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EMULSION FUEL AND OXIDATION CATALYST TECHNOLOGY FOR STATIONARY DIESEL ENGINES

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ABSTRACT

This paper presents recent results from comprehensive emissions measurements made on the EPA, Industrial Environmental Research Laboratory-RTP diesel-engine/generator set. The diesel set was equipped with two emission control systems: an oxidation catalyst in the exhaust and a fuel-oil/water emulsification unit in the fuel supply line. NO_x reductions resulting from emulsion fuel use are quantified along with resultant increases in organic emissions. The effects of the exhaust oxidation catalyst on the organic emissions are documented, including results of mutagenesis and cytotoxicity assays. Catalyst and emulsion effects on SO_2/SO_3 emissions are also quantified. Basic conclusions based on these reported results are that emulsion fuel provides control of diesel NO_x emissions, but at the expense of increased organic emissions. The oxidation catalyst will control CO and light gaseous hydrocarbons, but does not adequately control complex organics emitted by the diesel.

INTRODUCTION

The Combustion Research Branch (CRB) of EPA's Industrial Environmental Research Laboratory, Research Triangle Park (IERL-RTP), North Carolina, sponsors an on-going contract and in-house program to investigate emissions from stationary reciprocating internal combustion engines. This paper will describe the results obtained during in-house tests in applying fuel-oil/water emulsion and oxidation catalyst technology to a stationary diesel engine. The purpose of this work was to obtain comprehensive emission measurements of the diesel exhaust. These emissions measurements included criteria pollutants and particulates/organics.

EXPERIMENTAL APPROACH

A series of experiments were designed to evaluate the emissions from the CRB diesel-generator set and the effect of oil/water emulsion fuel combined with an oxidation catalyst on the levels of these emissions. Table 1 outlines the experiments conducted. All experiments were scheduled by assignment of their order with random numbers. A practical water/fuel ratio was selected for each load level based on prior experiments which determined water/fuel versus NO_x levels.

EXPERIMENTAL SYSTEM COMPONENTS

The diesel engine used for this study is part of an electrical generator package. The engine is a Caterpillar Model D334, prechamber ignition, turbocharged and after-cooled, four stroke cycle, six cylinder diesel with 638 in.^3 ($1.045 \times 10^{-2} m^3$) displacement rated at 165 kW electrical output for continuous service. Other pertinent data include:

Bore: 4.75 in. (120.65 mm)
Stroke: 6.00 in. (152.4 mm)
Compression Ratio: 17 to 1
Dry Weight: 2390 lb (1084.09 kg)
Standard Timing: 8° BTDC
Engine Speed: 1800 rpm (constant)

The catalytic reactor used in this study is an Engelhard Industries PTX-643D. This unit is a platinum metal catalyst on a monolith porous ceramic support with a honeycomb structure. The catalyst is enclosed in an Inconel band and a stainless steel outer housing.

Engine load is provided by an AVTRON Model K463 load bank connected to the diesel-generator set. This load bank provides load demands up to 225 kW in 5 kW increments.

The fuel used in the engine is a No. 2 diesel oil with an API gravity of 33.9°. The bound-nitrogen content of this fuel is 54 ppm, thus fuel nitrogen conversion to NO_x is not a major factor in the emission levels measured in this study. The sulfur content [0.24% (wt)] is sufficient to produce significant sulfate (SO_3, SO_4) emissions if SO_2 is oxidized in the engine or exhaust system. Other fuel properties were:

Carbon: 86.62% (wt)
Hydrogen: 13.15% (wt)
Ash: Trace (<0.01%)
HHV: 19,396 Btu/lb (45.07 MJ/kg)
Density: 0.8397 g/cm^3 @ 100°F (38°C)
Viscosity: 2.52 centipoise (2.52 mPa·s) @ 100°F (38°C)
Cetane Index: 43.5

The water for emulsion formation is deionized city water. Deionization is provided by a Continental Water Service anion and cation exchange resin system. Emulsion formation takes place in a mixer and gear pump unit located 2 m (6.5 ft) from the diesel engine fuel injection system.

SAMPLING AND ANALYTICAL SYSTEM

Instruments for determining the gaseous and particulate emissions from the diesel engine are listed in Table 2. In addition to these EPA-operated instruments, extensive analytical work was performed by contractors. Battelle Columbus Laboratories performed comprehensive analysis on selected diesel emission samples using liquid chromatography, infrared spectroscopy, and low resolution mass spectrometry (on the organic extract), and spark source mass spectrometry and atomic absorption (for inorganic analyses). Litton Bionetics performed bioassays on selected diesel emission samples including Ames Salmonella Assay for mutagenicity and CHO Clonal Assay for cytotoxicity.

EMISSION CHARACTERISTICS

Nitrogen Oxides

The experiments on this diesel engine indicate a baseline NO_x emission pattern with a 22.2 g/kg (450 ppm @ 15 percent O_2) peak at 40 kW load, and lower emissions (between 11.5 and 15 g/kg) at the other load levels studied. NO_x emissions for each of three control conditions (emulsion, catalyst, and emulsion + catalyst combined) are compared in Figure 1. The ratio of NO_x emissions for the catalyst runs indicates little effect on these emissions by the catalyst. A regression line through the data is close to the baseline. A water/fuel (W/F) ratio near the maximum that could be comfortably tolerated by the engine was selected for each load level studied. This W/F ratio varied:

Load, kW	W/F
0	0.39
40	0.31
80	0.49
120	0.60
160	0.27

Even with the variability in the W/F ratio, the NO_x reduction obtained at each load level was approximately 60 percent. The regression line through the data gave virtually no difference between the emulsion and the combined conditions: many of the data points were coincident. Evidently, the catalyst has no effect on NO_x emissions when emulsion fuel is used in the engine. A slight upward trend in the regression line with load is caused by the data at 160 kW where the W/F ratio was lower. This pattern of NO_x emission was expected based on prior tests. The NO_x emission levels are typical of what might be expected if a precombustion chamber diesel utilized water/fuel emulsion as a NO_x control method. The remainder of this paper will report the effects on other pollutant emissions that would result if this 60 percent NO_x control level were applied to this engine.

Carbon Monoxide

Experimental results indicated a CO baseline emission pattern with a 33.8 g/kg (735 ppm @ 15 percent O_2) peak at zero kW load, and rapidly decreasing emissions as load is added to the engine. This condition represents the lowest temperature regime in the engine, thus the CO oxidation is reduced at zero load. At half load (80 kW) and above, the baseline CO emission is nearly constant around 3 g/kg (70 ppm @ 15 percent O_2). The effect of the three control conditions on CO emissions is illustrated in Figure 2. Emulsion fuel at 80 kW and below increases CO emissions to greater than 45 g/kg (>1000 ppm @ 15 percent O_2), the limit of detectability. This condition is shown off-scale in the figure. At 120 and 160 kW, the increases in CO are still substantial but now measurable. Higher combustion temperatures at the higher load conditions provide for the better burnout of the CO. The effect of the oxidation catalyst is to reduce CO emissions nearly 90 percent at all loads above zero kW (where the exhaust temperature is too low for the catalyst to operate). When the catalyst is used with the emulsion fuel to combine NO_x and CO control, an average CO reduction of 55 percent is obtained. This "average," however, is the regression line through widely scattered data points, indicating that the control capability is highly variable. It is not clear from this limited data why this scatter occurs. Evidently the oxidation catalyst will counteract the adverse effect of emulsion fuel on CO emissions.

Total Gaseous Hydrocarbons

Experimental results indicate a total gaseous hydrocarbons (THC) baseline emission pattern similar to the CO pattern. There is a peak of 2.69 g/kg (37 ppm @ 15 percent O_2) at zero kW load, with emissions dropping rapidly with load to 0.21 g/kg (3 ppm @ 15 percent O_2) at full load. Again, this is caused by the low temperature engine regime at zero load as was the case with CO emission. The effect of the three control conditions on THC emissions is illustrated in Figure 3. Use of emulsion fuel, as for CO emissions, drastically increased the THC emissions at most load levels. The peak increases to 37.6 g/kg (520 ppm @ 15 percent O_2) at zero kW load, and the emissions remain above the baseline except at 160 kW. Data with the catalyst in operation indicate a reduction of 60 to 80 percent in THC emissions. Referring to Table 3, when the catalyst and emulsion fuel are both used, THC emissions are substantially reduced from the emulsion-only condition, but remain above baseline at half load (80 kW) and below. Thus, it appears that the catalyst does provide some countereffect to the emulsion on the hydrocarbon compounds that are detectable in a heated flame ionization analyzer. The heavier hydrocarbons emitted by the engine must also be considered.

Emission levels of hydrocarbons, as determined by the modified EPA Method 5, are listed in Table 4. The modified Method 5 train has an organic absorber (XAD-2) module added downstream of the filter. Inspection of this data essentially confirms the pattern of hydrocarbon emissions evident from the THC analyzer. The emulsion can produce large increases in both lighter (TCO) and heavier (GRAV) hydrocarbons, especially at less than full load operation of the diesel engine. The catalyst, in general, reduces hydrocarbon emissions affecting both lighter and heavier compounds. But the catalyst is able to overcome only part of the effect of the emulsion except at high load conditions.

Sulfur Oxides

Experimental results indicate that emissions of SO_2 are essentially constant over the load range of the machine for baseline operation. This is expected because SO_2 levels are usually fixed by the sulfur content of the fuel. The analytical instrument average was 4.72 g/kg (45 ppm @ 15 percent O_2), compared to a 4.77 g/kg value computed from the fuel sulfur content. The NO_x control methods, however, did affect SO_2 emissions. This effect involved conversion of some SO_2 to sulfate under some conditions. These results are illustrated in Figure 4. The emulsion fuel averaged about 3.4 percent conversion of SO_2 to sulfate, a relatively insignificant amount. The exception was at zero kW load where the high excess air condition gave a 21 percent conversion to sulfate. The oxidation catalyst, as may be expected, gave conversions up to 62 percent at full load. When the data for the emulsion plus catalyst are inspected, the result is essentially a combination of the two control methods taken individually even to the increase at zero kW load.

Particulates

Particulate emissions were measured using the Modified Method 5 sampling train. This method uses filtration at stack temperature to collect the particulate matter in the exhaust from the diesel engine. For baseline conditions (no NO_x control), the particulate level reached a maximum value of 119.5 mg/m^3 at zero kW load. There was a decline to 30 mg/m^3 at half load (80 kW), and the emissions then remained nearly constant to full load (160 kW). Effects of the control methods are illustrated in Figure 5. The results are difficult to interpret. Emulsion fuel increased particulates at zero kW load but gave reductions at most higher load conditions. (The emulsion run at 80 kW resulted in higher particulates and is also the high hydrocarbon run noted in Table 4. This may be an aberration that occurred on that run only and may not be representative of the emulsion effect.) The catalyst did not affect particulate at zero kW as would be expected since it is not up to operating temperature. At 40 kW, particulates were reduced, but for higher load levels, large increases in particulates occurred. This pattern was essentially repeated by the combined control condition. A similar pattern resulted from particulate mass determinations using the sulfate train filter (a less accurate measure than Method 5); thus the pattern may be real. Evidently, the catalyst gives rise to increased particulate emissions, and there appears to be an interaction between the catalyst and emulsion that further increases the emission. Future work will include in-depth analysis of the particulates to determine their composition.

Bioassay and Chemical Analyses

Bioassay and chemical analyses were limited to full load operation samples for baseline and catalyst runs by time constraints, except for polycyclic aromatic hydrocarbon (PAH) spot tests. The results of bioassay testing of three fractions of the diesel exhaust are given in Table 5. It is evident that both mutagenic (potentially carcinogenic) and toxic compounds are emitted by the diesel in baseline operation. The addition of the oxidation catalyst to the exhaust stream appears to increase the bioactivity of the organic compounds: both mutagenicity and toxicity were higher. The largest amount (20 times greater mass than any other organic containing part of the total sample) of organic was the organic module extract which contains all heavy organics not associated with particulates at stack temperature conditions. This fraction of the exhaust emissions was further fractionated to attempt identification of the compound types involved. The fraction bioassay data is presented in Table 6. Mutagens were contained in Fractions 3, 4, and 5. Chemical analyses indicated that these fractions contained nitrate and nitro-organic compounds. The analysts indicated that these compounds were commonly found in the diesel exhaust samples. All of the fractions tested appeared to be toxic. More detailed identification of the organic compounds present was not within the scope of this study.

The PAH spot test was applied to all of the runs made, but only the 80 kW emulsion run gave a positive response. Evidently this test was an abnormal condition; quite likely the amount of water added was greater than specified for the test because of a control malfunction. This condition indicates that there will be a stage in water addition where PAHs will begin to form, thus limiting NO_x control by water addition to the prechamber diesel engine.

At the time this paper was prepared, the possibility of nitro/nitrate organic mutagenic compounds being formed as an artifact in the sampling system was under further study.

CONCLUSIONS

Several conclusions can be drawn from the measurements.

- Emulsion fuel provides NO_x control in addition to the inherent control provided by the prechamber (staging) effect. There is also a reduction in particulate emissions.

- This NO_x/particulate control is achieved at the expense of increased CO, THC, TCO, and GRAV, especially at less than full load.

- An oxidation catalyst in the exhaust provides control of CO and hydrocarbons when used alone.

-When combined with emulsion fuel, the catalyst still provides CO control, but could only control hydrocarbons adequately at near full load operation.

-Additional side effects of the catalyst are creation of a sulfuric acid emission (important if S is present in the fuel) and increased particulate emission above half load on the machine.

-The oxidation catalyst appeared to increase particulate emissions at load levels above 40 kW, with or without emulsion fuel use.

-The oxidation catalyst appeared to increase the mutagenicity and toxicity of heavy organic compounds emitted, while reducing their amount.

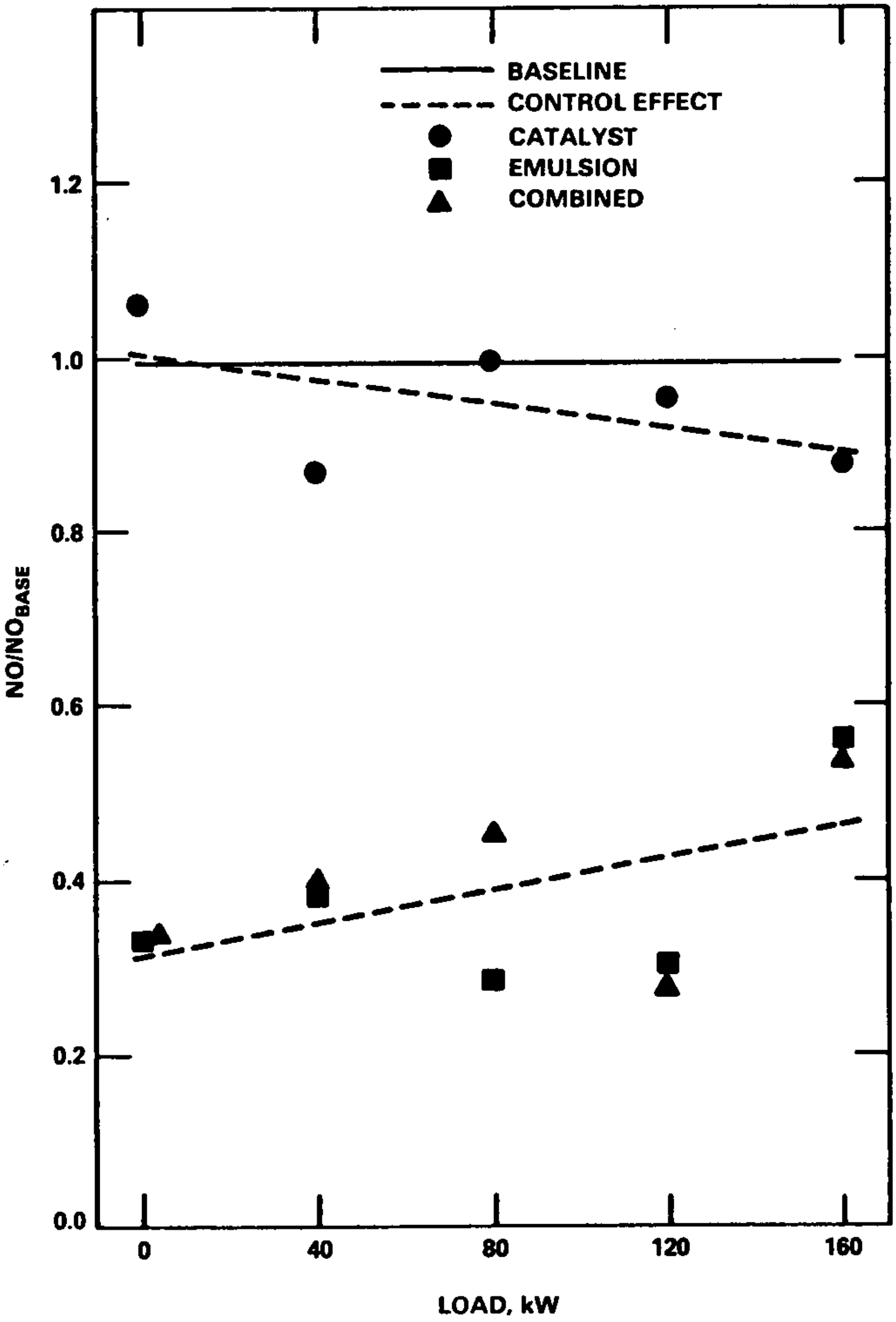

Figure 1. Effect of control on NO emissions.

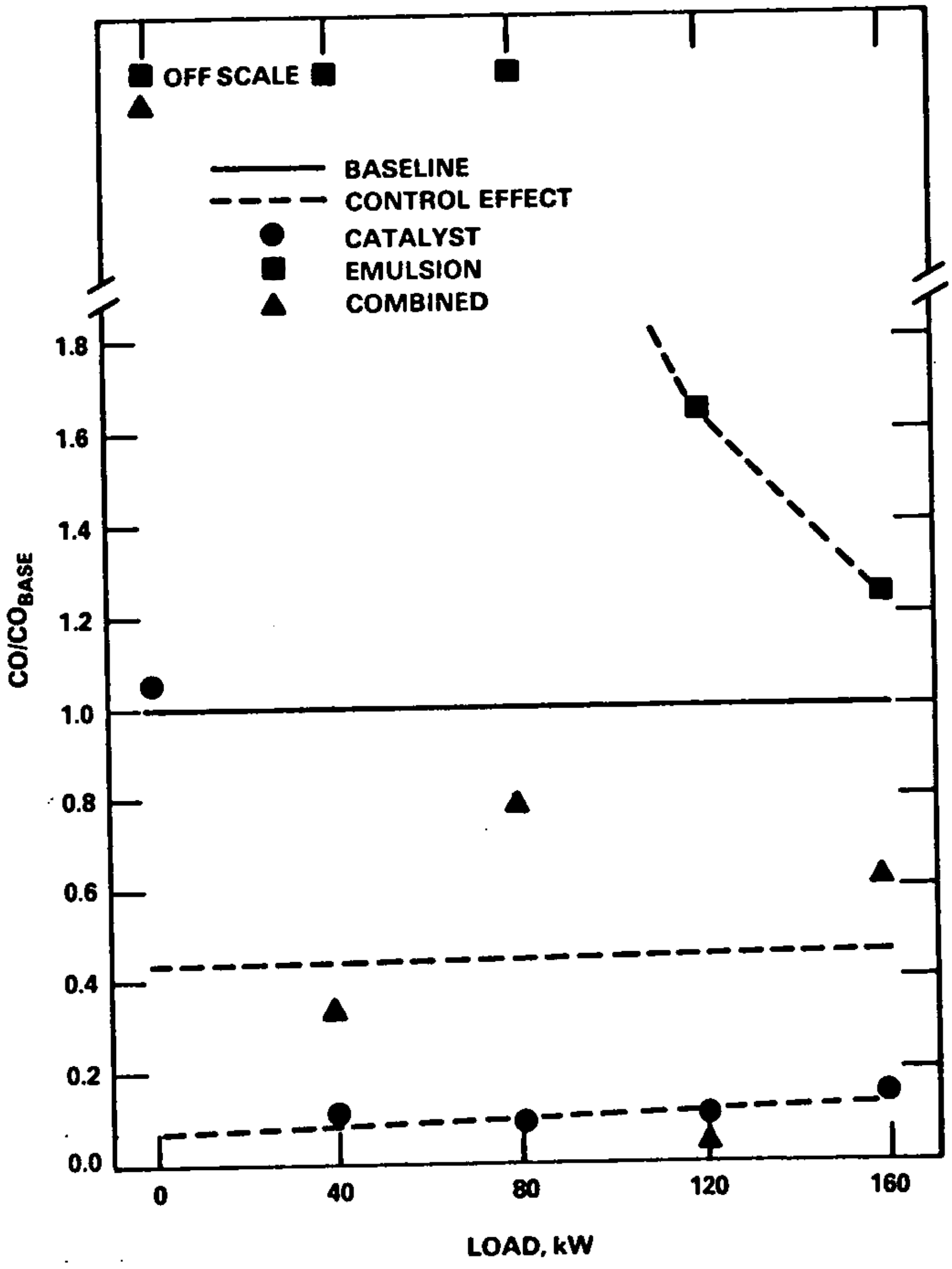

Figure 2. Effect of control on CO emissions.

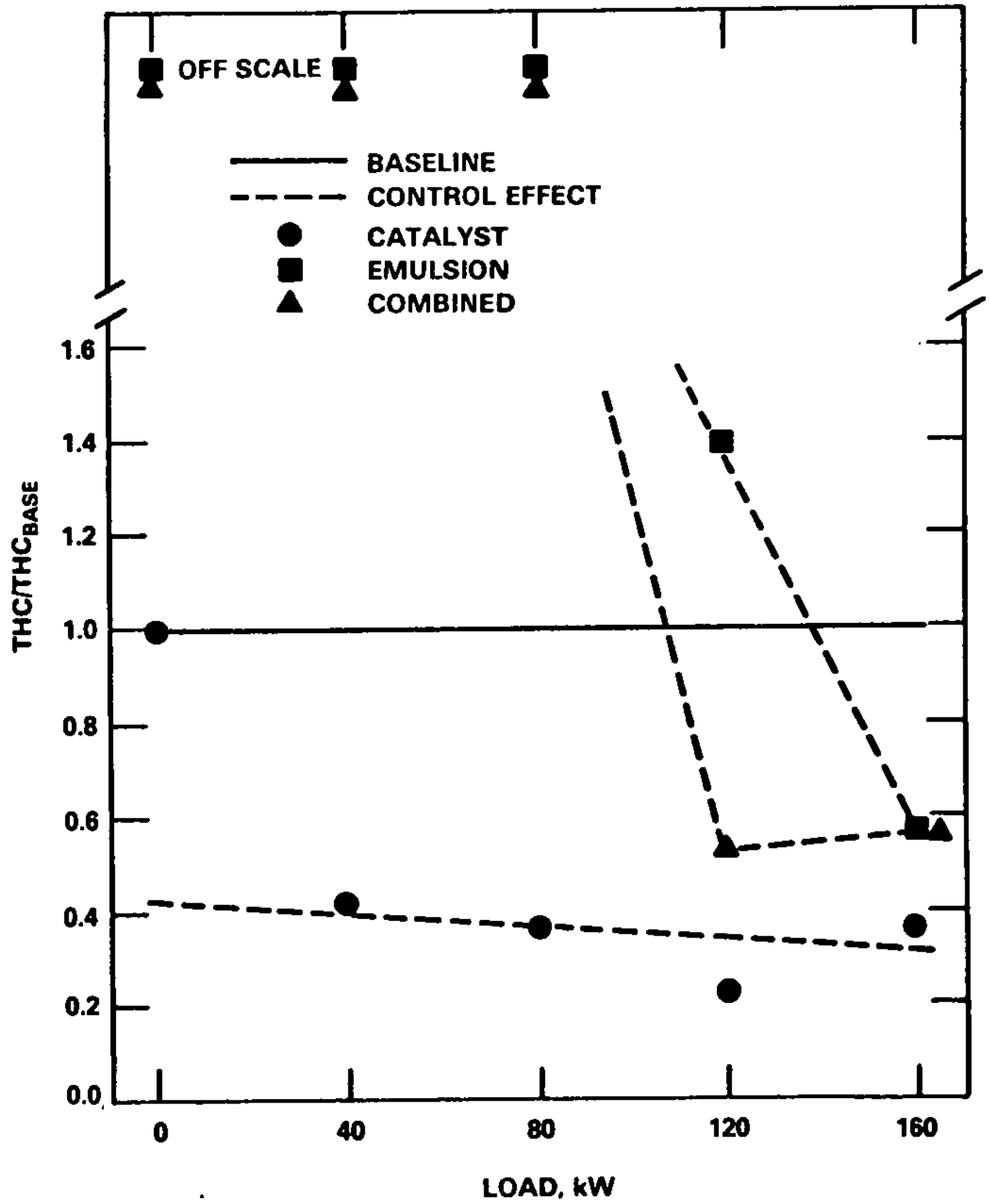

Figure 3. Effect of control on THC emissions.

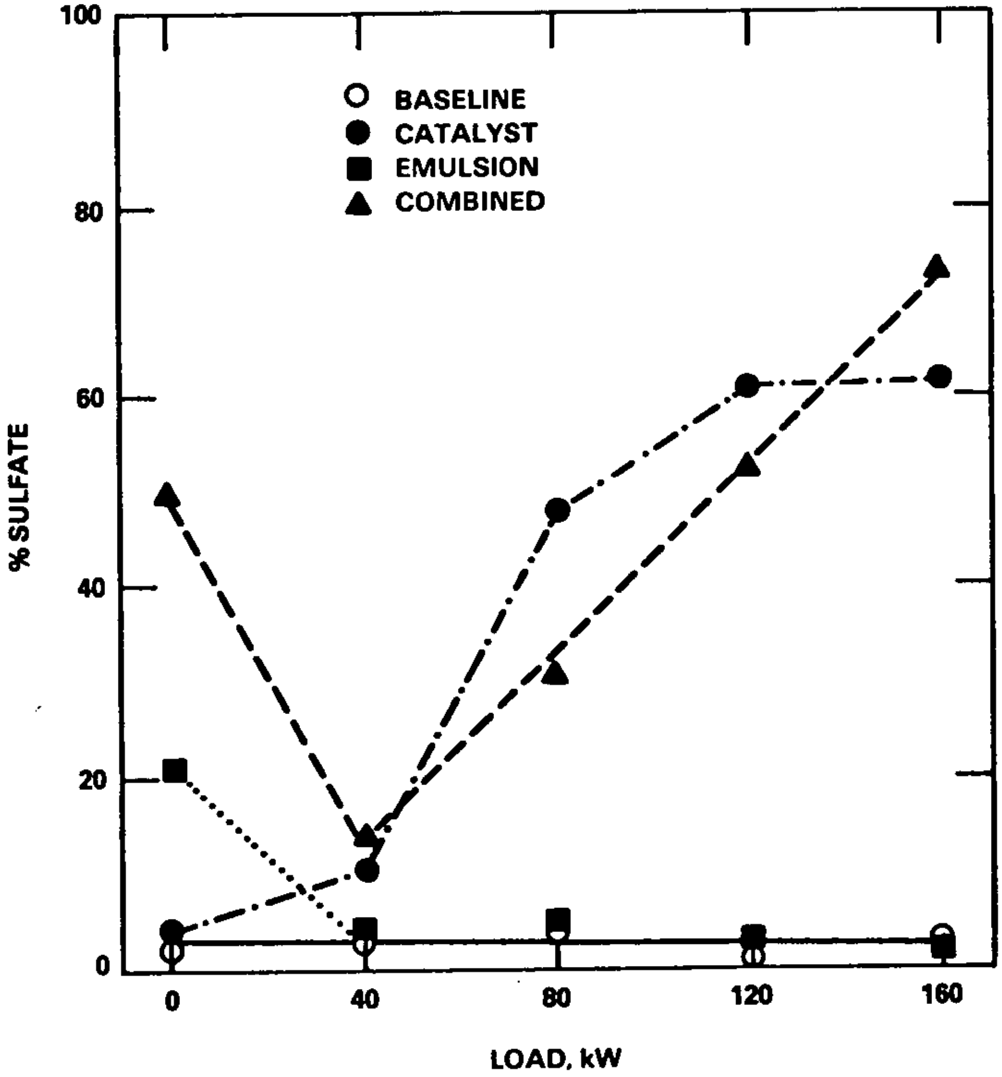

Figure 4. Conversion of SO_2 to sulfate.

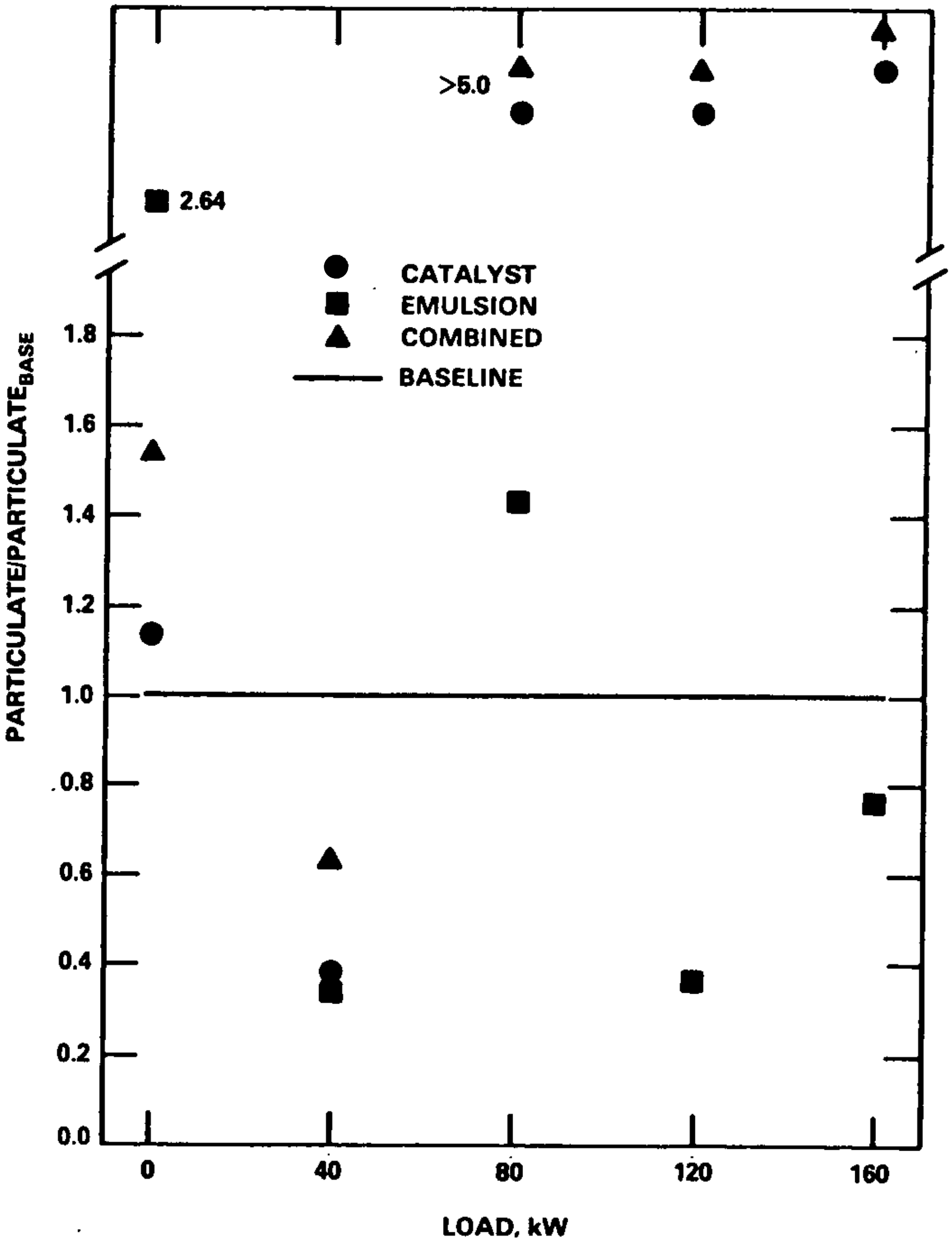

Figure 5. Effect of control on particulate emissions.

TABLE 1. EXPERIMENTAL PROGRAM

Experiment Set	Variables	Study Range
Baseline	Generator Load	Zero to 160 kW @ 40 kW intervals
Fuel Emulsion	Generator Load Water/Fuel Ratio	Zero to 160 kW @ 40 kW intervals One water/fuel ratio at each load
Catalyst	Generator Load	Zero to 160 kW @ 40 kW intervals
Catalyst + Fuel Emulsion	Generator Load Water/Fuel Ratio	Zero to 160 kW @ 40 kW intervals One water/fuel ratio at each load

TABLE 2. SAMPLING AND ANALYTICAL INSTRUMENTS

Flue Gas Constituent	Analyzer
O_2	Beckman Paramagnetic
CO_2	Beckman NDIR Model 865
CO	Beckman NDIR Model 865
Hydrocarbons	Scott Flame Ionization Model 415
NO_x	TECO Chemiluminescence
Particulates/Organics	RAC Staksampler + XAD-2 Module
Organic Extract	HP5840A Gas Chromatograph
SO_2	TECO Pulsed Fluorescent Model 40
SO_3/SO_4	Goksoyr-Ross Condensation Coil + Beckman Model 24 Spectrophotometer
Smoke (Opacity %)	Berkeley Model 107

TABLE 3. HYDROCARBON EMISSIONS (total gaseous, g/kg fuel)

	0 kW	40 kW	80 kW	120 kW	160 kW
Emulsion	37.59	5.73	9.25	0.56	0.12
Combined	37.59	2.58	1.95	0.21	0.12
Baseline	2.69	1.56	0.56	0.40	0.21
Catalyst	2.70	0.60	0.22	0.09	0.08

TABLE 4. HYDROCARBON EMISSIONS (XAD-2 EXTRACT)

Load, kW	Control	TCO[a] (mg/m^3)	GRAV[b] (mg/m^3)
0	Baseline	22.1	17.6
0	Emulsion	541	431
0	Catalyst	24.4	8.4
0	Emulsion + Catalyst	368	232
40	Baseline	28.8	24.1
40	Emulsion	268	184
40	Catalyst	4.28	0
40	Emulsion + Catalyst	100	109
80	Baseline	13.0	4.43
80	Emulsion	2820	155
80	Catalyst	2.33	1.41
80	Emulsion + Catalyst	105	42.8
120	Baseline	8.03	4.03
120	Emulsion	13.5	0.27
120	Catalyst	1.11	0
120	Emulsion + Catalyst	5.48	0.8
160	Baseline	4.49	0
160	Emulsion	6.72	2.07
160	Catalyst	0.693	2.01
160	Emulsion + Catalyst	1.42	1.83

[a] TCO = Total Chromatographable Organics (lighter than C_{17}, bp 300°C)
[b] GRAV - Gravimetric (heavier than C_{17}, bp 300°C)

TABLE 5. BIOASSAY ANALYSES (FULL LOAD)

Sample Description	Organic Module Extract (gaseous heavy organics)	Particulate Filter Extract (<3 μm particles)	Large Particle Extract (> 3μm particles)
Ames[a]/ Baseline	Low Mutagenicity Toxic	Low Mutagenicity Not Toxic	N.D.[d]
Ames/ Catalyst	Moderate Mutagenicity Toxic	Moderate Mutagenicity Not Toxic	N.D.
CHO[b]/ Baseline	Moderate to High Toxicity	Not Toxic	N.D.
CHO/ Catalyst	High Toxicity	Not Toxic	N.D.
RAM[c]/ Baseline	N.D.	N.D.	Low Toxicity
RAM/ Catalyst	N.D.	N.D.	Moderate Toxicity

[a] Ames *Salmonella* Mutagenesis Assay
[b] Chinese Hamster Ovary Cytotoxicity Assay in Culture
[c] Rabbit Alveolar Macrophage Cytotoxicity Assay in Culture
[d] Not Determined

TABLE 6. ORGANIC MODULE EXTRACT FRACTIONS (CATALYST)

Fraction No.	% of Sample	Bioassay Result
1	13.2	Not Mutagenic/High Toxicity
2	0.8	Not Mutagenic/N.D.[a]
3	1.9	Moderate to High Mutagenicity/N.D.
4	11.0	Moderate Mutagenicity/High Toxicity
5	13.1	Moderate to High Mutagenicity/High Toxicity
6	60.0	Not Mutagenic/High Toxicity

[a] Toxicity Not Determined