INERT GAS GENERATION UTILIZING DIESEL EXHAUST

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ABSTRACT

The generation of inert gas from 60 KW diesel engine exhaust by catalytic reduction of O_2 and NO_x has been demonstrated. Measured O_2 levels were < 10 V_{ppm} and NO_x levels were ≈ 0. 1 Vppm over a wide range of equivalence ratios. Durability of the catalytic converter was demonstrated up to 200 hours operating time at two diesel engine load conditions. Effective catalyst operating range was stoichiometric to rich fuel/air ratios. Optimum operation is at stoichiometric fuel/air ratios to minimize CO emissions. Alternative converter designs are proposed to allow operation over the full diesel engine load range with essentially zero emissions of O_2, NO_x and CO.

DISCLAIMER

1. INTRODUCTION

The generation of inert gas for blanketing operations has been accomplished by a number of different means. These include

- air separation,
- fuel combustion in a conventional flame burner to produce a nitrogen-carbon dioxide-oxygen mixture,
- catalytic treatment of the engine exhaust from a fuel-rich spark ignited engine to produce an essentially oxygen and NO_x free gas,
- fluidized bed combustion,
- pressure swing adsorption.

Each of these existing, commercial processes possess certain potential problems when applied to the application of inert gas to geothermal well drilling operations.

Although air separation plants are highly successful and well established sources of high grade nitrogen for large industrial operations, the design of movable, compact, low cost hardware to produce high grade nitrogen in the field is yet to be demonstrated.

Direct combustion of fuel oil to generate an inert gas is proven state of the art technology, and compact, rugged and portable units are commercially available. Inherently, these units are not capable of operating cleanly to produce an oxygen and NO_x free gas. Technical literature usually quotes oxygen levels of 1-1.5% in the generated inert gas. Further, although NO_x values are not usually provided, conventional flame burners typically generate in excess of 100 ppm of NO_x. It has been reported that the presence of NO_x can lead to severe corrosion. Thus, inert gas generation via direct combustion of fuel is unsuitable due to high levels of oxygen and NO_x in the effluent.

A third source of inert gas is the exhaust from spark ignited engines. These engines, when operated using natural gas, can produce a potentially useful effluent, with the added benefit that useful work is obtained from the engine. When operated under fuel lean conditions, the engine exhaust contains significant quantities of oxygen and NO_x, and is expected to perform in a similar manner to direct combustion gases. However, if the engine is operated under fuel rich conditions, using a special precious metal catalyst, the oxygen and NO_x in the exhaust can be reduced to as low as 1-3 ppm each. This process has been employed by Production Operators, using a proprietary Engelhard catalyst and has a demonstrated history of good operation. The primary defect of this process is the lack of availability of sweet natural gas required to run the fuel rich engines. Most drilling sites, whether for geothermal or oil well drilling, are remote and lack an acceptable source of sweet natural gas. In actual practice, drilling operations rely on trucked-in diesel fuel and are more likely to have a plentiful supply of diesel engine exhaust. Diesel engines operate under lean conditions, and have high oxygen concentrations in the engine exhaust.

Engelhard Industries had previously developed and successfully tested a new process for the production of inert gas utilizing a diesel engine exhaust. In this process, additional fuel is added to the exhaust sufficient to react with all the oxygen. The reaction takes place at or slightly rich of stoichiometric over an Engelhard catalyst. The purpose of the work carried out in this program was to demonstrate catalyst durability and provide scale up data for design of a 130,000 SCFH field test unit.

The results obtained in this program provide the data base needed to design a field test unit to be installed at a geothermal well site. This field unit would be used to verify that a catalytically treated diesel engine exhaust can be used to minimize drill pipe corrosion in a geothermal well drilling operation.

2. EXPERIMENTAL FACILITIES

The test facility comprised:

- diesel engine,
- exhaust manifold,
- diesel fuel injection system,
- catalytic reactor,
- exhaust stream analytical train.

A schematic flowsheet of the test rig is shown in Figure 1, a photograph of the catalytic reactor section in Figure 2, and piping and instrumentation details in Figure 3.

2.1 Diesel Engine/Load Bank

An Allis Chalmers DES-60 turbocharged diesel engine was utilized for this test program. An electrical generator/load bank system was used to vary the load on the engine from 0-60 KW in 12 KW increments. At full load, the engine was rated at 113 h.p.

2.2 Inert Gas Generator

The diesel engine produced an effluent gas containing 7-18 wt.% O_2 depending on the engine load. Diesel fuel was injected into the hot effluent gas and reacted on a proprietary Engelhard precious metal oxidation catalyst to consume the remaining oxygen and reduce the engine generated NO_x to nitrogen. A portion of the test rig containing the fuel injection location, mixing zone and catalyst location is shown in Figure 2. The reactor is designed to hold up to a 9 inch length of 9 inch diameter monolithic catalyst.

The process test unit was instrumented to monitor:

- diesel exhaust flow,
- catalyst exhaust flow,
- fuel flows to engine and catalytic reactor, .
- gas temperature,
- catalyst pressure drop,
- gas analysis downstream of catalyst.

Principal instrumentation locations are shown in Figure 3. Instrumentation consisted of:

- thermocouples for temperature measurement,
- pressure taps,
- analyzer train for exhaust analysis,
- rotometers for flow measurement,
- orifices with pressure taps for flow measurement,
- bag sample capability for sulfur analysis.

2.3 Analyzer Train

The instrumentation system provided the capability for measurement of the concentrations of HC, CO_2, CO, NO_x and O_2 in the exhaust. The system's instruments were capable of meeting or exceeding all emission measurement requirements.

The instrumentation system included the following:

- Beckman Model 402 Hydrocarbon Analyzer (flame ionization),
- Horiba Model AlA-21 CO_2 Non-Dispersive Infrared Gas Analyzer,
- Infrared Industries Model IR-703 CO-05-01-FI-RI Non-Dispersive Infrared CO Gas Analyzer,

- Aero Chem Chemiluminescence NO_x Monitor Model AA-3,
- Teledyne Model 311 Portable Trace Oxygen Analyzer.

Operating procedures necessary to assure the best possible accuracy and sensitivity were used.

3. EXPERIMENTAL PROGRAM

3.1 Variable Study

The effect of catalyst operating conditions on catalyst performance was studied to establish the range of acceptable operating conditions. The load on the engine was varied to change the catalyst inlet temperature, inlet oxygen concentration and exhaust gas flow rate. A bypass valve in the system allowed further flow rate adjustment. The fuel flow rate to the catalyst was systematically varied to change the fuel/air ratio in the system while the catalytic reactor's emissions were measured.

3.2 Durability Study

A 200 hour catalyst durability test was carried out on a new catalyst after the variable study was completed. Test time was accumulated in approximately 6 hour increments including start-ups and shutdowns because the test facility was manually operated. The system was operated for 100 hours at each of the engine load conditions of 48 and 60 KW.

4. RESULTS/DISCUSSION

4.1 Precommissioning Runs

After facility fabrication was completed, precommissioning work was carried out. This consisted of instrument calibration, trial test runs and characterization of the diesel engine and supporting equipment. The exhaust characterization of the Allis Chalmers DES-60 is presented in Table I.

As the engine load was increased, the exhaust temperature increased, the CO_2 and NO_x emissions increased, and the O_2 emissions decreased. The results are consistent since, as the engine load is increased, more fuel is combusted (lean fuel/air conditions) by the diesel engine.

4.1.1 Low Level O_2 Measurement Problems

Measurement of low levels of oxygen in a gaseous stream is made difficult by the presence of the system's surrounding ambient air, relatively rich in oxygen. Each system fitting or pipe bend becomes a potential site for oxygen leakage into the system.

During the test program, a zero baseline was established on the oxygen analyzer by passing an oxygen free calibration gas through the oxygen sampling system prior to each sample measurement. The oxygen free calibration gas (< 1 ppm O_2) was generated by combining nitrogen (99.9%) and hydrogen (99.95%) streams over an Engelhard Deoxo® catalyst. The hydrogen combined with any residual oxygen to form water which was removed from the stream using a dessicant.

Reactor effluent sample measurements were made after purging the oxygen sampling system with the oxygen free calibration gas until the oxygen analyzer reading had stabilized. A reactor effluent sample flow was then introduced, the calibration gas turned off, and the analyzer reading allowed to stabilize again. Results were reported as ppm over baseline and indicate the amount of O_2 added to the sampling system by the reactor effluent sample. The resolution of the O_2 measurement system was limited to about 10 Vppm.

4.2 Parametric Tests

Tests were carried out at several load settings of the diesel generator set. At each load setting, the total gas flow was adjusted to vary the catalyst inlet reference velocity. The fuel flow to the catalyst was varied to obtain a range of stoichiometries. The results obtained at 60 KW (100% load), 48 KW (80% load) and 36 KW (60% load) are presented in Figures 4 through 7.

4.2.1 Effect of Engine Load

Comparisons of Figures 4 through 7 indicated no discernable effect of engine load on catalytic reactor emissions even though, as shown in Table I, the O_2 and NO_x concentrations in the diesel exhaust varied with load. Since the objective was to deplete the 21% O_2 in the air injested by the engine, the proportion of fuel to the engine and catalytic reactor changed with load; however, the total fuel required did not.

The catalyst is currently limited to a maximum operating temperature of 2300°F. This limits the maximum catalytic reactor O_2 depletion to ≈10%. Therefore, for stoichiometric operation at engine load settings less than 48 KW where the diesel effluent may be ≥10% O_2, a system modification (two stage or recycle stream) would be required to prevent catalyst temperatures from exceeding 2300°F.

At the 60 and 48 KW load conditions, the O_2 concentration at the catalyst inlet was low enough to allow stoichiometric and fuel-rich operation to be carried out without the risk of excessive catalyst temperatures. Catalyst temperatures were closer to the recommended maximum at the 48 KW load condition.

4.2.2 Effect of Stoichiometry

Emission results indicated that both O_2 and NO_x essentially disappeared at slightly rich operating conditions (overall fuel/air ratio ≥0.069). At the optimum conditions for O_2 and NO_x reduction, CO levels exceeded 1-3% and increased as the operating conditions were made richer. A design modification would be necessary to reduce CO emissions.

4.2.3 Equilibrium Calculation/Measurements Comparison

An existing Engelhard computer program [1] was used to calculate equilibrium concentrations of the species present in the generated inert stream. Comparisons of the equilibrium concentration and actual gas sample measurements are shown in Figures 8 through 10.

Measured CO levels (Figure 10) are higher than predicted, possibly due to mixing problems (localized hot and cold spots), however, the visual appearance of the hot reactor showed that variations were very small.

Measured O_2 levels (Figure 9) compare with predicted values. Some scatter in the NO_x levels (Figure 8) is evident under fuel rich conditions.

4.2.4 Effect of Reference Velocity

As the total gas flow was varied at the 48 and 60 KW load conditions, there was no apparent effect on catalytic reactor performance. At the 36 KW load condition and a catalyst inlet reference velocity of 6 ft/sec, the gas flow was insufficient to prevent the combustion flame from propagating back into the diffuser section preceeding the catalyst and prevented operation. This occurrence (flashback) also prevented operation at the 24 KW load condition.

4.3 Durability Tests

The durability test study demonstrated 200 hours of successful catalytic NO_x and O_2 reduction. The emissions from the first 100 hours (60 KW engine load) and from the second 100 hours (48 KW engine load) were generally stable. At the conclusion of the test, NO_x and O_2 emission levels remained at less than 10 Vppm. NO_x and O_2 emissions are plotted as a function of time in Figure 11.

4.4 Further Exhaust Gas Treatment

The amount of further exhaust gas treatment is dependent on the specific intended use of the inert stream. Specification of the field system's gas composition requirements is necessary to prevent overdesign and thus enable a cost efficient total system to be recommended.

5. CONCLUSIONS

An experimental program has been carried out using an Engelhard convertor to reduce O_2 and NO_x in a diesel engine exhaust by combusting additional fuel over a catalyst to generate an inert gas. The primary results obtained were:

1. Oxygen and NO_x levels in a diesel exhaust stream can be reduced to low levels (≤ 10 ppm) by operating a catalytic convertor unit under fuel rich conditions.

2. 200 hours of catalyst durability have been successfully demonstrated.

3. There is no apparent effect of engine load or catalyst reference velocity on the convertor emissions.

4. Rising CO levels with increasing fuel/air ratio dictate operation (at fuel rich conditions) as close to stoichiometric conditions as temperature limits will permit to prevent excess CO formation.

5. Due to catalyst material temperature constraints, the single stage catalytic reactor cannot deplete O_2 levels in the diesel exhaust gas in excess of 10%.

REFERENCES

[1] I. T. Osgerby and R. P. Rhodes, "An Efficient Numerical Method for the Calculation of Chemical Equilibrium in the H/C/O/N/A System," ARO, Inc., Arnold Engineering Development Center (AEDC), TR-71-256.

[2] I. T. Osgerby and M. Durilla, "Inert Gas Generation from Diesel Exhaust Using a Catalyst System," Final Report, to be published. Sandia Contract 13-5071.

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Table 1

Allis Chalmers DES-60 Diesel Exhaust Characterization

Load (KW)	Temperature (°F)	CO_2 (%)	CO (%)	O_2* (%)	NO_x (ppm)
0	360	2.3	0.05	17.66	500
12	450	3.2	0.05	16.14	650
24	570	4.5	0.05	12.33	>1000
36	650	5.6	0.05	11.19	>1000
48	700	6.2	0.05	9.59	>1000

* Bag Samples

Figure 1

Schematic Flowsheet of Test Rig

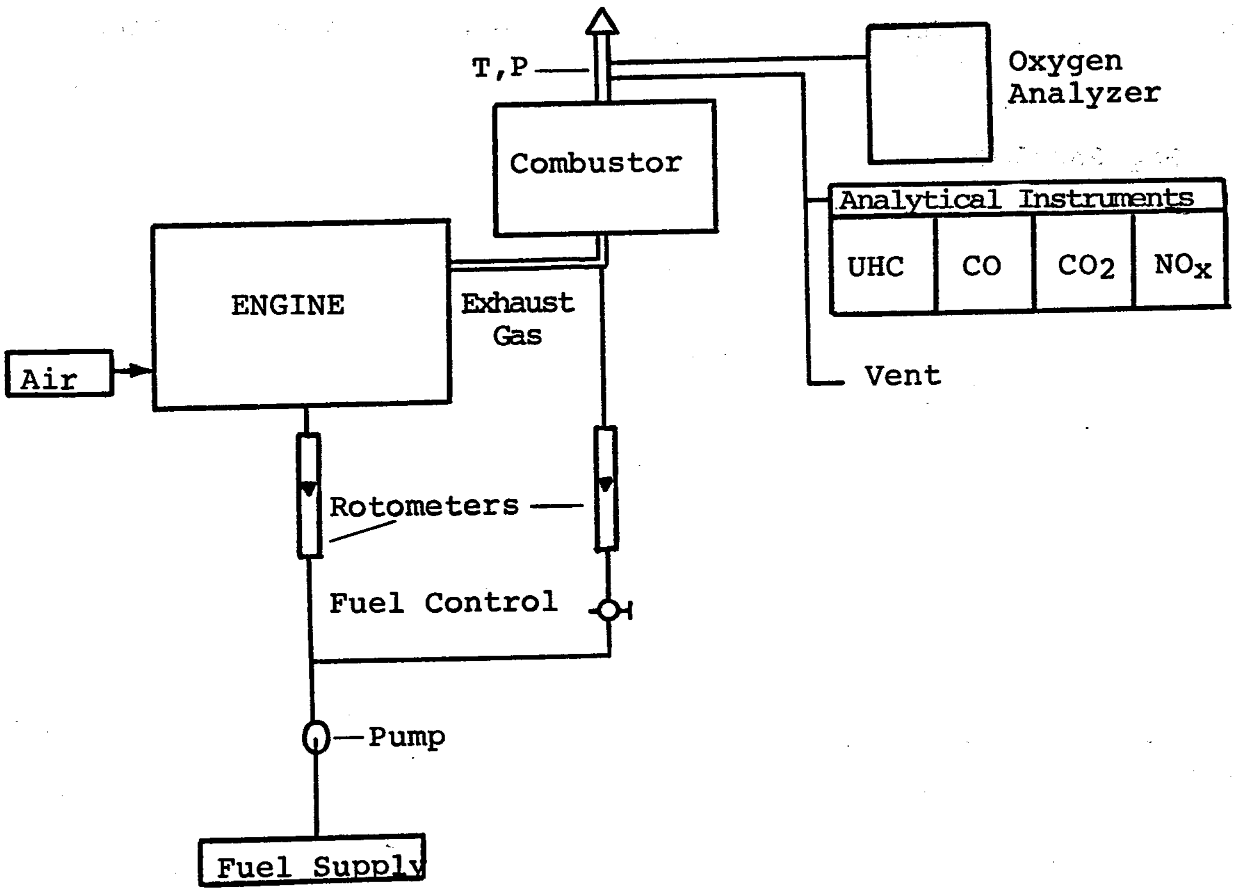


Figure 2

Diesel Inert Gas Generator Unit

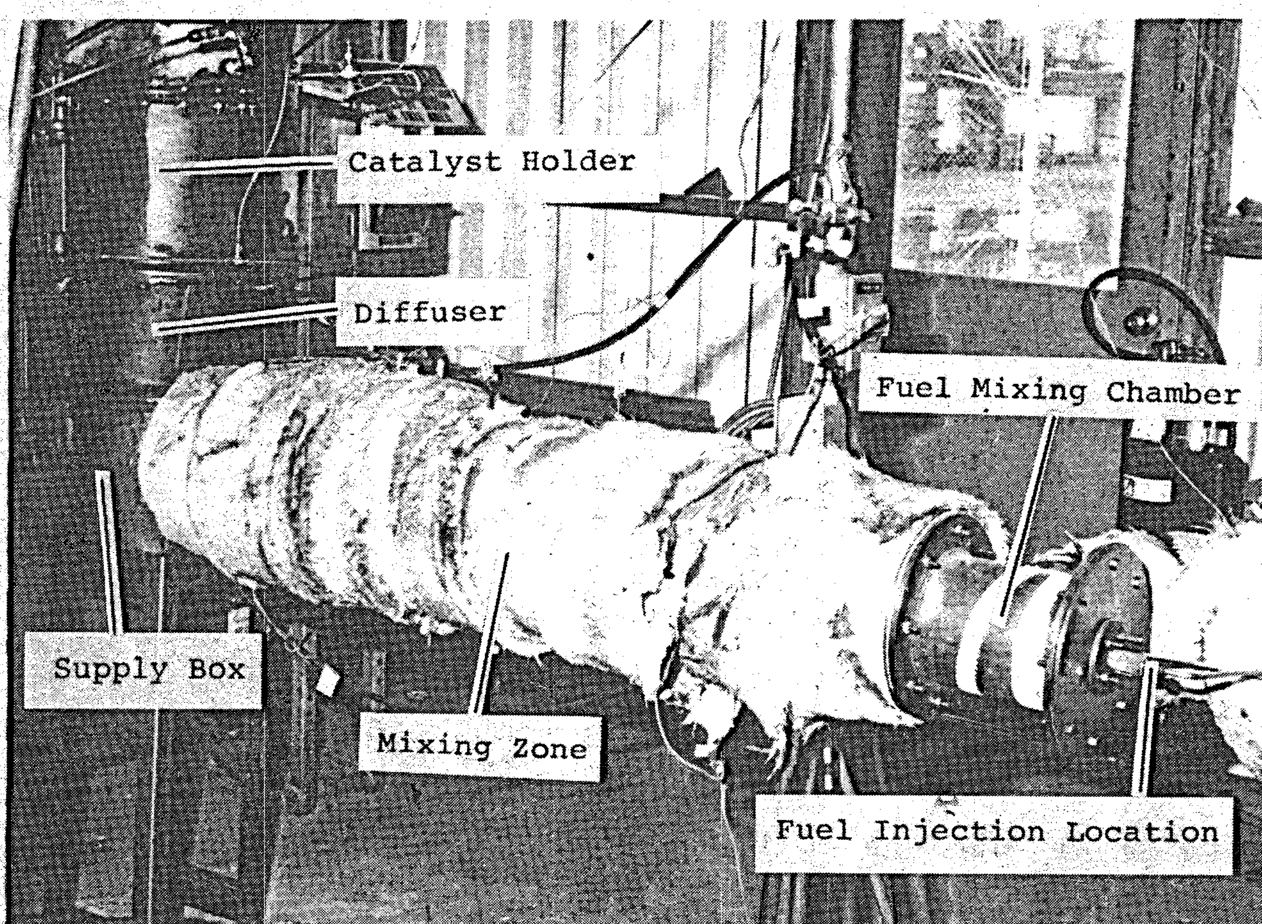


Figure 3

Diesel Inert Gas Generator Unit and Instrumentation

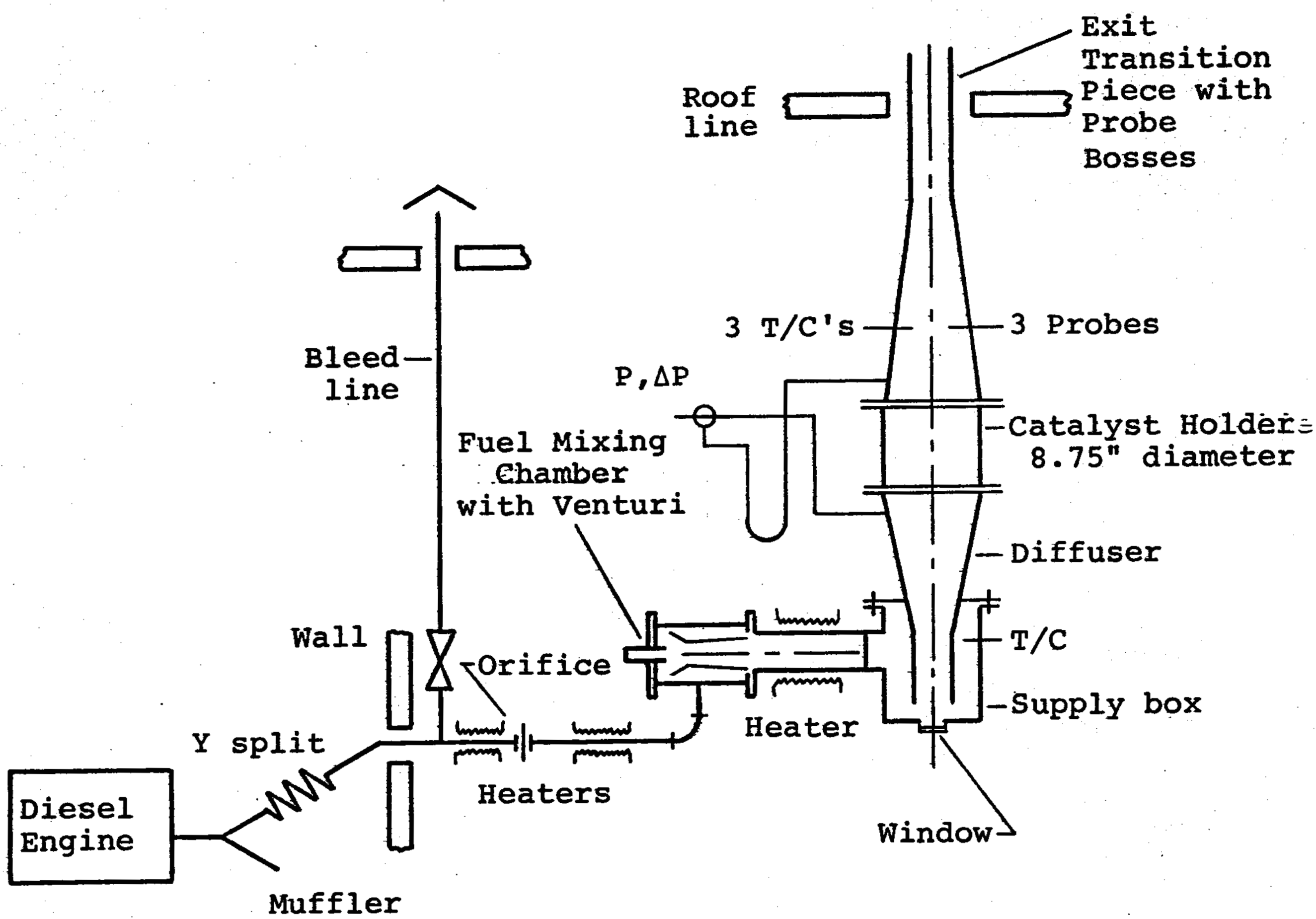
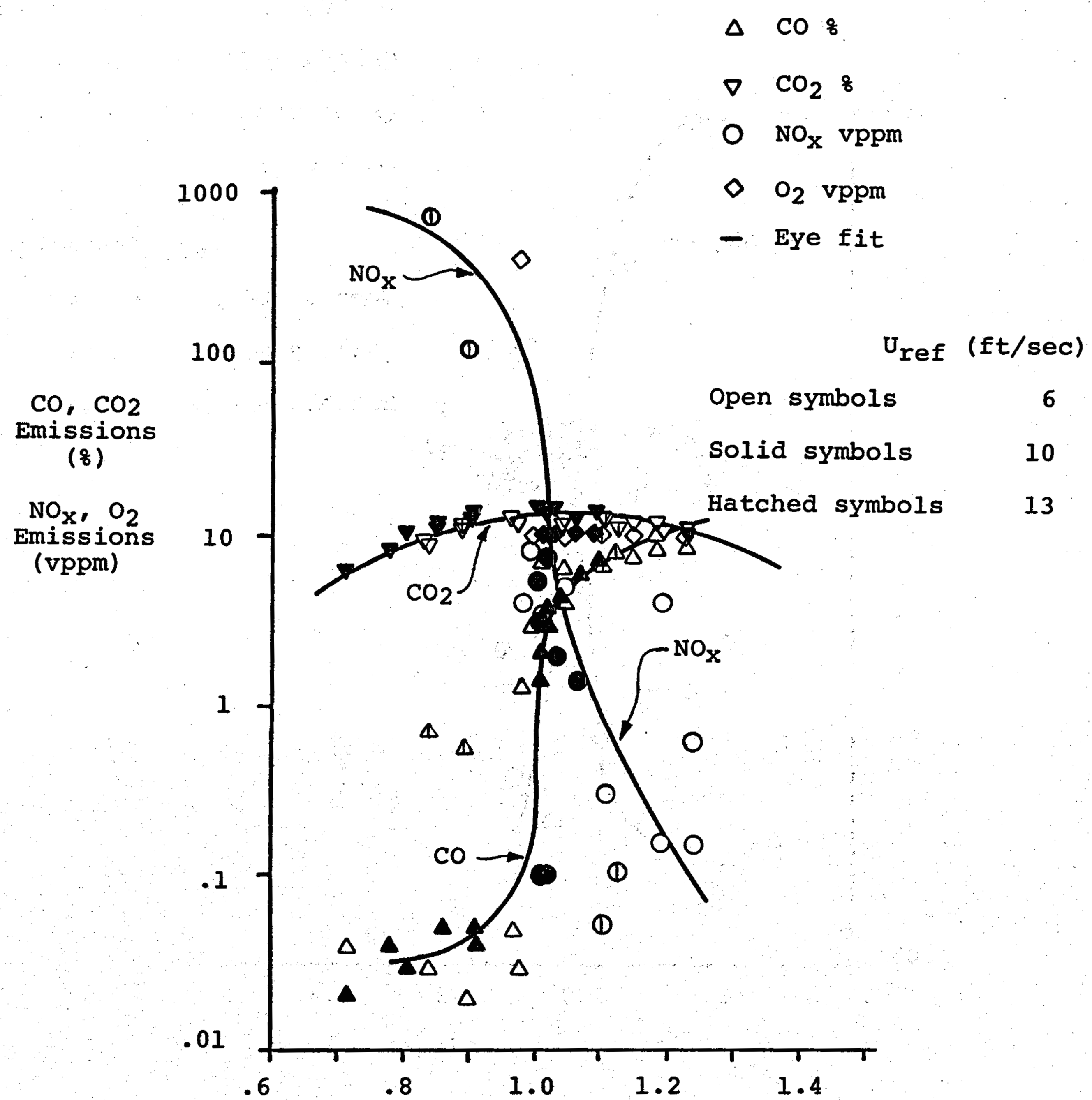


Figure 4

Parametric Tests - 60 KW Engine Load -

Emisions vs. Equivalence Ratio

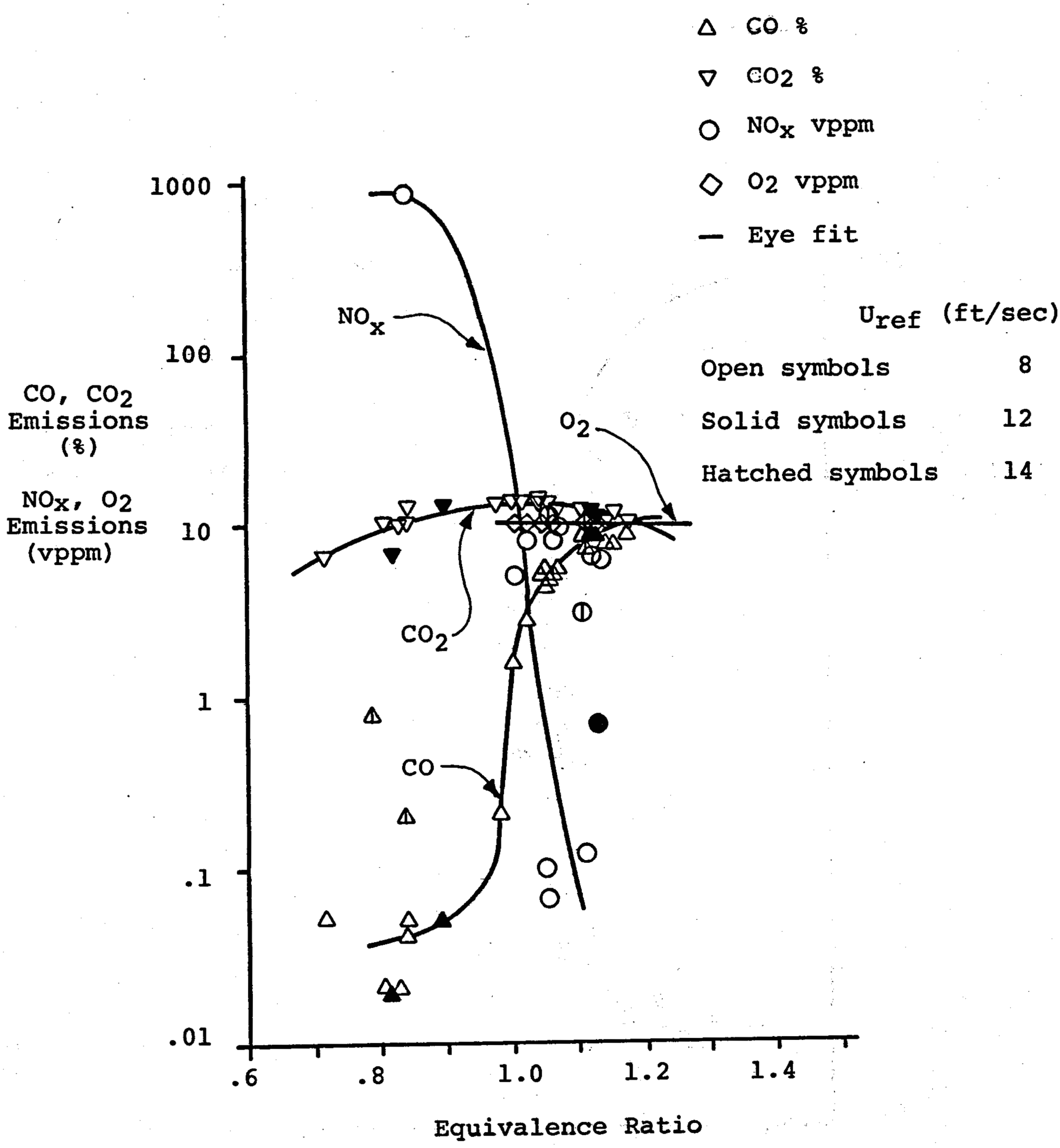


$$\frac{\text{(Fuel/air ratio) actual}}{\text{(Fuel/air ratio) stoichiometric}}$$

Figure 5

Parametric Tests - 48 KW Engine Load -

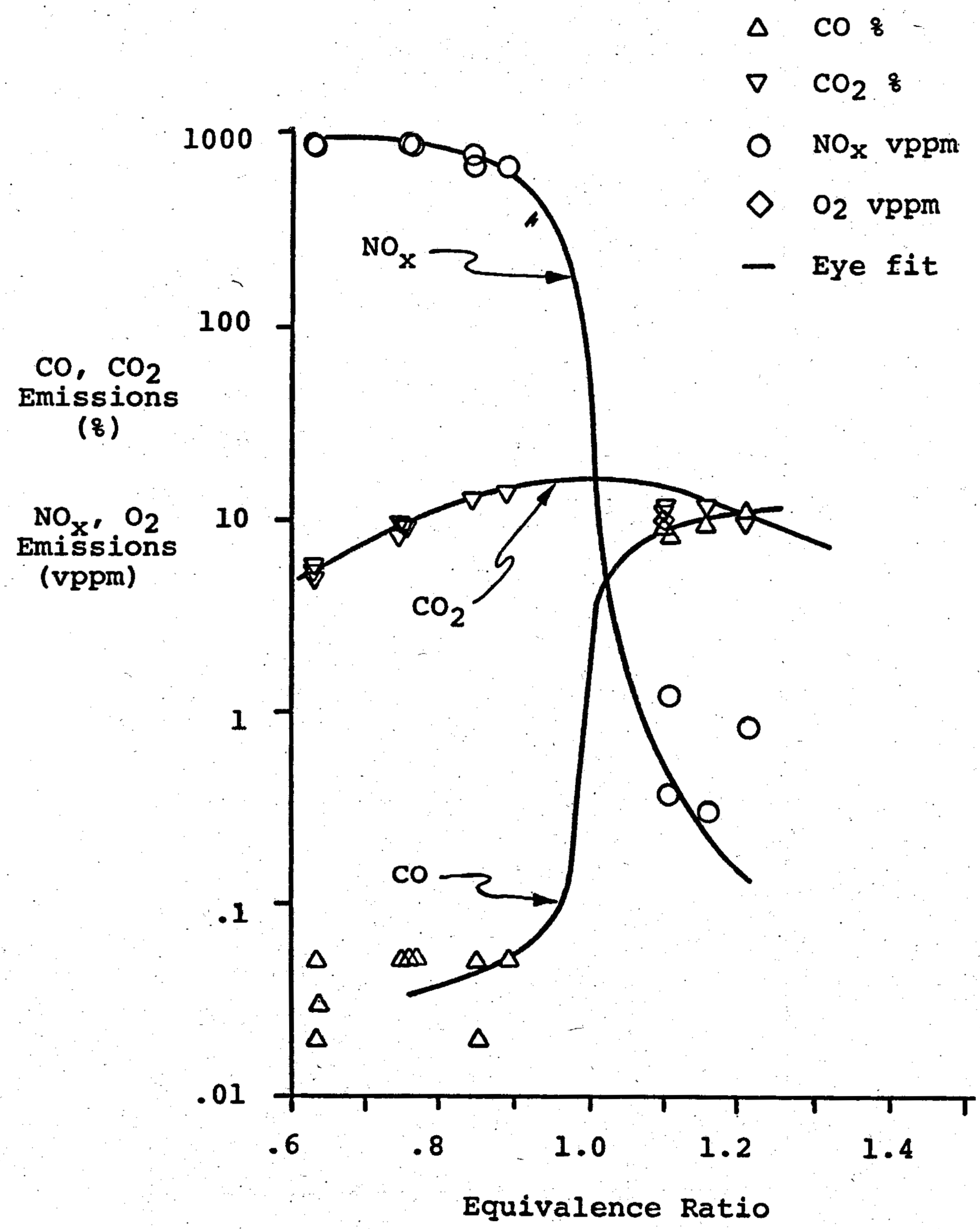
Emissions vs. Equivalence Ratio



$\frac{\text{(Fuel/air ratio) actual}}{\text{(Fuel/air ratio) stoichiometric}}$

Figure 6

Parametric Tests - 36 KW Engine Load -
Emissions vs. Equivalence Ratio



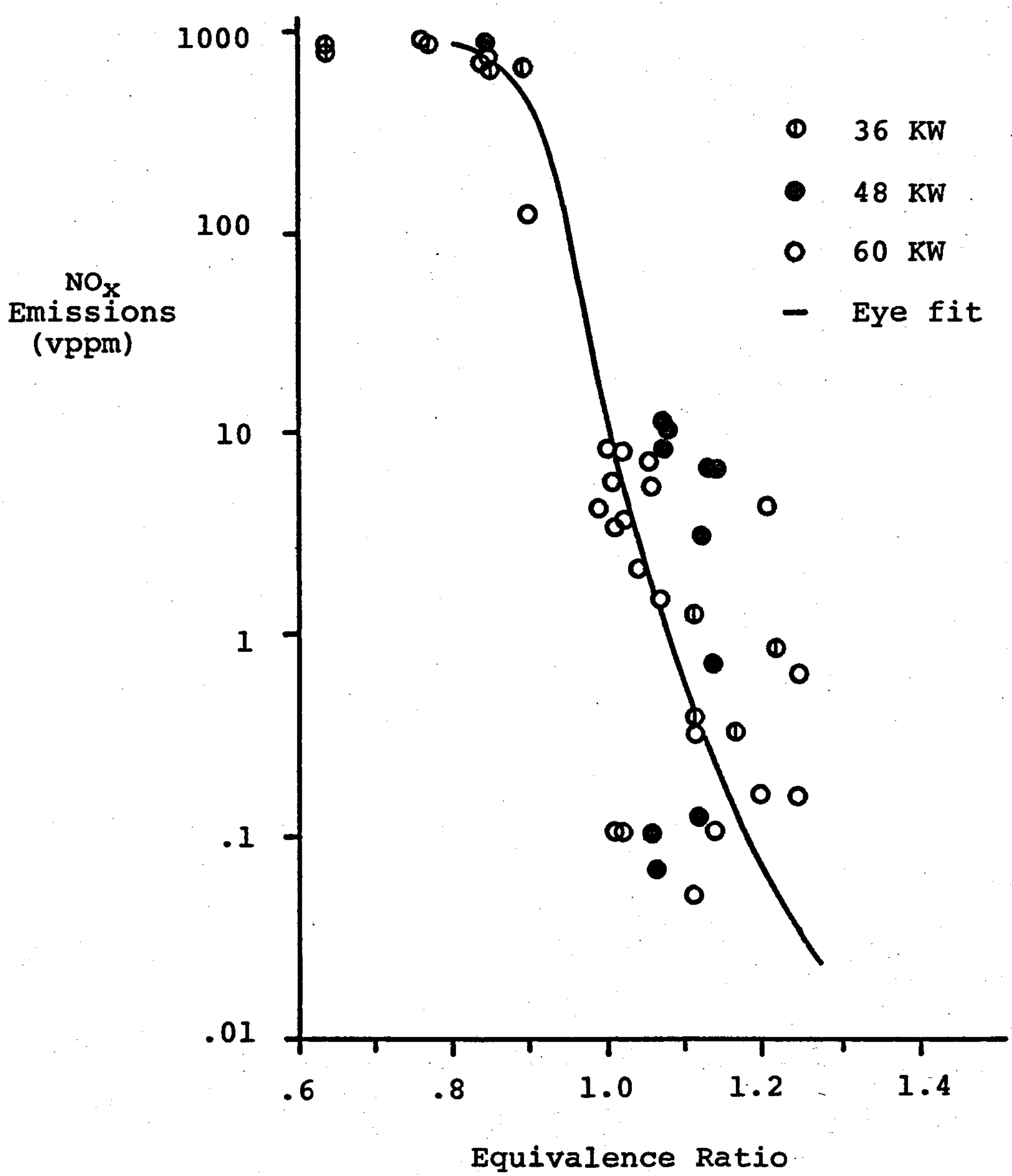
$$\frac{\text{(Fuel/air ratio) actual}}{\text{(Fuel/air ratio) stoichiometric}}$$

Figure 7

Parametric Tests

NO_x Emissions vs. Equivalence Ratio

Effect of Engine Load



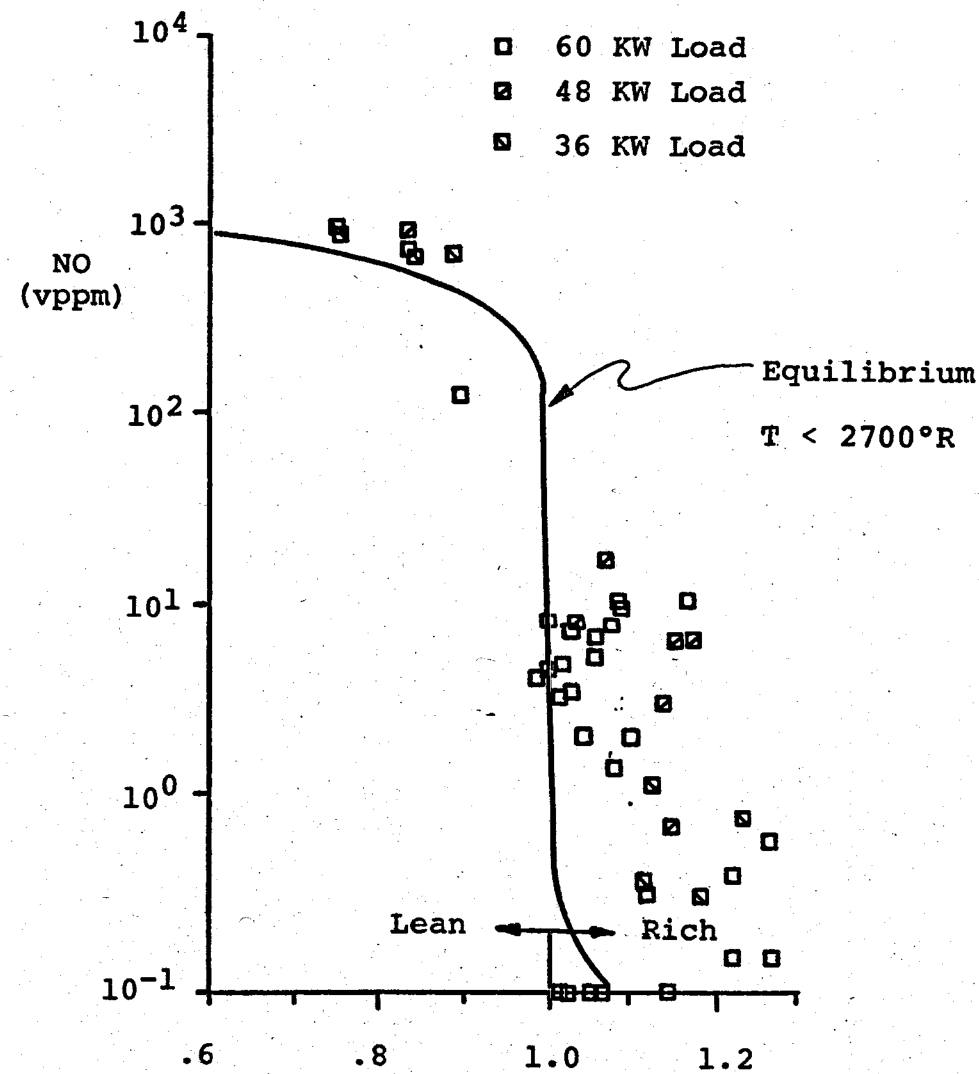
$$\frac{\text{(Fuel/air ratio) actual}}{\text{(Fuel/air ratio) stoichiometric}}$$

Figure 8

Reactor Exhaust NO_x:

Equilibrium vs. Measured Effect of Equivalence Ratio

Maximum Operating T_{ad} = 2700°R



Equivalence Ratio

$$\frac{\text{(Fuel/air ratio) actual}}{\text{(Fuel/air ratio) soichiometric}}$$

Figure 9

Reactor Exhaust O_2

Equilibrium vs. Measured Effect of Equivalence Ratio

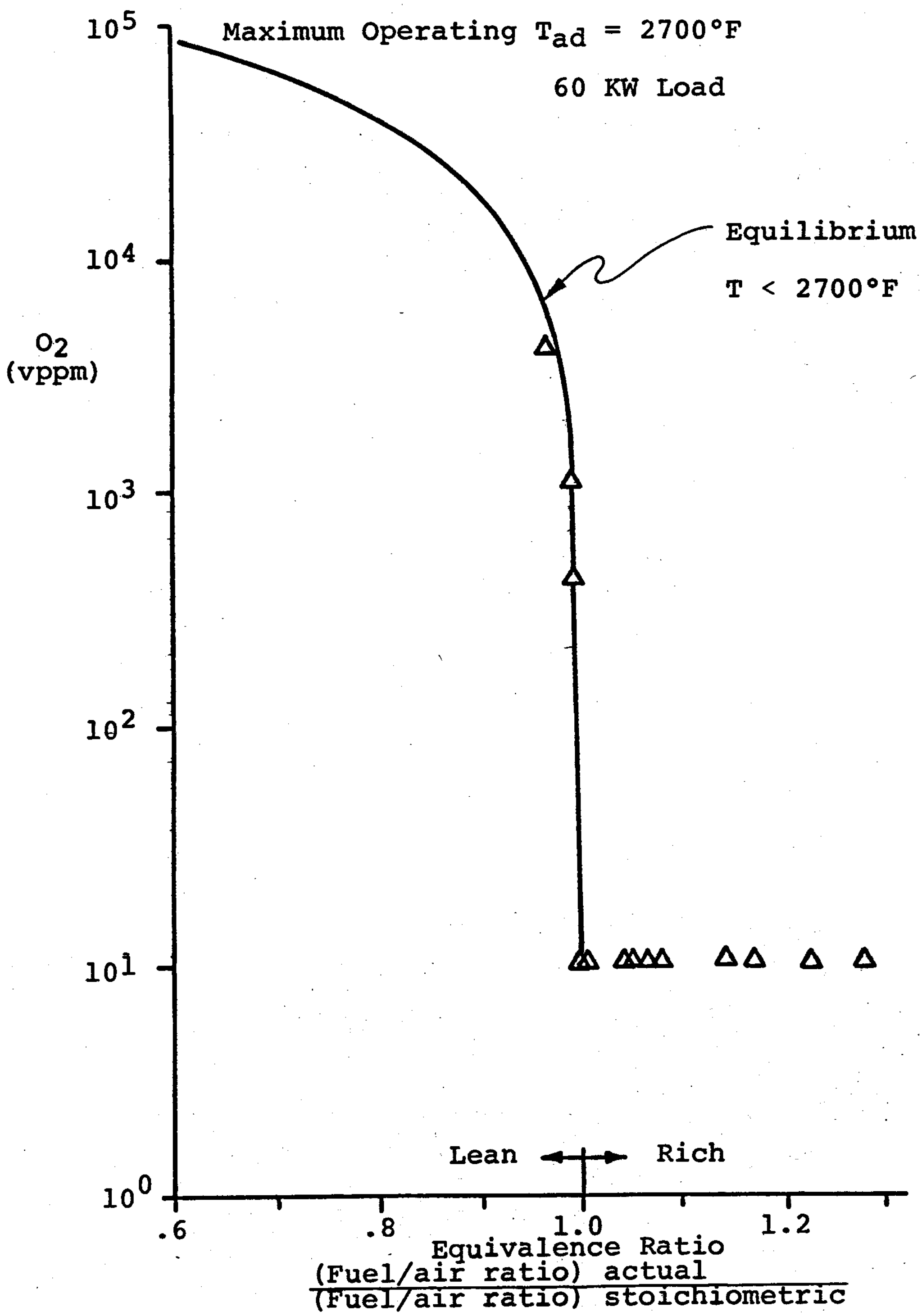
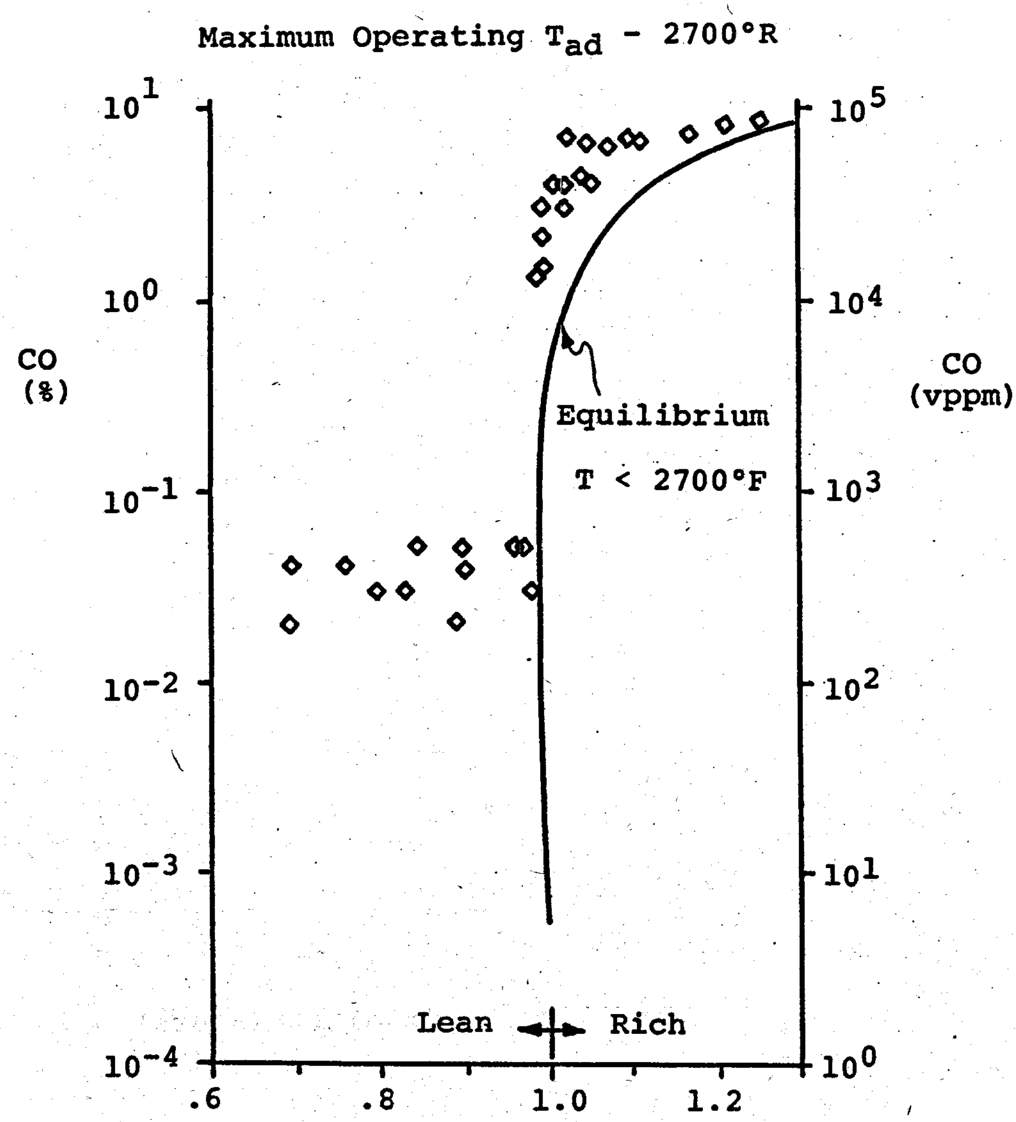


Figure 10

Reactor Exhaust CO:

Equilibrium vs. Measured Effect of Equivalence Ratio

60 KW Load



$$\frac{\text{(Fuel/air ratio) actual}}{\text{(Fuel/air ratio) stoichiometric}}$$

Figure 11

Durability Test Results

NO_x Emissions vs. Time