} = exhaust aldehyde mass concentration

V_{SAMP} = volume of exhaust sampled

Specific emission rates can then be determined as discussed above.

APPENDIX C - HPLC PROGRAM AND CHROMATOGRAM

```
F I L E   I N F O R M A T I O N

                PARAMETER FILE
Param. File Name    DATA:WDWW6FS.A
Last Change Date    24 Feb 93  2:45 pm

     Information : DNPH-ALDEHYDE PROGRAM WATERS GRADIENT
 Last Altered By : WDW

                DATA FILE
  Data File Name    DATA:WDW6.D

   Operator Name : WDW
     Sample Name :
Further Comments :

L I Q U I D   C H R O M A T O G R A P H                    initial parameters


           Flow :    1.500 ml/min
      Solvent  A :     60.0 %
               B :     40.0 %
              C1 :      0.0 %                                        : narrow

Oven Temperature :     40.0 C
    Max Pressure :      400 bar                      Min Pressure :    off

     Stop Time : no limit                          Column Switch :      0
     Post Time :     0.00 min                           Contacts :   0000

Injection Volume :     20.0 ul                          Slowdown :      2

L I Q U I D   C H R O M A T O G R A P H                          timetable

 Time (min)
      1.00          Solvent      A :   60.0 %     B :   40.0 %     C1 :    0.0 %
     10.00          Solvent      A :   40.0 %     B :   60.0 %     C1 :    0.0 %

D I O D E - A R R A Y   D E T E C T O R                    signals & spectra

       SIGNALS        A        B        C        D        E        F        G        H
Sample    (nm)
    Wavelength :     360      340      380      off      off      off      off      off
     Bandwidth :       4        4        4
Reference (nm)
    Wavelength :     550      550      550
     Bandwidth :     100      100      100


Store Spectrum :  peak controlled     about   20050 Records acquired during Run
     Threshold :    10.0 mAU

     Peakwidth :  0.100 min                      Sampling Interval      640 ms
     Stop Time : same as LC                   Spectrum Range from :     210 nm
                                                              to :     400 nm
```

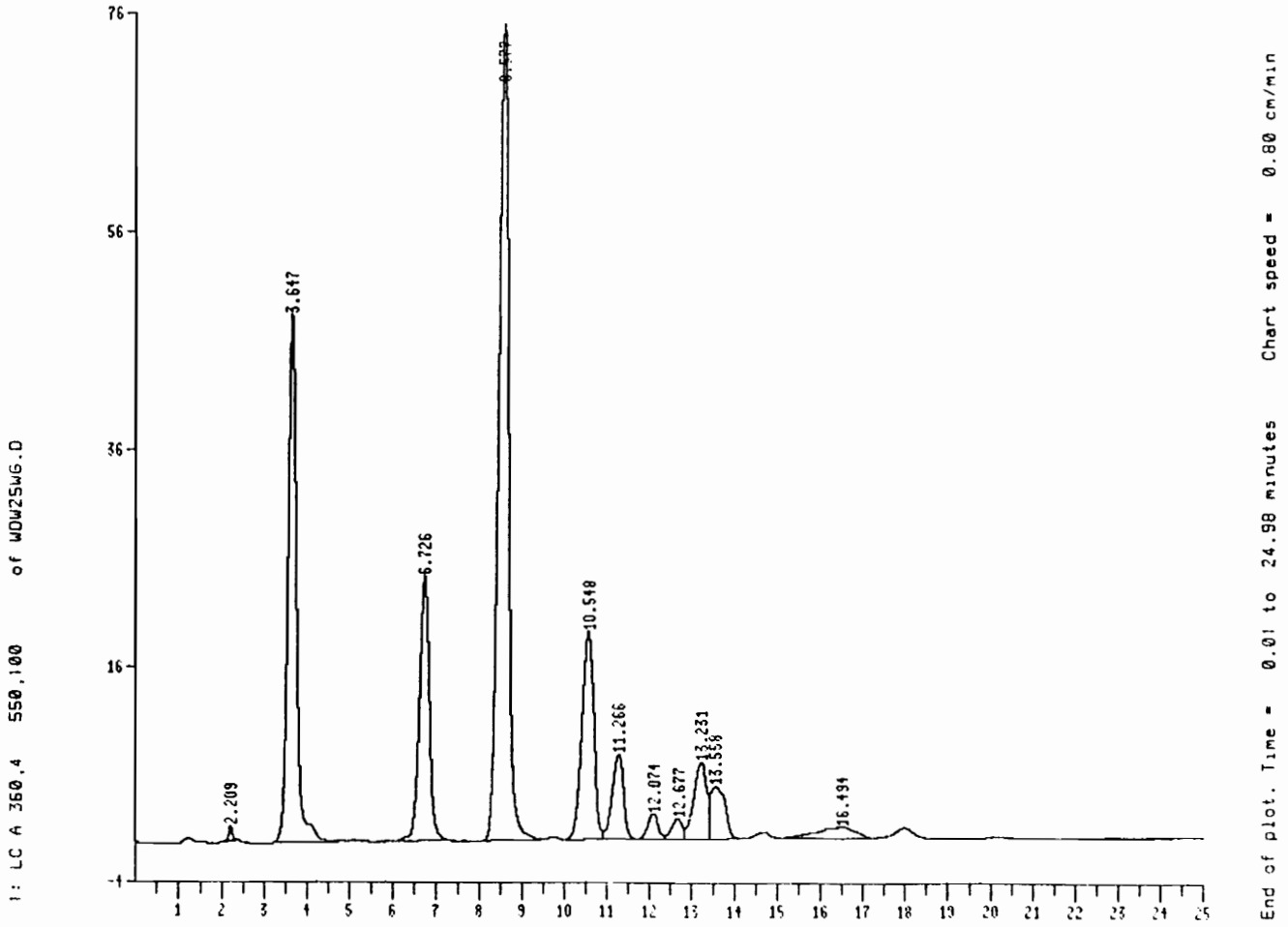


Figure 21 - Typical Chromatogram

APPENDIX D - COLLECTED DATA AND STATISTICAL RESULTS

Table D.I - Experiments Conducted

Date	Fuel	Catalyst	Engine Speed	Fuel Rate	Air Rate	Load Power	Standard Emissions	Sample Number	Aldehydes[a]	Sample Number
4/28/93	G100						X	T4/28-2	B	4/28-2,18
4/28/93	E10						X	T4/28-3	X	4/28/3
4/28/93	E25		X			X	X	T4/28-4	X	4/28-4
4/28/93	E50		X			X	X	T4/28-5	X	4/28-5
4/28/93	M10		X			X	X	T4/28-6	X	4/28-6
4/28/93	M25		X			X	X	T4/28-7	X	4/28-7
4/28/93	M50		X			X	X	T4/28-8	B	4/28-8,19
4/28/93	M50	X	X			X	X	T4/28-15	2	4/28-15,20
4/28/93	G100	X	X			X	X	T4/28-9	2	4/28-9,21
4/28/93	M10	X				X	X	T4/28-13	2	4/28-13,22
4/28/93	M25	X	X			X	X	T4/28-14	2	4/28-14,23
4/28/93	E10	X	X			X	X	T4/28-10	X	4/28-10
4/28/93	E25	X				X	X	T4/28-11	X	4/28-11

Table D.I Continued

Date	Fuel	Catalyst	Engine Speed	Fuel Rate	Air Rate	Load Power	Standard Emissions	Sample Number	Aldehydes	Sample Number
4/28/93	E50	X				X	X	T4/28-12	2	4/28-12,24
4/1/93	M10		X			X	X	4/1-4T		
4/1/93	M25		X			X	X	4/1-5T	X	4/1-1
4/1/93	M50		X			X	X	4/1-6T	X	4/1-2
4/1/93	E10		X			X	X	4/1-1T		
4/1/93	E25		X			X	X	4/1-2T		
4/1/93	E50		X			X	X	4/1-3T		
3/25/93	E10		X						X	3/25-1
3/25/93	E25								X	3/25-2
3/25/93	E50						X	3/25-3	B	3/25-3,7
3/25/93	M10		X						X	3/25-4
3/4/93	G100								X	3/4-1
3/4/93	E10		X						X	3/4-2
3/4/93	E25		X						X	3/4-3

Table D.I Continued

Date	Fuel	Catalyst	Engine Speed	Fuel Rate	Air Rate	Load Power	Standard Emissions	Sample Number	Aldehydes	Sample Number
3/4/93	E50		X						X	3/4-4
2/24/93	G100								3	2/24-1,2,3
2/24/93	G100			X						
2/10/93	G100			X	X					
2/10/93	G100			X			X	2/10-2	B	2/10-4,5
1/22/93	G100			X	X					
12/13/93	G100		X			X	X			
9/11/92	G100		X	X						
10/9/92	G100		X							
9/1/92	G100		X			X				
9/1/92	G100		X			X				
9/1/92	G100		X			X				

[a]A number in the aldehyde column indicates the number of multiple samples taken, a B indicates the installation of a breakthrough cartridge during sampling.

Table D.II - Measured Engine Speeds and Fuel Rates

Date	Speed[a] (RPM)	Fuel Rate[b] (mL/min)
9/1/92	3360	13.4
9/11/92	3360	
10/9/92	3360	
12/13/92	3360	
1/22/93		18.9
2/10/93		14.5
2/10/93		15.2
2/24/93		14.2
3/4/93	3160	
3/4/93	3160	
3/4/93	3140	
3/25/93	3140	
3/25/93	3120	
4/1/93	3129	
4/1/93	3110	
4/1/93	3160	
4/1/93	3120	
4/2/93	3120	
4/2/93	3120	
4/2/93	3120	
4/28/93	3120	
4/28/93	3020	
4/29/93	3320	
4/29/93	2940	
4/29/93	3140	
4/29/93	3200	
4/29/93	3120	
4/29/93	3010	
4/29/93	3110	

[a]Engine speed measured using a General Radio stroboscope.

[b]Fuel rate measured using a timed burette method.

Table D.III - Measured Electrical Power Outputs

Date	Voltage[a] (V)	Current[b] (A)	Power[c] (kW)
9/1/92	113.0	9.0	1.02
10/22/92	115.0	9.0	1.04
12/13/92	112.0	8.5	0.95
4/1/93	111.8	8.3	0.93
4/1/93	111.4	8.5	0.95
4/1/93	111.8	8.5	0.95
4/2/93	111.3	8.5	0.95
4/2/93	111.0	8.5	0.94
4/2/93	111.1	8.5	0.94
4/28/93	111.9	8.4	0.94
4/28/93	113.4	8.5	0.96
4/28/93	113.8	8.8	1.00
4/28/93	113.8	8.8	1.00
4/28/93	113.2	8.5	0.96
4/28/93	109.9	8.4	0.92
4/28/93	112.2	8.5	0.95
4/28/93	111.0	8.4	0.93
4/28/93	113.0	8.6	0.97
4/28/93	115.3	8.8	1.01
4/28/93	115.0	8.8	1.01
4/28/93	115.3	8.5	0.98

[a]Generator voltage measured using a Micronta digital multimeter.

[b]Load current measured using a Micronta clamp-on ammeter.

[c]Power calculated assuming a purely resistive load with a power factor of 1.0.

Table D.IV - Measured Air Intake Rates

Date	dP (in H20)	Intake Flow Rate (cfm)
1/22/93	0.07	5.3
1/27/93	0.06	4.5
2/10/93	0.07	5.3
3/25/93	0.05	3.8

Air flow rates measured using laminar flow meter built for this research.

Table D.V - Linear Coefficients from Regression Analyses

Trend	Slope	Intercept	r^2
Ethanol O_2	0.02	0.50	0.7390
Ethanol O_2, Catalyst	0.01	0.94	0.0891
Ethanol CO_2	0.07	9.94	0.9286
Ethanol CO_2, Catalyst	0.16	6.87	0.7107
Ethanol CO	-2.21	124	0.9710
Ethanol CO, Catalyst	-2.13	128	0.9905
Ethanol THC	-0.02	2.01	0.8637
Ethanol THC, Catalyst	-0.03	2.05	0.9495
Ethanol Form.	4.43	262	0.3476
Ethanol Form., Catalyst	5.69	308	0.4516
Ethanol Acet.	171.08	997	0.6045
Ethanol Acet., Catalyst	82.93	769	0.9392
Methanol O_2	0.04	0.65	0.6772
Methanol O_2,Catalyst	0.03	0.78	0.9567
Methanol CO_2	0.05	11.1	0.4393
Methanol CO_2,Catalyst	0.15	6.92	0.7104
Methanol CO	-2.08	94.2	0.6607
Methanol CO, Catalyst	-2.52	125	0.9968
Methanol THC	-0.02	1.73	0.6863
Methanol THC, Catalyst	-0.03	1.86	0.9825
Methanol Form.	0.91	272	0.0082
Methanol Form., Catalyst	0.91	272	0.0082
Methanol Acet.	-18.74	2749	0.0133
Methanol Acet., Catalyst	-14.45	1366	0.4333

Regression coefficients determined from a least squares line fit.

Form. - Formaldehyde

Acet. - Acetaldehyde

Table D.VI - T Test Results for Determination of Emission Trends Due to Alcohol Fuel Enhancement

Alcohol	Emission[a]	Catalyst	n	Σy2	Σy	Σxy	Calculated t-Value	t(n-2,α/2) for α=0.05	p-Value[b]
Ethanol	O_2	No	8	9.95	7.94	235	4.12	2.45	
Ethanol	O_2	Yes	4	6.54	4.54	110	0.442	4.30	0.70
Ethanol	CO_2	No	8	1,071	91.8	2,160	8.83	2.45	
Ethanol	CO_2	Yes	4	462	40.7	1,090	2.22	4.30	0.16
Ethanol	CO	No	8	62,860	623	6,970	-14.2	2.45	
Ethanol	CO	Yes	4	34,150	333	4,050	-14.4	4.30	
Ethanol	THC	No	8	20.2	12.1	191	-6.17	2.45	
Ethanol	THC	Yes	4	9.95	5.97	89.8	-6.13	4.30	
Ethanol	Form.	No	9	1,262,500	3,120	73,230	1.93	2.37	0.09
Ethanol	Form.	Yes	6	1,334,200	2,620	74,180	1.82	2.78	0.14
Ethanol	Acet.	No	9	3.18E08	38,060	1,272,970	3.27	2.37	
Ethanol	Acet.	Yes	6	6.14E07	15,810	578,670	7.86	2.78	

Table D.V Continued

Alcohol	Emission[a]	Catalyst	n	Σy2	Σy	Σxy	Calculated t-Value	t(n-2,α/2) for α=0.05	p-Value[b]
Methanol	O_2	No	8	21.8	11.4	346	3.55	2.45	
Methanol	O_2	Yes	4	10.5	5.95	174	6.65	4.30	
Methanol	CO_2	No	8	1,205	97.5	2,220	2.17	2.45	0.07
Methanol	CO_2	Yes	4	457	40.5	1,080	2.22	4.30	0.16
Methanol	CO	No	8	38,590	400	2,590	-3.42	2.45	
Methanol	CO	Yes	4	29,590	287	2,510	-25.0	4.30	
Methanol	THC	No	8	15.1	10.3	159	-3.62	2.45	
Methanol	THC	Yes	4	7.13	4.78	57.0	-10.6	4.30	
Methanol	Form.	No	9	1,083,700	2,610	52,170	0.240	2.37	0.82
Methanol	Form.	Yes	8	935,340	2,680	58,550	0.303	2.45	0.77
Methanol	Acet.	No	9	1.37E08	21,560	346,540	0.307	2.37	0.77
Methanol	Acet.	Yes	8	1.04E07	8,480	139,160	2.14	2.45	0.08

[a]Values of emissions used for statistical calculations were: concentrations of oxygen (O2) and carbon dioxide (CO2), specific emission rates of carbon monoxide (CO), total hydrocarbons (THC), formaldehyde (Form.), and acetaldehyde (Acet.).

[b]P values (α values at which the null hypothesis of zero slope was rejected) were calculated for those regression lines which did not show a non-zero slope at the 95% confidence interval. Confidence interval = 100(1 - p).

Table D.VII - F Test Results for Comparison of Emissions With and Without Platinum Catalyst

Alcohol	Emission	$\Sigma(Err.)^2$ No Catalyst	$\Sigma(Err.)^2$ Catalyst	$\Sigma(Err.)^2$ Reduced	n Reduced	Calculated f-Value	p Value
Ethanol	O_2	0.543	1.26	2.04	12	0.530	0.61
Ethanol	CO_2	1.15	13.9	26.1	12	2.92	0.11
Ethanol	CO	414	61.5	556	12	2.32	0.54
Ethanol	THC	0.246	0.0519	0.307	12	0.117	0.89
Ethanol	Form.	1.19E05	1.06E05	2.45E05	15	0.506	0.62
Ethanol	Acet.	6.20E07	1.20E06	9.00E07	15	2.32	0.14
Methanol	O_2	1.80	0.0708	1.89	12	0.043	0.96
Methanol	CO_2	10.1	13.2	43.7	12	3.50	0.08
Methanol	CO	6310	9020	7780	12	0.906	0.44
Methanol	THC	0.568	0.025	0.719	12	0.854	0.46
Methanol	Form.	3.26E05	3.98E04	3.74E05	17	0.141	0.87
Methanol	Acet.	8.45E07	7.75E05	9.24E07	17	0.542	0.59

[a]$\Sigma(Err.)^2$ indicates the sum of the squares of the errors of the data from the least squares regression line.

[b]The reduced data set consisted of data collected with and without the catalyst for the pollutant of interest.

Statistical calculations were made and hypotheses formed on the basis of information contained in the reference: (Neter and Wasserman, 1974).

APPENDIX E - STANDARD PROCEDURE FOR WET TEST METER

1. Level meter with spirit level bubble.
2. Fill meter with distilled water to the point that sight glass indicator just indents water meniscus. Use value at bottom of sight glass for final water adjustments.
3. Fill manometer U-tube with distilled water to "0" midscale. Move scale for final zero adjustment.
4. Connect flow tube so that gas bubbles through distilled water before entering wet test meter.
5. Manually set all pointers to "0".
6. Record ambient temperature, meter fluid temperature, barometric pressure, manometer gas pressure and time per revolution.
7. Calculate in order to correct measured ambient saturated flow rate to standard flow rate.

$$P_{meas} = P_{amb} + P_{mano} - P_v$$

P_{AMB}=ambient gas pressure,

P_{mano}=manometer pressure,

P_v =water vapor pressure at ambient temperature (from Table E.I).

$$Q_S = \frac{P_{meas}}{P_S}\frac{T_S}{T_{meas}}Q_{meas}$$

Q_S=standard flow rate,

P_S=standard pressure,

T_s=standard temperature,

Q_{meas}=measured flow rate.

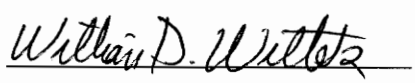
Table E.I - Water Vapor Pressure Data

Temperature (^{o}F)	Vapor Pressure (in Hg)
40	0.248
50	0.362
60	0.521
70	0.739
80	1.03
90	1.42
100	1.93

This procedure and these data were obtained from Dr. J. Martin Hughes, 1993.

VITA

William David Willets was born on January 21, 1963 in St. Petersburg, Florida. He attended elementary, junior high, and high schools in Roanoke County Virginia and graduated from William Byrd High School in 1981. William received an Associate in Science degree in Engineering from Virginia Western Community College in 1983. In December 1985 he received his Bachelor of Science in Aerospace and Ocean Engineering from Virginia Polytechnic Institute and State University. After selling, supporting, and servicing business and personal computer systems for Tandy Corporation, he held a managerial position in the Consumer Electronics Division of VPI Facilities at Virginia Tech. William entered the graduate program at Virginia Tech in May 1991 in pursuit of a Master of Science degree in Environmental Engineering. During his career as a graduate student, William served as teaching assistant for and taught a summer session of Air Resources Engineering. He worked for two years as the senior technician on the Engineering Fundamentals PC Support Team. He was also a member of the American Society of Civil Engineers and the Gamma Beta Phi national honor and service society. He is a member of the Air and Waste Management Association and serves on the Curriculum Development and Review Committee. William is currently employed as an environmental engineer with the State of North Carolina where he conducts reviews for air permit applications.



William D. Willets