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THE ECONOMICAL PRODUCTION OF ALCOHOL FUELS FROM COAL-DERIVED SYNTHESIS GAS

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Executive Summary

At WVU, three types of catalysts were produced and evaluated during this reporting period: (1) vapor-phase-synthesized molybdenum nitrides mixed with clay or silica,(2) temperature-program-decomposed vanadium nitrides doped with potassium acetate, and (3) reduced carbon-supported molybdenum-nickel catalysts doped with potassium. Catalysts in the first category have high activity, but low selectivity toward alcohols. The second type of catalyst is active for alcohol synthesis if appropriate doping level and reaction conditions were employed. Reduced Mo-Ni-K/C catalysts are promising materials for higher alcohol synthesis, even though they produce some unidentified higher-molecular-weight products.

In catalyst synthesis, the compounds, VN and NbN, were prepared by temperature programmed decomposition (TPD) of the respective M(V) oxides. Pure phase VN forms readily at 750°C, while the formation of single phase NbN requires temperatures of 900°C. VN and potassium activated VN were evaluated as catalysts.

We have set up a new Varian GC/MS this quarter and are making progress in identification of oxygenates and hydrocarbons using chemical ionization (CI). We experienced problems with the Rotoberty reactor, namely rotor-locking and leaking at elevated temperatures. These problems were referred to the manufacturer and were solved. We are now producing data on this reactor.

We have started converting the plug-flow reactor which had been isolated from sulfur to a membrane reactor so that we can explore new reactor concepts for converting syngas to liquid fuel products.

At UCC&P, we have met or exceeded three of four catalyst development targets with catalysts tested to date. We are not yet close on the fourth target, oxygenate selectivity, unless we compromise the other three targets.

We completed screening of three series of catalysts including an Engelhard support impregnated with various levels of cesium, a Union Carbide-manufactured catalyst support impregnated with cesium, and the Engelhard support impregnated with copper and cesium. Maximum isobutanol space time yield was 24 g/kg-cat/hr.

In Task 2, during the past three months, much has been accomplished in fuel testing. Several tests have been run on pure indolene, and the data have been analyzed from these tests. The two limiting alcohol blends have been made, sent out for analysis and the results obtained. The emissions sampling system is undergoing changes necessary for running alcohol fuels. A cylinder pressure measurement system has been installed.

Most of the past three months has been devoted to final preparation of a Topical Report describing and evaluating the seven design cases.

TASK 1. REACTION STUDIES

1.1 Introduction

The objective of Task 1 is to prepare and evaluate catalysts and to develop efficient reactor systems for the selective conversion of hydrogen-lean systhesis gas to alcohol fuel extenders and octane enhancers.

Task 1 is subdivided into three separate subtasks: laboratory setup; catalysis research; and reaction engineering and modeling. Research at West Virginia University (WVU) is focused on molybdenum-based catalysts for higher alcohol synthesis (HAS). Parallel research carried out at Union Carbide Chemicals and Plastics (UCC&P) is focused on transition-metal-oxide catalysts.

1.2 Accomplishments, Results and Discussion

1.2.1 Laboratory and Equipment Setup

After the Rotoberty reactor was re-installed in the system that had been exposed to sulfides and two test runs using standard methanol catalysts supplied by Union Carbide and BASF were successfully made, we experienced two major problems with this reactor. The first one was with the rotor. It locked at relatively high temperatures (greater than 330°C). The second one was with the reactor seals. A very good seal could be made at room temperature, but the seal failed at elevated temperatures. These problems were referred to the manufacturer and were solved. Now we are producing data on this reactor.

In order to explore and to evaluate new reactor concepts that could be used for converting syngas to liquid fuel products, the plug-flow reactor that had been isolated from sulfur is being converted to a membrane reactor. We expect to finish the conversion in October. This modification will allow rapid conversion between a packed-bed and membrane-reactor configurations.

We have purchased a Varian GC-MS for product identification. We are making progress in identification of different oxygenates and hydrocarbons from liquid products collected from prior catalysts studies. The GC-MS is on a cart so that it may be operated independently or moved to either one of the reactor units for on-line product analysis.

1.2.2 Molybdenum-Based Catalyst Research

A total of 15 catalysts were screened this quarter. They were: (a) vapor phase synthesized molybdenum nitrides mixed with clay or silica (total of 3);(b) temperature-programmed decomposed vanadium nitrides doped with potassium acetate (total of 4); and (c) reduced carbon-supported molybdenum-nickel catalysts doped with potassium nitride (total of 8). For all these catalysts, product identification with the gas chromatograms remains a problem, due to formation of some unidentified, heavier products. Calculation of yields and selectivities is difficult at the

present time. Only overall CO conversions and GC area percentages have been reported.

Catalysts in group (a) are active for CO hydrogenation, but they produce very little alcohols, probably because of dehydration of alcohols on clay or silica. Vanadium nitride, VN, without alkali gives very low activity and produces exclusively hydrocarbons. Appropriate doping of KAc significantly increased both activity and selectivity to alcohols. However, excessive doping of KAc resulted in a dramatic decrease in both activity and selectivity to alcohols. Group (c) contains 2 non-calcined, 5 calcined and 1 nitrided catalysts. The effects of Mo content, K precursor and doping level, Ni concentration, pretreatment conditions and calcination on the catalytic performance of this type of catalyst have been investigated. Detailed discussions can be found in monthly status reports MS47, MS48 and MS49.

Although alcohol production rates cannot be determined for all these catalysts, it is still possible that some of these catalysts satisfy the minimum criteria for further study.

In our catalyst preparation research, VN was prepared by heating V_2O_5 (3.0938 g) in flowing ammonia (170 mL/min) from 25 to 750°C at 2°C/min, then holding the temperature at 750°C for 2 hours. Nb_2O_5 heated under these conditions yielded a mixture of oxide products. Therefore the maximum temperature was increased to 900°C to facilitate conversion of the Nb_2O_5 to NbN.

Four catalysts were prepared with VN: VN, $K_{0.4}$VN, $K_{0.7}$VN and $K_{1.1}$VN. These were all prepared by adding potassium acetate to the VN as a solid then adding methanol ($K_{0.4}$ and $K_{0.7}$) or water ($K_{1.1}$) to the mixture and mixing the slurry together.

1MRC169A ($K_{0.7}$VN) was evaluated in two separate reactor runs. In the first run, the activity approached 60% at 400°C, and the selectivity to higher alcohols was around 20% at the same temperature. The activity and the selectivity to higher alcohols was still increasing at 400°C. In order to determine the optimum temperature conditions, a second run of 1MRC169A was completed up to 425°C. The catalyst evaluated in this second run was very different from the first. The activity was around 1% and the selectivities were also very low. An XRD pattern was obtained on the used 1MRC169A catalyst after the second run. The two phases identified were potassium bicarbonate and VN. The bicarbonate is a product of the thermal decomposition of the potassium acetate in the reactor environment. Due to the hygroscopic nature of the alkali acetates, it appears reasonable that atmospheric water is reacting with the alkali activated vanadium nitride catalysts to cause the deactivation. Work on the vanadium based catalysts is continuing.

1.2.3 Transition-Metal-Oxide Catalyst Research

Last quarter we tested an Engelhard Zn/Cr support (designated 2WMH61B) at 1000 psig pressure with 1:1 H_2:CO syngas at 12,000 GHSV from 260 - 440 °C. The first isobutanol was detected at 400 °C, but was being produced at a rate of only 5 g/kg-cat/hr. At 440 °C, the isobutanol rate was up to 9 g/kg/hr. The support was also tested after impregnating with

potassium at various levels. The maximum isobutanol space time yield was about 4 g/kg/hr at the lower temperature of 340°C and 1000 psig. Tests were not run at higher temperatures for the potassium-impregnated catalysts.

This quarter, we completed a series of runs testing the effect of impregnating the Engelhard support (2WMH61A) with cesium at various levels. The best performer in terms of isobutanol yield was 2WMH74A which had been impregnated with 5 parts Cs per 100 parts support (pph). It had an isobutanol space-time yield of 10 g/kg/hr at 340°C and 1000 psig; however, hydrocarbon selectivity was 70%. Again, tests were not run at higher temperatures for these catalysts.

We completed a series of runs using a support manufactured at UCC&P (2WMH94). We impregnated this support with various levels of cesium (0, 5, 7.5 and 10 pph). The best single result in terms of isobutanol yield occurred with 5 pph Cs at 440°C, 1000 psig and 12,000 GHSV: 22 g isobutanol/kg/hr. However, hydrocarbon selectivity was 83%. The result with the same catalyst at 400°C was nearly as good in terms of isobutanol space time yield (19 g/kg/hr), and its hydrocarbon selectivity was only 50%. Interestingly, no isobutanol was formed with this catalyst at 340°C and lower.

We also ran experiments using the Engelhard support impregnated with copper and cesium. Copper concentration was varied at 0, 0.5 and 1.0 pph while cesium concentration was kept constant at 5.0 pph. This series of runs produced our highest isobutanol space-time yield to date at 24 g/kg/hr (5 pph Cs, 0.5 pph Cu at 400°C, 1000 psig and 12,000 GHSV). Unfortunately, hydrocarbon selectivity was still unacceptably high at 84%.

At UCC&P, our general goal for this project has been to produce an oxygenate mix suitable for use as a fuel additive. Consequently, our initial general catalyst targets were 1) total oxygenate space-time yield greater than 320 g/kg/hr; 2) selectivity to oxygenates greater than 90% (CO_2-free, carbon basis); 3) oxygenate product less than 70 mole percent methanol; and 4) carbon monoxide conversion per pass greater than 20%. We had no initial isobutanol target because we were not looking at this product as a precursor to MTBE. If we were interested in producing the precursors to MTBE, we would also be interested in generating products with a methanol-to-isobutanol ratio of less than one.

With these fuel-additive targets in mind, we can take a look at where we stand in our catalyst development efforts. Table A compares our targets with 1) our best run to date in terms of isobutanol space time yield and 2) what is probably our best run to date in terms of overall performance.

Table A. Comparison of Experimental Data with Catalyst Targets

Target Area	Target Value	Highest Isobutanol Space Time Yield	Best Overall Performance
Catalyst	---	2WMH98A	2WMH102A
Temperature (°C)	---	400	340
1) Oxygenate Space Time Yield	>320 g/kg-cat/hr	178	356
2) Selectivity to Oxygenates	>90%	16	35
3) Product Molar Methanol Content	<70%	60	70
4) CO Percent Conversion	>20%	33	30

It is apparent from Table A that we have met three of the four target goals with2WMH102A. However, the selectivity result is a long way from the target. It is also apparent that having the highest isobutanol space-time yield does not ensure that all the fuel-additive goals are met. Incidentally, it is possible at this time to meet the 90% oxygenate selectivity target, but the product would contain mostly methanol.

1.3 Conclusions and Recommendations

Catalyst screening has stopped at WVU. We have set up a Berty-type reactor and have solved new-reactor, start-up problems. We have begun kinetic studies with sulfided Mo-Co-K/C catalysts to learn how to optimize reaction conditions for producting higher alcohols.

We are converting the no-sulfur reactor at WVU to operate either in a plug-flow or membrane reactor mode. Simultaneously, we are learning how to analyze reaction products with GC-MS using both electron ionization and chemical ionization. We will return to studying Mo-Ni-K/C and other promising catalysts when the reactor conversion is complete and we have improved our product analysis capabilities.

The transition-metal-oxide catalysts studied this quarter did not meet success criteria. Conditions that produced isobutanol also produced large quantities of hydrocarbons.

1.4 Future Plans

During the next quarter at WVU, we expect to obtain good kinetic data on sulfided Mo-Co-K/C catalysts to better understand an efficient catalyst for producing linear alcohols. We also expect to have solved analytical problems with the GC-MS and to have more complete data on non-sulfide catalysts that produce oxygenate products.

In the next quarter at UCC&P, we will continue testing copper-based catalysts. We are also in the process of manufacturing a new catalyst support that will be evaluated.

TASK 2. PROCESS SYNTHESIS AND FUEL EVALUATION.

2.1 Introduction

During the past three months, much has been accomplished in fuel testing. Several tests have been run on pure indolene, and the data have been analyzed from these tests. The two limiting alcohol blends have been made, sent out for analysis and the results obtained. The emissions sampling system underwent, and is undergoing, changes necessary for alcohol fuels. A cylinder pressure measurement system has been installed.

Most of the past three months has been devoted to final preparation of a Topical Report describing and evaluating the seven design cases. The abstract of this report follows.

2.2 Accomplishments, Results, and Discussion

2.2.1 Design

Most of the past three months has been devoted to final preparation of a Topical Report describing and evaluating the seven design cases. The abstract of this report follows.

This project is a combination of process simulation and catalyst development aimed at identifying the most economical method for converting coal to syngas to linear higher alcohols to be used as oxygenated fuel additives. There are two tasks. The goal of Task 1 is to discover, study, and evaluate novel heterogeneous catalytic systems for the production of oxygenated fuel enhancers from synthesis gas, and to explore, analytically and on the bench scale, novel reactor and process concepts for use in converting syngas to liquid fuel products. The goal of Task 2 is to simulate, by computer, energy efficient and economically efficient processes for converting coal to energy (fuel alcohols and/or power). This report contains results from Task 2.

The first step for Task 2 was to develop computer simulations of alternative coal to syngas to linear higher alcohol processes, to evaluate and compare the economics and energy efficiency of these alternative processes, and to make a preliminary determination as to the most attractive process configuration. Seven cases were developed using different gasifier technologies, different methods for altering the H_2/CO ratio of the syngas to the desired 1.1/1, and with the higher alcohols as the primary product and as a by-product of a power generation facility. Texaco, Shell, and Lurgi gasifiers were used as to gasify coal, and steam reforming of natural gas, sour gas shift conversion, or pressure swing adsorption was used to alter the H_2/CO ratio of the syngas. In addition, a case using only natural gas was prepared in order to facilitate comparison between coal and natural gas as a source of syngas.

There are significant differences among the production costs for processes converting coal to syngas to higher alcohol fuel additives for cases involving Texaco, Lurgi, and Shell gasifiers, between cases involving natural gas reforming or sour gas shift conversion to alter the H_2/CO ratio, and for different plant capacities. The best case, on the basis of manufacturing cost, is one of the hybrids, a Shell gasifier with natural gas.

Production of 5.1 billion liters/yr (32 MM bbl/yr) of alcohol fuels from coal is considered the maximum feasible process scale. As expected, there are economies of scale favoring larger-scale over smaller-scale processes. However, resource and marketing constraints limit the maximum scale at which a plant could be constructed.

Production of higher alcohol fuel additives from natural gas is more economical, for the next 20 years, than production from coal at any scale at current or predicted (by DOE) natural gas prices. Production of higher alcohol fuel additives from coal and natural gas hybrids is more economical than production from natural gas at West Virginia natural gas prices ($3.00/MM BTU). The break even natural gas price for production of higher alcohols by natural gas versus the Shell gasifier/natural gas hybrid is $2.45/MM BTU. Furthermore, if a plant life of 10 years were used, which is more typical in the chemical process industry, then all of the manufacturing costs for the cases using coal gasification will increase, making natural gas the clearly superior option.

Capital and operating costs are estimated on the basis of conventional technology, equipment, processes, and environmental controls. Thus, it is possible that future emission control requirements could significantly increase capital and operating costs of all coal-based processes described.

The manufacturing cost of the alcohol derived from natural gas is highly dependent on the natural gas price. Capital costs are lower for natural gas cases than for coal-based cases. Therefore, raw material costs for the natural gas cases are a larger portion of the total annualized cost.

If the cost of natural gas exceeds $2.45/MM BTU, the coal/natural gas hybrid (Shell gasifier) is more economical than the natural gas only design. If the cost of natural gas exceeds $4.94/MM BTU, the all coal design (Shell gasifier) is more economical than the hybrid. This is primarily a result of the high capital investment for the gasifier and accompanying cryogenic oxygen plant. This higher investment outweighs the benefit of using coal, which is a cheaper raw material. The only way for coal based processes to be more competitive than natural gas under all conditions is either for the relative price of coal and natural gas to change or for a major development to occur in coal gasification technology. Price variations would have greater impact on the natural gas reference cases, since raw material costs for these cases are a larger portion of the total annualized cost. Therefore, the competitiveness of the coal-based cases would be enhanced more by increases in the price of natural gas than by decreases in coal cost.

The most energy efficient design, by wide margin, uses only natural gas. If pollution credits based on CO_2 or other combustion products are obtainable in the future, this process will benefit relative to the coal cases. The major question is whether an increase in natural gas prices would be completely offset by any potential gains realized by pollution credits.

2.2.2 Fuel Testing

2.2.2.1 Explanation of Exhaust Sampling Rig and Testing Method

A flow diagram of the exhaust sampling system is shown in Figure 1. An explanation of the symbols used in Figure 1 follows:

- P - pumps for drawing in the raw exhaust and the dilution air.
- MFC - Mass Flow Controller. These set the mass flow rate of mixture flowing through a particular line.
- BX, DX - filters which protect the MFC's from harmful constituents.
- V - 3-way valves for switching between warm-up / bypass mode and sample mode.
- $\dot{m}$ - mass flow rate of mixture through a particular line.

The system is capable of capturing exhaust emissions from an engine fueled by either pure gasoline or a blend of gasoline and alcohol. Whether running on either pure gasoline or a blend of gasoline and alcohol, the system performs the following two tasks:

1. It draws in a sample of raw exhaust exiting the engine and dilute the exhaust with fresh air from a bottle.
2. It captures a diluted exhaust sample in a bag.

When sampling an engine fueled by a blend of gasoline and alcohol, the following three tasks are also performed by the system:

1. It draws a sample of the diluted exhaust through an in-line HFID (Heated Flame Ionization Detector) to determine the concentration hydrocarbon emissions.
2. It captures unburned alcohols in the diluted exhaust in water contained in the bubblers.
3. It captures aldehydes and ketones in the Dinitrophenylhydrazine (DNPH) cartridge.

The in-line HFID is needed when running blends of gasoline and alcohol because the reading obtained from the HFID will be affected by unburned alcohol, and unburned alcohol will settle on the walls of the tedlar bag. Therefore, a different hydrocarbon concentration would be obtained from the tedlar bag than would be obtained from the in-line HFID. The other constituents (CO, CO_2, NO_x) will not be affected, and bag sampling is acceptable.

Hydrocarbons measured by the HFID and not measured as unburned CH_3OH (methanol) or C_2H_5OH (ethanol) are reported as RHC (Residual HydroCarbons). RHC is calculated from the following [1]:

$$RHC = HFID - r_{CH_3OH}C_{CH_3OH} - r_{C_2H_5OH}C_{C_2H_5OH} \quad (1)$$

where the r's are the HFID response factors for the particular alcohol, and the C's are the concentrations of the particular alcohol in the exhaust obtained from the gas chromatography analysis of unburned alcohol trapped in the bubblers. The alcohol response factors are determined by analyzing a known concentration of a particular alcohol using the HFID (calibrated on propane) and observing the reading. Hence:

$$r = \frac{HFID\ reading \in ppm}{Alcohol\ concentration\ (C_1) \in mixture,\ ppm} \quad (2)$$

The EPA (Environmental Protection Agency) uses a quantity known as the OMHCE (Organic Matter HydroCarbon Equivalent) to denote the total hydrocarbon mass emitted from the engine as unburned and partially burned fuel. For a blend containing methanol and ethanol, OMHCE is [1]:

$$OMHCE = RHC + \frac{13.8756}{32.042}m_{CH_3OH} + \frac{13.8756}{23.034}m_{C_2H_5OH} + \frac{13.8756}{30.0262}m_{HCHO} + \frac{13.8756}{22.03}m_{CH_3CHO} \quad (3)$$

where: m's are masses of the particular constituents

- 13.876 - molecular weight of gasoline associated with each carbon atom
- 23.034 - molecular weight of C_2H_5OH per carbon atom
- 32.0262 - molecular weight of HCHO per carbon atom
- 22.03 - molecular weight of CH_3CHO per carbon atom

The raw exhaust sampling line is heated to prevent condensation in the line which would dissolve any unburned alcohol before it reaches the bubblers and the HFID. Once the exhaust is diluted, the dew point is sufficiently lowered so that no condensation occurs at room temperature. The three-way valves in the system are used to allow the system to be warmed up and conditioned with exhaust before any sample is taken. The sample trapped in the tedlar bag is analyzed in a gas analysis bench to determine the concentration of CO, CO_2, and NO_x.

2.2.2.2 Calculation of Raw Exhaust Gas Emissions

Since the HFID and the analysis of the bag sample gives the concentration of the various constituents in the diluted exhaust, a method must be derived for calculating the concentration of the constituents in the raw exhaust exiting the engine. It should be noted that the volume

flowrates used below are standard volume flowrates controlled by the mass flow controllers. Therefore, these standard volume flowrates can be treated as mass flowrates. The standard conditions set in the mass flow controllers are 70 °F and 1 atmosphere.

Consider some time interval, *t*. Then, the total volume of diluted exhaust drawn by the sampling system, V_{DE}, is:

$$V_{DE}=\dot{V}_{DE}t \tag{4}$$

where: $\dot{V}_{DE}$ = standard volume flowrate of diluted exhaust

The total volume of constituent *i* in the diluted exhaust, V_{DE}^{i}, drawn by the sampling system is:

$$V_{DE}^{i}=V_{DE}C_{DE}^{i} \tag{5}$$

where: C_{DE}^{i} = concentration of constituent *i* in the diluted exhaust

Combining (4) & (5):

$$V_{DE}^{i}=\dot{V}_{DE}tC_{DE}^{i} \tag{6}$$

The total volume of constituent *i* in the diluted exhaust will come from two sources: the raw exhaust stream and the dilution air. Thus, the total volume of constituent *i* in the diluted exhaust coming from the dilution air, $V_{DE_{DA}}^{i}$, is:

$$V_{DE_{DA}}^{i}=\dot{V}_{DA}tC_{DA}^{i} \tag{7}$$

where: $\dot{V}_{DA}$ = standard volume flowrate of dilution air

C_{DA}^{i} = concentration of constituent *i* in the dilution air

Likewise, the total volume of constituent *i* in the diluted exhaust coming from the raw exhaust, $V_{DE_{RE}}^{i}$, is:

$$V_{DE_{RE}}^{i}=\dot{V}_{RE}tC_{RE}^{i} \tag{8}$$

where: $\dot{V}_{RE}$ = standard volume flowrate of raw exhaust

C_{RE}^{i} = concentration of constituent *i* in the raw exhaust

Applying conservation of mass on the diluted exhaust stream:

$$\dot{V}_{DE} = \dot{V}_{RE} + \dot{V}_{DA} \tag{9}$$

$$V^i_{DE} = V^i_{DE_{RE}} + V^i_{DE_{DA}} \tag{10}$$

Rearranging (8):

$$C^i_{RE} = \frac{V^i_{DE_{RE}}}{\dot{V}_{RE} t} \tag{11}$$

Substituting (10) into (11):

$$C^i_{RE} = \frac{V^i_{DE} - V^i_{DE_{DA}}}{\dot{V}_{RE} t} \tag{12}$$

Substituting (6) and (7) into (12):

$$C^i_{RE} = \frac{\dot{V}_{DE} t C^i_{DE} - \dot{V}_{DA} t C^i_{DA}}{\dot{V}_{RE} t} \tag{13}$$

Substituting (9) into (13) and canceling out t:

$$C^i_{RE} = \frac{\left(\dot{V}_{RE} + \dot{V}_{DA}\right) C^i_{DE} - \dot{V}_{DA} C^i_{DA}}{\dot{V}_{RE}} \tag{14}$$

Rearranging (14):

$$C^i_{RE} = \left(1 + \frac{\dot{V}_{DA}}{\dot{V}_{RE}}\right) C^i_{DE} - \frac{\dot{V}_{DA}}{\dot{V}_{RE}} C^i_{DA} \tag{15}$$

Defining parameter δ:

$$\delta = \frac{\dot{V}_{DA}}{\dot{V}_{RE}} \tag{16}$$

Substituting (16) into (15):

$$C^i_{RE} = (1 + \delta) C^i_{DE} - \delta C^i_{DA} \tag{17}$$

Rearranging (17):

$$C_{RE}^{i} = C_{DE}^{i} + \delta\left(C_{DE}^{i} - C_{DA}^{i}\right) \tag{18}$$

Equation (18) gives the concentration of constituent *i* in the raw exhaust stream in terms of known quantities. The next step is to calculate the mass flowrate of exhaust coming out of the engine. Neglecting blowby past the piston rings and any losses from the cylinder head, conservation of mass on the engine gives:

$$\dot{m}_E = \dot{m}_A + \dot{m}_F \tag{19}$$

where: $\dot{m}_E$ = mass flowrate of exhaust exiting the engine
$\dot{m}_A$ = mass flowrate of air entering the engine (known)
$\dot{m}_F$ = mass flowrate of fuel entering the engine (known)

Applying the ideal gas equation of state on the exhaust gas stream exiting the engine, we get:

$$\dot{V}_E = \frac{\dot{m}_E \overline{R} T}{M_E P} \tag{20}$$

where: $\dot{V}_E$ = volumetric flowrate of exhaust
$\overline{R}$ = universal gas constant
T = temperature
P = pressure
M_E = molecular weight of the exhaust mixture

Combining (19) & (20):

$$\dot{V}_E = \frac{\left(\dot{m}_A + \dot{m}_F\right)\overline{R} T}{M_E P} \tag{21}$$

The standard volume flowrate of constituent *i* in the exhaust exiting the engine:

$$\dot{V}_E^{i} = \dot{V}_E C_{RE}^{i} \tag{22}$$

Combining (21) and (22):

$$\dot{V}_E^{i} = \frac{\left(\dot{m}_A + \dot{m}_F\right)\overline{R} T}{M_E P} C_{RE}^{i} \tag{23}$$

Combining (18) and (23):

$$\dot{V}_E^i = \frac{(\dot{m}_A + \dot{m}_F)\overline{R}T}{M_E P}\left[C_{DE}^i + \delta\left(C_{DE}^i - C_{DA}^i\right)\right] \tag{24}$$

Using the density, the mass flowrate of each constituent i in the exhaust exiting the engine can now be calculated:

$$\dot{m}_E^i = \frac{(\dot{m}_A + \dot{m}_F)\rho^i \overline{R}T}{M_E P}\left[C_{DE}^i + \delta\left(C_{DE}^i - C_{DA}^i\right)\right] \tag{25}$$

The density ρ^i is the density of constituent i at temperature T and pressure P. Dividing the right hand side of (25) by the engine power output, ξ, the mass flow of exhaust per unit time per unit power is:

$$\dot{m}_E^i = \frac{(\dot{m}_A + \dot{m}_F)\rho^i \overline{R}T}{M_E P\xi}\left[C_{DE}^i + \delta\left(C_{DE}^i - C_{DA}^i\right)\right] \tag{26}$$

A check on the units in equation (26) yields:

$$\dot{m}_E^i = \frac{(\dot{m}_A + \dot{m}_F)\ \text{g of exhaust}}{\text{s}} \left| \frac{\rho^i\ \text{kg of i}}{\text{m}^3\ \text{of i}} \right| \frac{8.314\ \text{N-m}}{\text{gmol-°K}} \left| \frac{(T+459.67)\ \text{°R}}{} \right| \frac{\text{gmol of exhaust}}{M_E\ \text{g of exhaust}} \left| \frac{}{P\ \text{atm}} \right| \frac{}{\xi\ \text{BHP}} \left| \frac{\left[C_{DE}^i + \delta\left(C_{DE}^i - C_{DA}^i\right)\right]\ \text{m}^3\ \text{of i}}{1{,}000{,}000\ \text{m}^3\ \text{of exhaust}} \right| \frac{\text{°K}}{1.8\ \text{°R}} \left| \frac{\text{atm-m}^2}{101325\ \text{N}} \right| \frac{1000\ \text{g of i}}{\text{kg of i}} \left| \frac{3600\ \text{s}}{\text{hr}} \right.$$

Finally:

$$\dot{m}_E^i = 1.641\,056\,007\,895\,39 \times 10^{-4}\ \frac{(\dot{m}_A + \dot{m}_F)\rho^i(T+459.67)}{M_E P\xi}\left[C_{DE}^i + \delta\left(C_{DE}^i - C_{DA}^i\right)\right] \tag{27}$$

where: $\dot{m}_E^i \doteq$ grams/BHP-hr = emission of specie i from the engine
$\dot{m}_A$ & $\dot{m}_F \doteq$ grams/sec
$T \doteq$ °F
$\rho^i \doteq$ kg/m^3
$M_E \doteq$ grams/gmol
$P \doteq$ atmospheres
$\xi \doteq$ Brake Horsepower

$$\delta = \frac{\dot{V}_{DA}}{\dot{V}_{RE}} \doteq \frac{\text{standard volume flowrate of dilution air}}{\text{standard volume flowrate of raw exhaust into sampling system}}$$

(NOTE: symbol $\doteq$ means "has units of")

Mass emission rates from the engine can now be calculated from the concentrations measured in the diluted exhaust taken in by the sampling system. Only one more point needs to be considered. The Code of Federal Regulations [1] uses a humidity correction factor, K_H, on the NO_x calculation:

$$K_H = \frac{1}{1 - 0.0047\left(\frac{43.478 R_i P_d}{P_B - \left(P_d \frac{R_i}{100}\right)} - 75\right)} \tag{28}$$

where: R_i = relative humidity of the engine intake air, in percent
P_d = Saturated vapor pressure, in mm Hg, at the engine intake air dry bulb temperature
P_B = Barometric pressure, in mm Hg

The NO_x concentration obtained from equation (27) is multiplied by K_H from equation (28) to get the corrected NO_x concentration.

2.2.2.3 Calculation of Molecular Weight of Exhaust

The molecular weight of the raw exhaust gas, Mw_{RE}, which is needed in the calculation using equation (27) is computed as follows [2]:

The chemical formula of the fuel is given by $C_\alpha H_\beta O_\gamma N_\delta$. At low temperatures and carbon to oxygen ratios less than one, the overall combustion reaction can be written as:

$$\phi\varepsilon C_\alpha H_\beta O_\gamma N_\delta + (0.21\ O_2 + 0.79\ N_2) \rightarrow \nu_1 CO_2 + \nu_2 H_2O + \nu_3 N_2 + \nu_4 O_2 + \nu_5 CO + \nu_6 H_2$$

Convenient approximations for lean and rich combustion are:

For $\phi<1$: $\nu_5 = \nu_6 = 0$
For $\phi>1$: $\nu_4 = 0$

where ϕ is the equivalence ratio, ε is the molar fuel-air ratio, and the coefficients ν_i, i=(1,6), that describe the product composition. The mole fraction of the ith component, Y_i, is given by:

$$Y_i = \frac{\nu_i}{N} \quad , \quad N = \sum_i \nu_i$$

The molecular weight of the exhaust gas is given by:

$$Mw_{RE} = \sum_i Y_i Mw_i$$ where Mw_i is the molecular weight of the species i.

For the lean or stoichiometric cases, atom-balance equations are sufficient to determine the product composition. For the rich case, the following reaction is introduced:

$$CO_2 + H_2 \leftrightarrow CO + H_2O$$

and the equilibrium constant for this reaction $K = \frac{\nu_2 \nu_5}{\nu_1 \nu_6}$ is given at temperature T in Kelvin as:

$$K = e^{2.743 + \frac{1000}{T}\left(-1.761 + \frac{1000}{T}\left(-1.611 + \frac{1000}{T}0.2803\right)\right)}$$

Solution for both rich and lean cases are given in Table 1.

Table 1: **Low temperature combustion products**

i	Specie	$\phi \leq 1$	$\phi > 1$
1	CO_2	$\alpha\phi\varepsilon$	$\alpha\phi\varepsilon - \nu_5$
2	H_2O	$\beta\phi\varepsilon/2$	$0.42 - \phi\varepsilon(2\alpha - \gamma) + \nu_5$
3	N_2	$0.79 + \delta\phi\varepsilon/2$	$0.79 + \delta\phi\varepsilon/2$
4	O_2	$0.21(1-\phi)$	0
5	CO	0	ν_5
6	H_2	0	$0.42(\phi - 1) - \nu_5$

In the rich case , ν_5 is given by the solution of a quadratic equation, which is given by:

$$\nu_5 = \frac{-b + \sqrt{b^2 - 4ac}}{2a}$$

where

$a = 1\text{-}K$

$b = 0.42-\phi\epsilon(2\alpha-\gamma)+K(0.42(\phi-1)+ \alpha\phi\epsilon)$
$c = -0.42\alpha\phi\epsilon(\phi-1)K$

2.2.2.4 Results of Testing

Several baseline tests (tests run on pure indolene) have been conducted, and the results are given in Table 3 and Figures 2 - 9. From left to right, Table 2 gives the following information about the baseline tests:

- Test Number
- Date when test was conducted
- Engine Parameters - speed, torque output, power output
- Ambient Air Entering Engine - barometric pressure, dry-bulb temperature, humidity, volume flowrate, mass flowrate
- Mass flow rate of fuel
- Air/Fuel ratio on a mass basis
- Equivalence Ratio
- Molecular weight of fuel calculated from procedure outlined earlier
- Temperatures - engine coolant, intake manifold, exhaust manifold, crankcase oil
- Mass Flow Controllers' Settings on Sampling Cart
- Dilution Factor, δ, calculated from equation (16)
- Concentration of each exhaust constituent in the diluted exhaust
- Concentration of each exhaust constituent in the bottled dilution air
- Concentration of each exhaust constituent in the raw exhaust (ppm) from equation (18)
- Engine emissions calculated from equation (27)
- Brake Specific Fuel Consumption

The figures give the following information:

Figure 2 - Carbon monoxide emissions (g/BHP-hr) vs. equivalence ratio
Figure 3 - Carbon dioxide emissions (g/BHP-hr) vs. equivalence ratio
Figure 4 - Nitric oxide emissions (g/BHP-hr) vs. equivalence ratio
Figure 5 - Hydrocarbon emissions (g/BHP-hr) vs. equivalence ratio
Figure 6 - Brake specific fuel consumption vs. equivalence ratio
Figure 7 - Exhaust gas temperature vs. equivalence ratio
Figure 8 - Molecular weight of exhaust gas mixture vs. equivalence ratio
Figure 9 - Engine torque output vs. equivalence ratio

In addition to running baseline tests on pure indolene, the two limiting blends have been made and sent out to Ashland Automotive and Product Application Laboratories for several types of tests. The results are listed in Table 2 below along with the same properties of pure indolene:

Table 2: **Properties of Two Limiting Blends and Pure Indolene**

	Blend #1 90% Indolene 1% Methanol 7.5% Ethanol 1.2% Propanol 0.2% Butanol 0.1% Pentanol	Blend #2 90% Indolene 0% Methanol 8.5% Ethanol 1.2% Propanol 0.2% Butanol 0.1% Pentanol	Baseline 100% Indolene
	3.69% Oxygen by wt.	3.53% Oxygen by wt.	0% Oxygen by wt.
RON	99.4	99.2	96.7
MON	89.6	90.0	87.2
RVP (psi)	8.89	9.12	8.9
API Gravity	58.4	58.3	59.0
Sp. Gravity	0.7451	0.	.7426
Sulfur (Wt%)	0.008	0.007	0.0061
Aromatics (V%)	29.4	28.4	30.6
Olefins (V%)	3.1	3.1	5.4
Saturates (V%)	67.5	68.5	64.0
IBP (°F)	83	95	94
10% Evap (°F)	125	124	131
50% Evap (°F)	199	204	221
90% Evap (°F)	299	303	307
FBP (°F)	394	393	398

2.3 Conclusions

2.4 Future Work

Now that baseline tests have been conducted, tests need to be run on the two limiting blends to obtain the same kinds of data recorded on the baseline tests. The in-line HFID is now being added to the exhaust sampling system, and that work should be completed within the next couple of weeks. In addition, the cylinder pressure measurement instrumentation is in the process of being installed and tested. Data from the two limiting blends should be available within the next month.

2.4 References

1. Code of Federal Regulations. CFR 40. Office of the Federal Register, National Archives and Records Administration, Revised July 1, 1993.

2. Ferguson, C.R., "Internal Combustion Engines, Applied Thermosciences," John Wiley & Sons, New York, 1985.

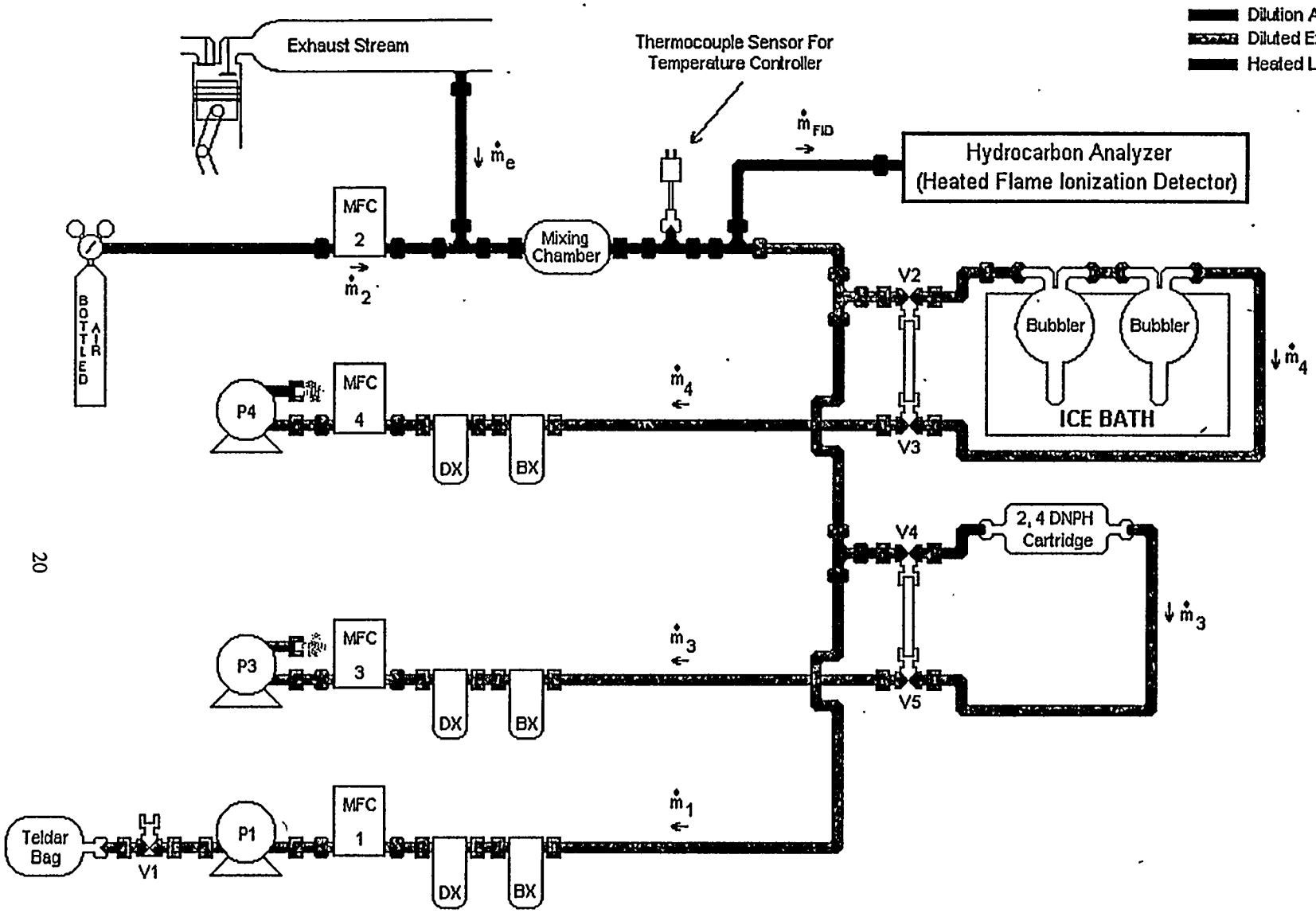

Figure 1 - Exhaust Gas Emissions Sampling System

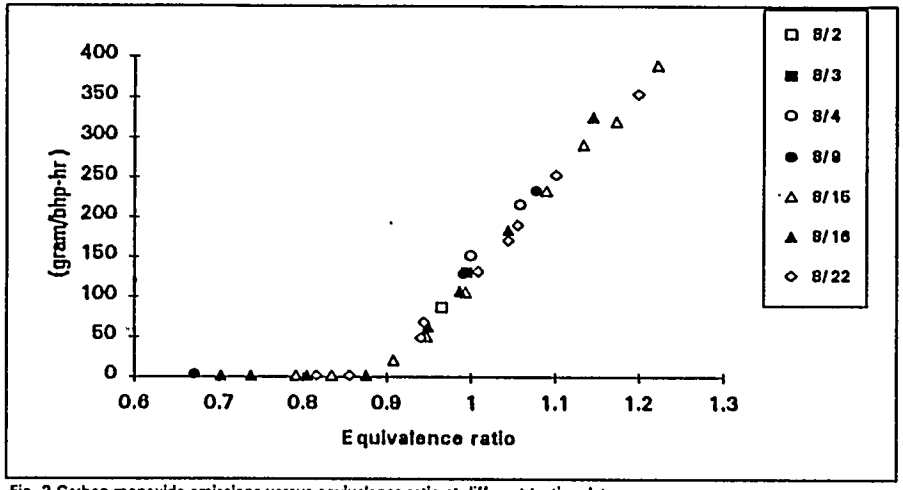

Fig. 2 Carbon monoxide emissions versus equivalence ratio at different testing dates

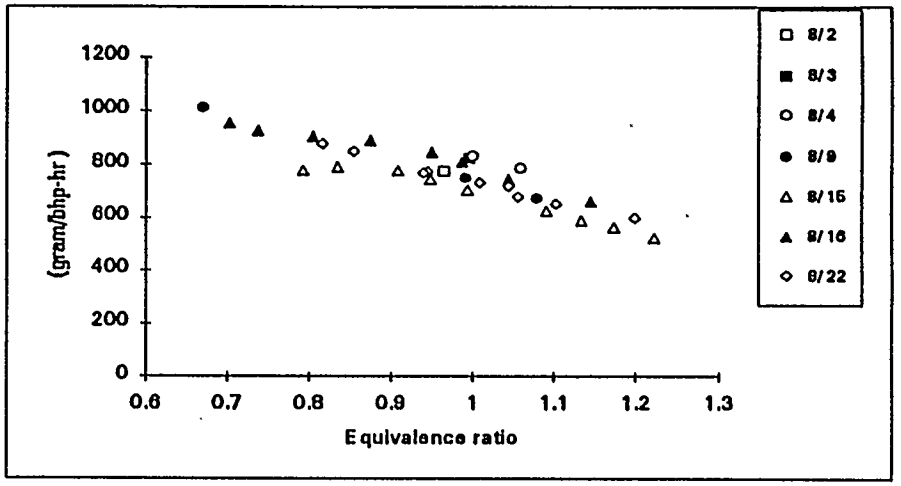

Fig. 3 Carbon dioxide emissions versus equivalence ratio at different testing dates

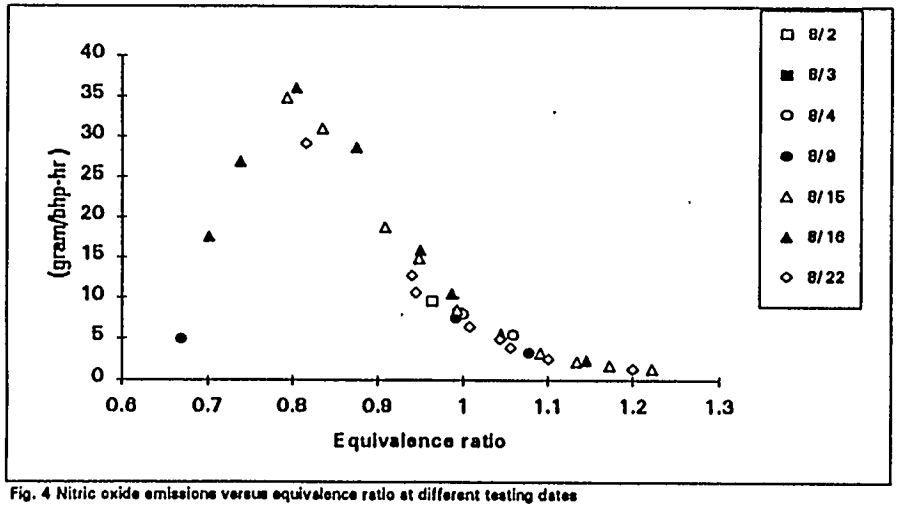

Fig. 4 Nitric oxide emissions versus equivalence ratio at different testing dates

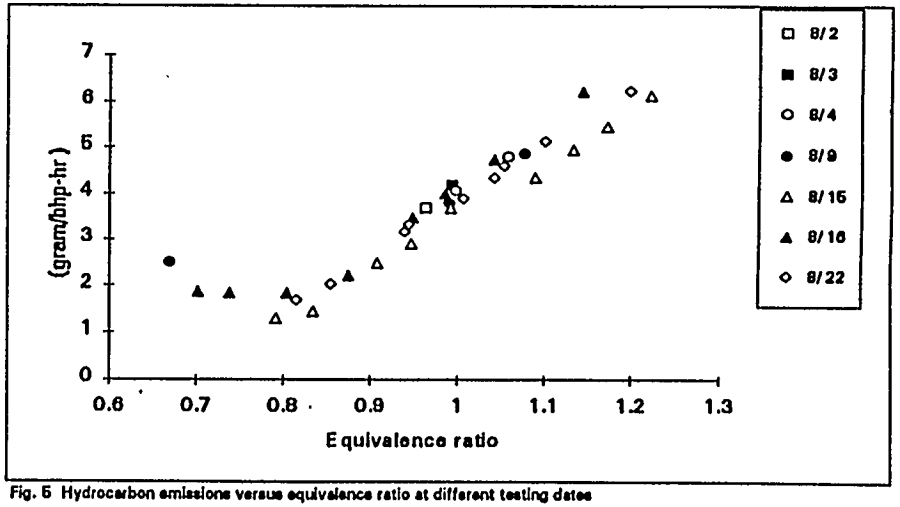

Fig. 5 Hydrocarbon emissions versus equivalence ratio at different testing dates

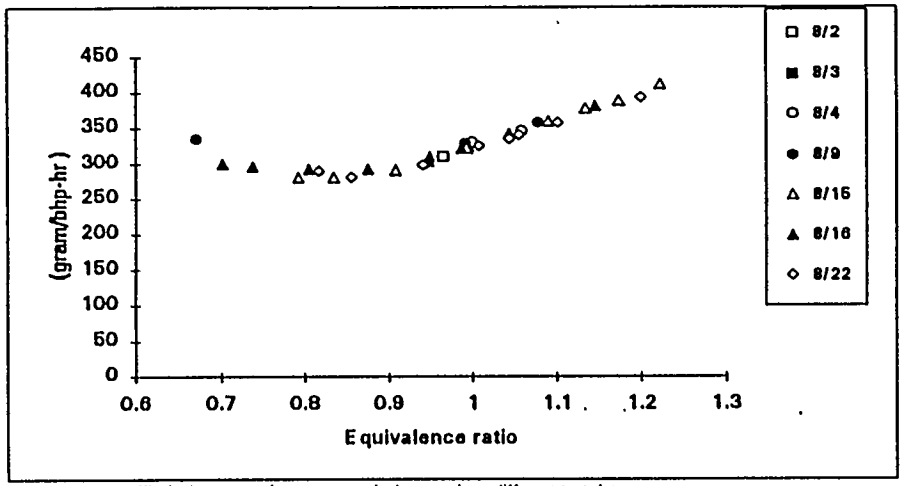

Fig. 6 Brake specific fuel consumption versus equivalence ratio at different test dates

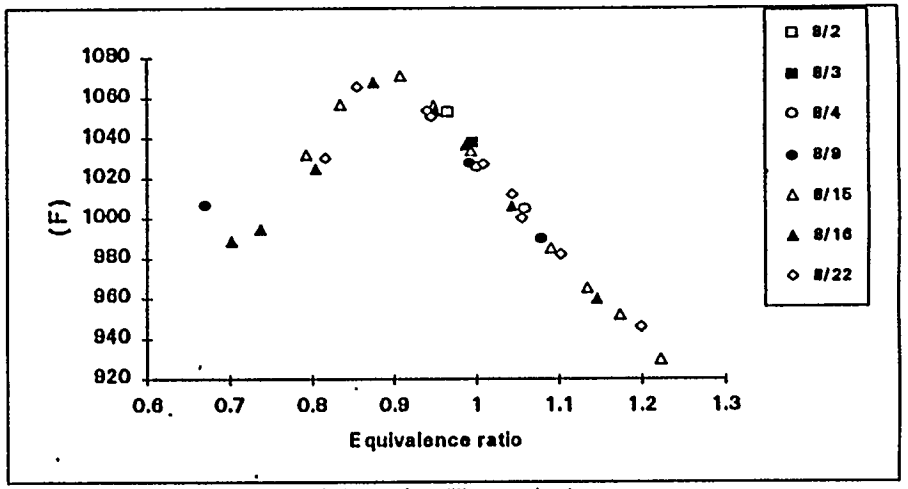

Fig. 7 Exhaust gas temperature versus equivalence ratio at different testing dates

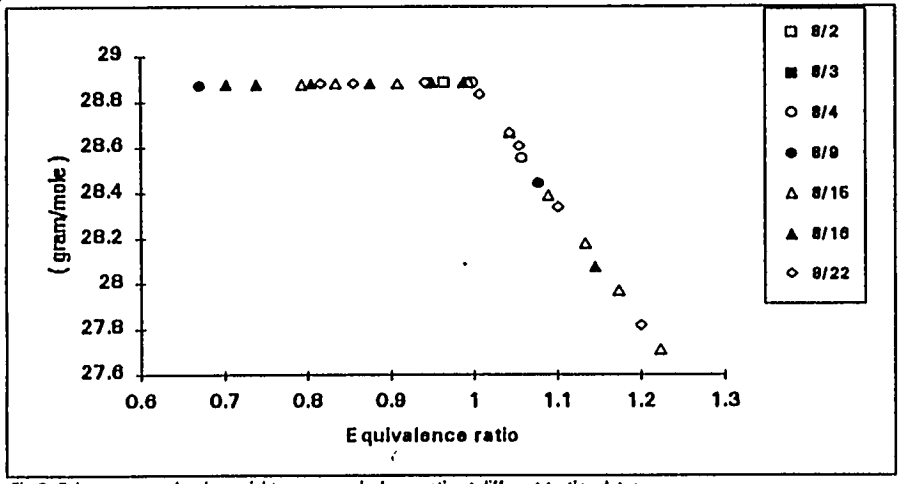

Fig 8. Exhaust gas molecular weight versus equivalence ratio at different testing dates

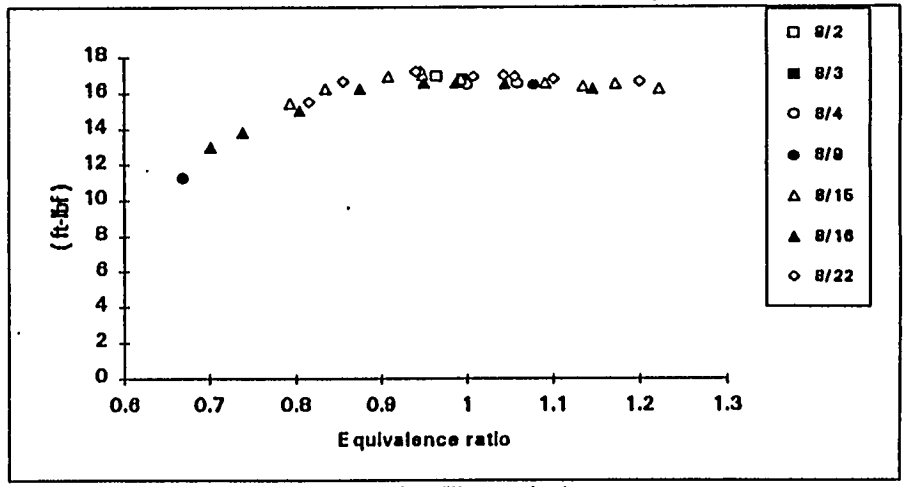

Fig 9. Measured engine torque versus equivalence ratio at different testing dates

Table3: Baseline Engine Test Results

Fuel Composition (Volume Fractions)

Indolene:	1
Methanol:	0
Ethanol:	0
Propanol:	0
Butanol:	0
Pentanol:	0

Stoichiometric A/F:	14.51
Fuel Density (kg/m3):	0.742
Spark Timing (deg btdc):	25
Compression Ratio:	7:1

Num.	Date	Engine			Air					Fuel	Air to Fuel	Equiv.	Fuel	Temperature				Mass flow controllers' flow rates			
		Speed (rpm)	Torque (ft-lbf)	Power (hp)	Pressure (inch Hg)	Tmprtr (F)	Hmdty ratio (grains/lbm)	Vol. flow (cfm)	Mass flow (gram/sec)	Mass Flow (gram/sec)	ratio (mass basis)	ratio	Mol. weight	Coolant (f)	Intake (f)	Exhaust (f)	Oil (f)	Mdot1 (slpm)	Mdot2 (slpm)	Mdot3 (slpm)	Mdot4 (slpm)
1	8/2/95	901	16.94	2.91	29.36	88	100	7	3.762	0.25	15.05	0.96	28.89	208	116	1053	144	8.58	9.52	0.52	2
2	8/3/95	900	16.82	2.88	29.38	86	92	7	3.778	0.259	14.59	0.99	28.89	208	115	1038	143	8.58	9.48	0.54	2
3	8/4/95	901	16 44	2.82	29.31	87	100	7	3.762	0.259	14.53	1.00	28.89	208	115	1026	143	8.58	9.48	0.52	2
4	8/4/95	901	16 54	2.84	29.32	90	108	7	3.743	0.273	13.71	1.06	28.55	208	115	1005	149	8.58	9.52	0.54	2
5	8/9/95	901	16 57	2.84	29.27	82	85	7	3.792	0.259	14.64	0.99	28.89	208	111	1028	142	8.58	9.5	0.52	2
6	8/9/95	901	16.45	2.82	29.26	85	92	7	3.769	0.28	13.46	1.08	28.45	208	111	990	145	8.64	9.52	0.52	2
7	8/9/95	897	11.25	1.92	29.26	85	92	7.2	3.877	0.179	21.66	0.67	28.87	208	118	1007	148	8.64	9.52	0.52	2
8	8/15/95	899	16 83	2 88	29.27	87.7	100	7.03	3.768	0.258	14.61	0.99	28.89	207.9	114.9	1034	146	8.58	9.52	0.52	2
9	8/15/95	898	16 59	2.84	29.27	88.6	104	7.04	3.767	0.283	13.31	1.09	28.39	207.9	112.9	985	149	8.58	9.52	0.54	2
10	8/15/95	900	16.41	2 81	29.27	89	108	7.06	3.776	0.295	12.80	1.13	28.18	207.8	112.3	965	151	8.58	9.52	0.54	2
11	8/15/95	901	16.27	2.79	29.26	89.7	108	7.09	3.785	0.319	11.87	1.22	27.71	207.8	111.3	930	152	8.58	9.52	0.54	2
12	8/15/95	900	16 53	2.83	29.26	90.7	108	7.08	3.773	0.305	12.37	1.17	27.97	207.9	112.8	952	153	8.58	9.52	0.54	2
13	8/15/95	900	17	2.91	29.25	91.6	115	7.08	3.766	0.246	15.31	0.95	28.89	207.9	117.1	1056	154	8.58	9.52	0.54	2
14	8/15/95	900	16 95	2.90	29.25	91.9	115	7.07	3.758	0.235	15.99	0.91	28.88	207.9	118.4	1071	155	8.58	9.52	0.54	2
15	8/15/95	900	16.25	2.78	29.25	92.4	118	7.11	3.776	0.217	17.40	0.83	28.88	207.9	119.7	1057	155	8.58	9.52	0.54	2
16	8/15/95	901	15.44	2.65	29.25	93	120	7.15	3.793	0.207	18.32	0.79	28.88	207.9	120.7	1032	156	8.58	9.52	0.54	2
17	8/16/95	903	12.99	2.23	29.24	88.4	103	7.19	3.845	0.186	20.67	0.70	28.87	208	122.2	989	148	8.58	9.52	0.52	2.02
18	8/16/95	900	13 83	2.37	29.23	89.1	105	7.18	3.834	0.195	19.66	0.74	28.88	208	122	995	150	8.58	9.52	0.52	2.02
19	8/16/95	900	15.05	2.58	29.23	90.1	108	7.11	3.789	0.21	18.04	0.80	28.88	207.9	121.1	1025	151	8.58	9.52	0.54	2.02
20	8/16/95	901	16 27	2.79	29.23	90.7	108	7.07	3.764	0.227	16.58	0.88	28.88	207.9	119.7	1008	153	8.58	9.52	0.54	2.02
21	8/16/95	900	16 6	2.84	29 23	91.9	116	7.05	3.745	0.245	15.29	0.95	28.89	207.8	118.3	1054	154	8.58	9.52	0.54	2.02
22	8/16/95	900	16 64	2.85	29.23	91.2	113	7.05	3.750	0.265	14.71	0.99	28.89	207.9	117.8	1037	155	8.58	9.52	0.54	2.02
23	8/16/95	900	16 54	2.83	29.22	92	116	7.07	3.754	0.27	13.90	1.04	28.66	208	117	1006	156	8.58	9.52	0.54	2.02
24	8/16/95	900	16.28	2.79	29.22	94.3	127	7.09	3.749	0.296	12.66	1.15	28.07	208	115.6	960	157	8.58	9.52	0.54	2.02
25	8/22/95	905	16 65	2.87	29.39	85	92	7.03	3.802	0.224	16.98	0.85	28.88	208.6	116.7	1066	149	8.58	9.52	0.52	2
26	8/22/95	900	15.55	2.66	29.39	84.1	89	7.06	3.825	0.215	17.79	0.82	28.88	208.5	116.1	1030	147	8.58	9.52	0.52	2
27	8/22/95	900	17.21	2.95	29.39	85.3	92	6.99	3.779	0.246	15.36	0.94	28.89	208.5	114.1	1051	160	8.58	9.52	0.54	2
28	8/22/95	903	16 96	2.92	29.39	85.5	92	7.01	3.788	0.263	14.40	1.01	28.83	208.5	113.2	1027	161	8.58	9.52	0.52	2
29	8/22/95	900	17.24	2.95	29.39	87.3	100	7.02	3.781	0.245	15.43	0.94	28.89	208.5	114.3	1054	164	8.58	9.52	0.54	2
30	8/22/95	900	17	2 91	29 39	86.2	96	7.01	3.783	0.272	13.91	1.04	28.66	208.5	112	1012	162	8.58	9 52	0.52	2
31	8/22/95	901	16 81	2.88	29 39	86.4	96	7.01	3.782	0.287	13.18	1.10	28.34	208 6	111.5	982	163	8.58	9.52	0.52	2
32	8/22/95	901	16.67	2 86	29 39	86.4	96	7.02	3.787	0.313	12.10	1.20	27.62	208.5	110.2	946	163	8.58	9.52	0.54	2
33	8/22/95	901	16 97	2.91	29.39	87	100	7.02	3.783	0.275	13.76	1.05	28.61	208.5	111.8	1000	163	8.58	9.52	0.52	2

Table3: Baseline Engine Test Results

Standard Conditions
Pressure (atm) = 1
Temperature (f) = 68

Relative Humdity: 0.500

Density (kg/m3) of Species at Standard Conditions

CO: 1.164
CO2: 1.83
NOx: 1.913
HC: 0.5768

N.	Dilution Factor	Diluted Exhaust Bag Emission Conc.				Dilution Air Bag Emission Conc.				Exhaust Gas Emissions				Exhaust Gas Emissions (gram/bhp-hr)					Fuel
		CO (ppm)	CO2 (ppm)	NOx (ppm)	HC (ppm)	CO (ppm)	CO2 (ppm)	NOx (ppm)	HC (ppm)	CO (ppm)	CO2 (ppm)	NOx (ppm)	HC (ppm)	CO	CO2	NOx uncrrctd.	NOx crrctd.	HC	BSFC gram/bhp-hr
1	6.03	2580	14852	152	224	6	385	0	4	18089.2	102020	1067.85	1549.57	87.134	772.599	8.454	9.579	3.699	309.7
2	5.78	3796	15584	133	250	7	400	0	4	26625.9	107072	934.367	1732.23	130.125	822.680	7.505	8.156	4.195	323.5
3	5.85	4350	16411	123	270	16	1470	0	42	30463.7	106435	864.114	1643.77	151.551	832.455	7.065	8.006	4.052	330.6
4	5.95	6181	15573	80	312	16	1470	0	42	43327.1	100548	562.025	1938.84	216.458	789.744	4.615	5.462	4.800	346.4
5	5.94	3706	14938	125	255	16	1470	0	42	25939.4	96087	878.165	1638.39	128.974	751.113	7.176	7.530	3.790	328.0
6	5.80	6589	13307	53	311	16	1470	0	42	46193.4	84628.7	372.342	1931.81	234.879	676.519	3.111	3.382	4.867	357.2
7	5.80	80	13735	53	134	16	1470	0	42	465.62	87635.5	372.342	688.329	3.432	1015.396	4.510	4.901	2.514	335.4
8	6.03	3137	14386	134	253	16	1470	0	42	21942	92209	941.392	1624.34	107.004	706.957	7.545	8.549	3.684	322.4
9	5.95	6583	12424	50	282	16	1470	0	42	46151.3	78425.3	351.266	1728.08	233.960	625.046	2.927	3.388	4.341	359.2
10	5.95	8016	11539	33	311	16	1470	0	42	56218.5	72207.9	231.835	1931.81	291.083	587.788	1.973	2.335	4.956	377.7
11	5.95	10411	10137	18	366	16	1470	0	42	73044.2	62358.4	126.456	2318.2	390.648	524.316	1.111	1.316	6.144	411.4
12	5.95	8805	11051	25	338	16	1470	0	42	61761.5	68779.6	175.633	2121.49	320.440	561.031	1.498	1.773	5.454	387.6
13	5.95	1516	15364	218	210	16	1470	0	42	10564	99079.7	1531.52	1222.25	50.715	748.621	12.095	14.895	2.910	304.0
14	5.95	649	15954	276	185	16	1470	0	42	4463.03	103225	1938.99	1046.62	21.412	778.604	15.289	18.829	2.488	291.3
15	5.95	48	15581	428	120	16	1470	0	42	240.81	100604	3006.84	589.975	1.205	791.595	24.732	30.996	1.463	280.5
16	5.95	47	14659	452	106	16	1470	0	42	233.785	94126.9	3175.44	491.62	1.232	780.056	27.509	34.888	1.284	281.3
17	5.95	59	14282	212	98	10	695	2	14	354.241	96148	1477.32	604.127	2.232	952.431	15.298	17.616	1.886	299.8
18	5.95	55	14774	339	102	10	695	2	14	326.139	99604.4	2369.53	632.228	1.935	929.182	23.107	26.900	1.859	296.2
19	5.88	51	15749	488	110	10	695	2	14	298.038	106454	3416.3	688.43	1.613	905.860	30.389	35.968	1.846	293.1
20	5.88	70	16758	423	140	10	695	2	14	431.519	113543	2959.66	899.19	2.153	890.745	24.272	28.727	2.223	292.8
21	5.88	1827	16282	230	217	10	695	2	14	12775	110199	1603.77	1440.14	62.529	848.000	12.901	15.981	3.493	310.1
22	5.88	3139	15540	164	247	10	695	2	14	21992.2	104986	1069.85	1650.9	107.776	808.876	8.617	10.490	4.009	321.9
23	5.88	5265	14188	80	285	10	695	2	14	36928	95487.6	549.975	1917.86	184.347	749.418	4.512	5.589	4.744	342.9
24	5.88	8909	12122	32	356	10	695	2	14	62528.3	80973.3	212.759	2416.66	325.496	662.687	1.820	2.409	6.234	382.0
25	6.03	57	16306		131	10	695	2	14	340.19	110367		835.962	1.666	849.881			2.029	281.1
26	6.03	49	15595	447	104	10	695	2	14	283.987	105372	3128.27	646.278	1.503	876.624	27.205	29.122	1.695	290.5
27	5.95	2092	15303	180	213	10	695	2	14	14636.7	103321	1252.51	1412.04	69.704	773.569	9.803	10.654	3.332	300.3
28	6.03	3867	14269	107	243	10	695	2	14	27106.6	96056.6	739.658	1622.8	131.658	733.493	5.904	6.417	3.906	324.7
29	5.95	1513	15274	208	204	10	695	2	14	10569.1	103117	1449.22	1348.81	50.262	770.957	11.327	12.835	3.179	298.6
30	6.03	4979	13894	82	268	10	695	2	14	34918.8	93422.2	564.025	1798.43	170.930	718.966	4.638	5.034	4.362	336.1
31	6.03	7201	12407	42	307	10	695	2	14	50529.1	82975.5	283.013	2072.42	253.589	654.693	2.334	2.590	5.154	358.3
32	5.95	9722	10998	22	358	10	695	2	14	68239.9	73076.8	142.506	2430.71	354.554	596.929	1.217	1.350	6.258	394.0
33	6.03	5554	13156	62	282	10	695	2	14	38958.4	88237.5	423.519	1896.78	191.332	681.298	3.418	3.874	4.616	340.1