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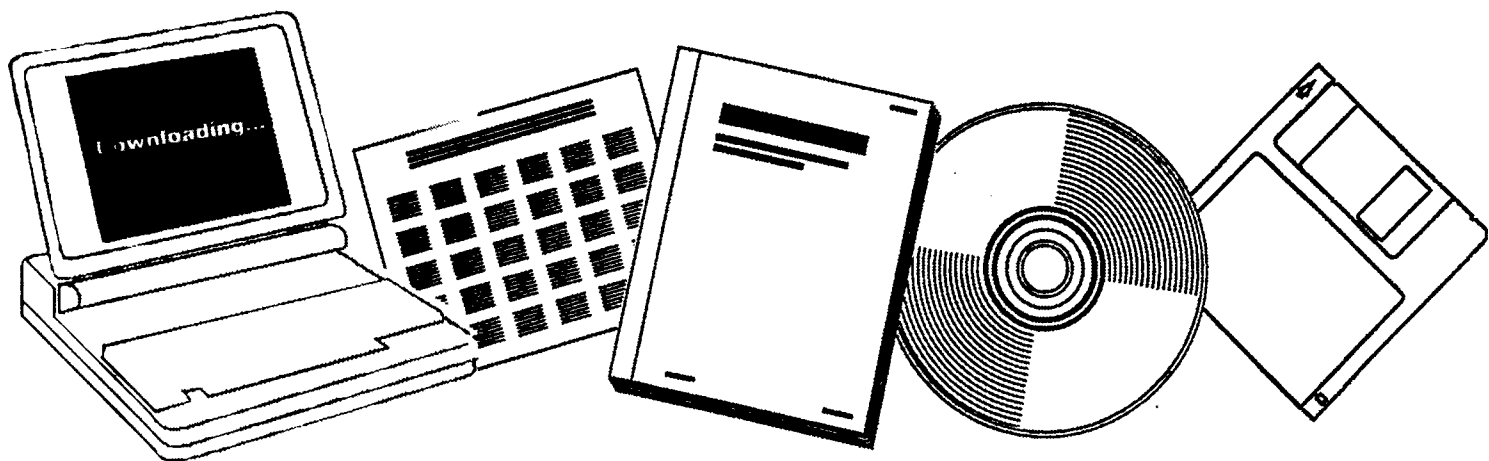
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**FUNDAMENTAL CHARACTERIZATION OF ALTERNATE
FUEL EFFECTS IN CONTINUOUS COMBUSTION
SYSTEMS. SUMMARY TECHNICAL PROGRESS
REPORT, AUGUST 15, 1978-JANUARY 31, 1980**

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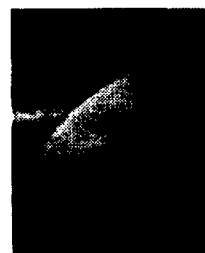
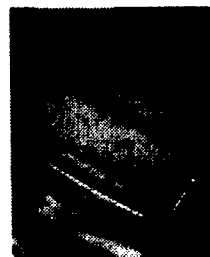
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FUNDAMENTAL CHARACTERIZATION OF ALTERNATE FUEL
EFFECTS IN CONTINUOUS COMBUSTION SYSTEMS

SUMMARY TECHNICAL PROGRESS REPORT

FOR PERIOD AUGUST 15, 1978-JANUARY 31, 1980

by

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FOREWORD

With increased emphasis on the utilization of U.S. energy resources for national self-reliance, alternative (synthetic) fuels are expected to play a major role in future energy developments. Future electric power generation with combined cycle gas turbines can make a major contribution to national energy goals if these systems could be made to accept synthetic liquid fuels having minimum upgrading. Development of such fuel-flexible gas turbines will encourage the utilization of synthetic fuels as they enter the marketplace, have major impact on future conservation of petroleum supplies, and reduce the cost of power production.

Characteristics of the basic feedstocks from which future liquid fuels for gas turbines will be made are significantly different from typical petroleum properties. Liquid synfuels, especially those derived from coal, are likely to be more aromatic and have low hydrogen content. In the combustion system, these characteristics can be expected to promote the formation of soot. This can result in decreased combustor life due to enhanced flame radiation, increased smoke or visibility of the exhaust plume, increased emission of particulate material, and increased deposit forming tendency. Consequently, it is imperative that the process of soot formation within the combustion system be controlled.

Another significant difference between conventional petroleum and synthetic fuels is nitrogen content. Organically-bound nitrogen is effectively converted to NO_x ¹ in conventional combustion systems. NO_x is also formed thermally by fixation of N_2 and O_2 from the air which participates in the combustion process but, for high nitrogen fuels such as synthetics with minimum upgrading, the NO_x due to fuel nitrogen is usually the dominant contribution. While existing stationary gas turbine standards make some allowance for fuel NO_x contributions, conventional combustors would not be capable of meeting the limitations if high nitrogen synthetic fuels are employed. The extent of fuel nitrogen conversion to NO_x must be reduced.

This program addresses the combustion community's need to better understand fuel related combustion variations: A multi-year effort is being conducted to satisfy two primary objectives: a) to provide an improved understanding of the relationships between fuel properties and combustion characteristics and b) to develop analytical modeling/correlation capabilities for the prediction of fuel effects. The work is limited to investigation of alternate liquid fuels used in continuous combustion systems, with gas turbine systems receiving special attention.

The program philosophy is to relate fundamental combustion phenomena to fuel characteristics using analytical models developed with and eventually verified by data obtained in carefully designed experiments. This approach is illustrated schematically on the next page. The model can be envisioned as a combination of chemical and fuel related elements, thermodynamic and heat transfer elements, and gas phase elements.

¹ NO_x is the general symbol which represents the sum of NO and NO_2 emission from a source.

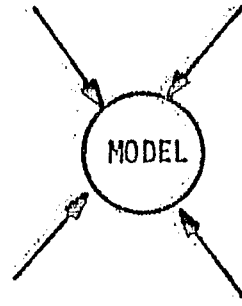
Schematic Representation of a Combustor Model

CHEMICAL AND FUEL RELATED ELEMENTS

- * Fuel Vaporization and Spray Dynamics
- * Fuel Pyrolysis
- * Soot Formation
- * Bound N \rightarrow NO_x Conversion
- * H₂ and CO Oxidation
- * Soot Oxidation
- * Aerodynamic/Chemical Interactions

THERMODYNAMIC AND HEAT TRANSFER ELEMENTS

- o Conduction
- o Convection
- * Radiation
- o Turbulence Effects
- o Energy Balance and Temperature Determination



GAS PHASE ELEMENTS

- o Mass and Species Conservation
- o Momentum Conservation
- o Energy Conservation
- o Species Diffusion
- o Turbulence Model

SOLUTION SCHEME

- o Simplification of Equations
- o Solution Procedure
- o Criteria for Solution Acceptance

A solution scheme provides the mathematical procedures for solving the many complex mathematical relationships. The subject program focuses on the fuel related elements appearing in the upper left portion of the schematic but includes devoting sufficient attention to other elements to result in the development of a successful model. The program proceeds along two parallel, strongly-interactive paths involving both modeling and experimental tasks. ER&E is responsible for overall program direction and experimentation, while Science Applications, Inc. (SAI) is responsible for analytical modeling under subcontract to ER&E.

These results will allow engine designers to better understand fuel effects in existing systems and will provide a vital tool necessary for the future development of fuel flexible systems. Four key goals of the DOE Principal Alternate Fuels Planning Network will be pursued in this program:

- Quantify engineering chemical kinetics of alternative fuels
- Develop combustion models for alternative fuels
- Characterize and quantify emissions from alternative fuels
- Evaluate combustion performance of alternative fuels

While the primary thrust in this program is towards the gas turbine application, many direct contributions will be made to alternate fuel usage in other applications such as spark ignition and diesel engines. Specific contributions will include improved understanding of soot formation/oxidation chemistry and information regarding fuel nitrogen-to-NO_x conversion.

The first major report on this program (1) was written to account for the period August 15, 1977 to September 30, 1978. This report covers the period October 1, 1978 to January 31, 1980. During much of this time period the contract was officially in a hiatus period during which negotiations for contract renewal took place. However, the work effort continued at both Exxon and SAI, albeit on a much lower level of effort than had been planned. Despite these developments, the work performed was quite successful and this second major report contains much valuable information.

The report is organized into three parts.

Part A: Experimental Program Progress

Part B: Analytical Program Progress

Part C: Technical Papers During Reporting Period

The Principal Investigator wishes to acknowledge the efforts of Messrs. R. W. Schroeder and R. J. Kuriskin who have obtained the experimental results described. Their skills and dedication have been essential to this development. The efforts of D. C. Rigano in developing data reduction procedures and in supervising the operation of the Liquid Fuel Jet Stirred Combustor are also appreciated.

ABSTRACT

The overall objective of this contract is to assist in the development of fuel-flexible combustion systems for gas turbines as well as Rankine and Stirling cycle engines. The primary emphasis of the program is on liquid hydrocarbons produced from non-petroleum resources. Fuel-flexible combustion systems will provide for more rapid transition of these alternative fuels into important future energy utilization centers (especially utility power generation with the combined cycle gas turbine). The specific technical objectives of the program are: a) develop an improved understanding of relationships between alternative fuel properties and continuous combustion system effects, and b) provide analytical modeling/correlation capabilities to be used as design aids for development of fuel-tolerant combustion systems. This is the second major report of the program. Key experimental findings during this reporting period concern stirred combustor soot production during operation at controlled temperature conditions, soot production as a function of combustor residence time, an improved measurement technique for total hydrocarbons and initial stirred combustor results of fuel nitrogen conversion. While the results to be presented concern a stirred combustor which utilizes premixed fuel vapor/oxidant mixtures, a new combustor which combusts liquid fuel injected into the reactor as a spray has been developed and will be described. Analytical program progress includes the development of new quasiglobal models of soot formation and assessment of needs for other submodel development.

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PART C - TECHNICAL PAPERS DURING REPORTING PERIOD

"Fundamental Characterization of Alternative Fuel Effects in Continuous Combustion Systems," Edelman, R. B., Turan, A., Harsha, P. T., Wong, E., and Blazowski, W. S.

"The Interrelationship between Soot and Fuel NO_x Control in Gas Turbine Combustors," Blazowski, W. S., Sarofim, A. F., and Keck, J. C.

"Dependence of Soot Production on Fuel Blend Characteristics and Combustion Conditions," Blazowski, W. S.

"Dependence of Soot Production on Fuel Structure in Backmixed Conditions, Blazowski, W. S.

PART A: EXPERIMENTAL PROGRAM PROGRESS

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1. INTRODUCTION

Experimental work during the first year of this program focused on soot production in highly backmixed combustion (1). The experimental device used was the Jet Stirred Combustor. This device is designed to provide a combustion volume in which temperature and composition are uniform throughout the reactor. It "backmixes" thoroughly the combustion products with the incoming fresh fuel-air mixture. Results included an evaluation of the fuel-rich combustion and soot formation characteristics of a number of pure hydrocarbons. In all cases a premixed fuel vapor/air mixture was injected into the reactor. Groups of the hydrocarbons tested were found to behave similarly and three categories of hydrocarbons were defined. The groupings were as follows:

<u>Group 1</u>	<u>Group 2</u>	<u>Group 3</u>
Ethylene	Toluene	1-methyl-naphthalene
Hexane	O-xylene	
Cyclohexane	N-xylene	
N-octane	P-xylene	
Iso-octane	Cumene	
1-octene	Tetralin	
Cyclo-octane	Dicyclopentadiene	
Decalin		

The first group produced large amounts of exhaust total hydrocarbons without sooting and in no case was significant (i.e., measurable at the mg/l level) soot observed. Many percent THC* could be detected at mixture ratios below that at which soot appeared.

The second group produced measurable soot. For these fuels, the leanest mixture ratio at which soot is observed (the incipient soot limit) was found to correspond to the conditions at which significant concentrations of exhaust hydrocarbons were first detected (hydrocarbon breakthrough). In these cases, the measured hydrocarbon concentration was less than one percent at the incipient sooting limit.

Another commonality in the second group is that the incipient soot limit of these fuels occurred at an equivalence ratio of about 1.4 and the amount of soot produced as fuel-air mixture ratio was increased beyond the incipient sooting limit was similar (within a factor of two) for all fuels in this group. 1-methyl-naphthalene was significantly different in this respect producing much higher soot quantities than those in the second category and having an even lower soot formation equivalence ratio. Consequently, this double-ring aromatic represents a third soot formation category.

Blends of iso-octane and toluene were tested to determine the behavior of a two-component mixture with Group 1 and Group 2 hydrocarbons. Mixtures with 50 or more percent toluene produced soot while a 25% toluene blend did not. Clearly, for the mixtures which did soot, increases in the volume percent toluene result in increased soot production at all equivalence ratios.

* THC = Total hydrocarbons present in the exhaust products; expressed in volumetric concentration as if their composition was entirely methane.

It was also determined that with less toluene in the blend, the concentration of hydrocarbons at the incipient limit tended to be low for the highly sooting blends but increased sharply for those blends which did not soot. For example, with 50% toluene, the THC concentration was 2.4% at the incipient soot limit, while with 100% toluene this value was 0.2%. These results indicate a combination of Group 1 and 2 behaviors and imply that a combination of the analytical descriptions for toluene and iso-octane might be a reasonable approach for prediction of the sooting characteristics of such fuel blends.

Experimental efforts since the last major report (Sept. 30, 1978) have been in five areas:

- Soot production results were obtained at variable equivalence ratio but constant temperature using the Jet Stirred Combustor. This was done by varying the O₂/N₂ ratio of the oxidant. Previous results were not acquired at controlled temperatures; data was taken at whatever temperature resulted from combustion with air. The new results will be used to develop quasiglobal soot formation expressions.
- A study of the effect of residence time on soot production was made. These results also provide information for quasiglobal models. In addition, they highlight the controlling influence of THC breakthrough in backmixed combustor soot formation.
- A procedure was developed to extend the range of the total hydrocarbon analyzer to 10% (as methane). It was learned earlier that the analyzer response was non-linear above concentrations of about 2%, causing an underestimation of hydrocarbon concentrations in some runs.
- A stirred combustor system which accepts a liquid fuel spray was constructed and commissioned. This device will allow future study of the effects of inhomogeneity present during spray combustion. The new unit is described in Section 3.
- Initial Jet Stirred Combustor results of fuel nitrogen conversion were acquired. The findings are very interesting and provide results to which proposed models can be compared and tested.

The balance of the experimental portion of this report (Part A) provides a definition of the experiments conducted, description of the new Liquid Fuel Jet Stirred Combustor, summary of results, and discussion of experimental findings.

2. EXPERIMENTAL DESCRIPTION

Selection of the experimental method to be used in an investigation of soot formation or fuel nitrogen conversion is strongly influenced by study objectives. The desire here is to develop an engineering model for continuous combustion systems, specifically gas turbine combustors. In such devices, the combustion process is stabilized by some region where combustion products are backmixed with the incoming fuel-air mixture. This is accomplished by air swirl, a flameholder, or an air injection pattern arranged to entrain combustion products. The backmixed "primary zone" is operated at a stoichiometric or fuel-rich mixture ratio to provide high temperatures which further enhance stability and facilitate ignition. The processes of soot formation and fuel nitrogen conversion to fixed nitrogen intermediates are usually limited to this zone.

The predominance of soot formation research has involved laminar premixed flames or diffusion flames. Soot formation in laminar premixed flames occurs in a region having fuel and oxygen concentration and temperature profiles unique to this combustion process. The temperature and species concentration histories are much different than those occurring during combustion in a practical system. The fact that soot formation in backmixed combustion is not represented by the laminar premixed flame was demonstrated by Wright (2). Incipient soot formation limits were found to occur at higher mixture ratios in the backmixed combustor. Soot formation in laminar diffusion flames also occurs in a unique fashion. The physical separation of fuel from the oxygen causes fuel pyrolysis and soot formation to occur in the absence of oxygen. This situation could not occur within the turbulently-mixed primary zone of a practical combustion system.

The behavior of fuel nitrogen is also dependent upon temperature and species concentration histories. Objections to the characteristics of laminar premixed flames and diffusion flame experiments must also be raised for fuel nitrogen investigations which address the gas turbine-type combustion process.

A study of soot formation and fuel nitrogen behavior which intends to simulate the mixing characteristics (or the temperature/concentration histories) of a turbine-type combustion system should utilize a backmixed combustion experiment. Further, use of the backmixed combustion experiment usually requires assuming the reactor is homogeneous in both temperature and species concentration; each operating condition is characterized by a single set of temperature and concentration data rather than profiles of these parameters. This is an essential advantage in this study to develop simplified or "engineering chemistry" submodels involving quasi-global steps for soot formation and fuel nitrogen conversion. It would be a fatal disadvantage if our objective were to evaluate the elemental reactions important to these processes; such studies must resort to the laminar premixed and diffusion flames where extraction of detailed information is possible.

2.1 The Jet Stirred Combustor

The experimental effort during the past year concerned a Jet Stirred Combustor similar to that previously used by Wright (2) and identical

to that used in the first year of this program (1). The device used was a modification of the Longwell-Weiss reactor (3) with hemispherical geometry. The reaction zone was 5.08 cm in diameter and had 25 radial exhaust ports of 3.2 mm diameter. Combustion experiments were conducted at atmospheric pressure with a range of residence time of 2.0 to 6.0 ms. Fuel and air were metered separately, preheated to the desired inlet temperature prior to injection (liquid fuels are prevaporized), and injected into the reactor zone through forty small holes or sonic jets which stir the reactor contents and produce a mixture of essentially uniform temperature and composition.

Measured quantities included gaseous species concentrations (CO , CO_2 , THC , H_2 , O_2), the incipient soot equivalence ratio, and soot production (mg/l). During the past year improvements to the THC measurement technique have been made and the capability to determine HCN and NH_3 was added. These developments are discussed in Sections 2.2 and 2.3. Two other minor changes to the gas analysis system have been made since the last reporting. First, a new NDIR analyzer for CO was acquired with ranges of 0-10, 0-20 and 0-100%. Previously the maximum range was 0-10%. Secondly, a gas chromatograph was added to determine H_2 . The Carle Model 8706-A utilizes a three-column separation technique employing silica gel and molecular sieves.

The fact that fuel enters the combustion volume as a gas represents a major difference between the JSC and practical systems in which the fuel enters as a spray. Because this difference is expected to influence the applicability of the current results to practical systems, a stirred combustor allowing fuels to be introduced as a spray was built. The Liquid Fuel Jet Stirred Combustor (LFJSC) is described in Section 3. Another difference which detracts from the direct applicability of these results is operation of the current JSC at atmospheric pressure only. A new combustor is being designed for testing during 1980 which will span the pressure range from 0.1 to 4 atmospheres.

2.2 THC Measurement Improvements

During the past year a substantial nonlinearity in our flame ionization measurement of total hydrocarbons was found. At hydrocarbon concentrations greater than 2 volume percent (as CH_4) the flame ionization detector would saturate and further increases in THC would receive less than a proportional increase in instrument response. Consequently, measurements of THC quantities over 2% would be undervalued. Because of this, the modification to our THC measurement technique described below was made and data in question was retaken.

The total hydrocarbon measurement is done with a Beckman Model 402 Heated Flame Ionization Detector (FID). The principle employed here is to inject a small quantity of sample into a hydrogen flame positioned within an electric field. The amount of sample injected is controlled by an orifice and regulated upstream sample pressure. The hydrocarbons present in the sample undergo a chemi-ionization reaction resulting in $\text{CHO}^+ + e^-$. Since the electrons are much more mobile than the positive ions, a net current proportional to the THC concentration is measured across the electric field. However, if the amount of hydrocarbons entering the flame is too large the hydrocarbons will not be able to react within the flame and the instrument response to THC will become non-linear.

The solution to the nonlinearity problem is to either reduce the sample flow to the hydrogen flame to assure linear operation at higher THC concentration, or to dilute the sample flow in a controlled manner so that the H₂ flame always sees less than 2% THC. Flow reduction by substituting a smaller orifice would be much easier and, in fact, the desired method if a clean combustion experiment were being considered. But in our situation where soot production is high and some tar-like hydrocarbons might be present, a smaller flow restriction would be inadvisable. So we have constructed a dilution scheme for our hydrocarbon measurement.

The schematic of the dilution scheme is shown in Figure 1. Most of the modifications have been made within our existing sample conditioning oven which is held at 150°C. After the sample is pressurized by the metal bellows pump it passes through a three-way valve, to a metering valve used to control sample pressure, and through a metering orifice. Sample pressure is adjusted to 30 kPa just upstream of the orifice. Since the pressure downstream of the orifice is controlled by a regulator within the FID (at about 14 kPa) this procedure assures a constant flow of sample through the system. The flow of the N₂ diluent introduced at this point is held constant using the same control technique; pressure before a metering orifice is automatically controlled and the FID regulated pressure is experienced downstream of the orifice. The N₂ is heated to oven temperature as it passes through a coil before mixing with the sample, thus avoiding the possibility of water or hydrocarbon condensation during mixing. Since the volumetric flows of sample and N₂ are held constant, a constant, repeatable dilution results.

The system is calibrated with a C₂H₄/N₂ mixture prepared on-line with metered quantities of C₂H₄ and N₂. This mixture is preheated in a coil within the oven as was the N₂, and can be selected to enter the balance of the measurement train instead of the sample by turning the three-way valve. This measurement scheme has allowed us to extend the linear range of the FID to ten volume percent (as methane).

2.3 HCN and NH₃ Measurements

Experiments concerning the fate of fuel nitrogen during combustion must be concerned with total fixed nitrogen, TFN = NO + NO₂ + HCN + NH₃. Large quantities of HCN and NH₃ can be produced in the first stage of the rich-lean combustors now being considered for control of fuel NO_x. These species are likely to be oxidized to NO in the fuel-lean second stage. Consequently, the first stage must minimize production of total fixed nitrogen (NO + HCN + NH₃) if high overall conversion of fuel nitrogen to NO_x is to be avoided.

NO is determined using a chemiluminescent instrument (TECO Model 10A) as discussed in previous reports. In this technique, sample gas enters a chamber where the NO reacts with O₃ produced within the instrument and fed to the chamber. The NO and O₃ produce an activated NO₂ which emits light of a characteristic frequency upon decay. The amount of light produced is proportional to the amount of NO present and, since the sample inflow is held constant, the light intensity is proportional to the concentration of NO in the sample. NO₂ is usually determined using the same procedure, but after the sample has been passed through a stainless steel tube at about 900°C which converts NO₂

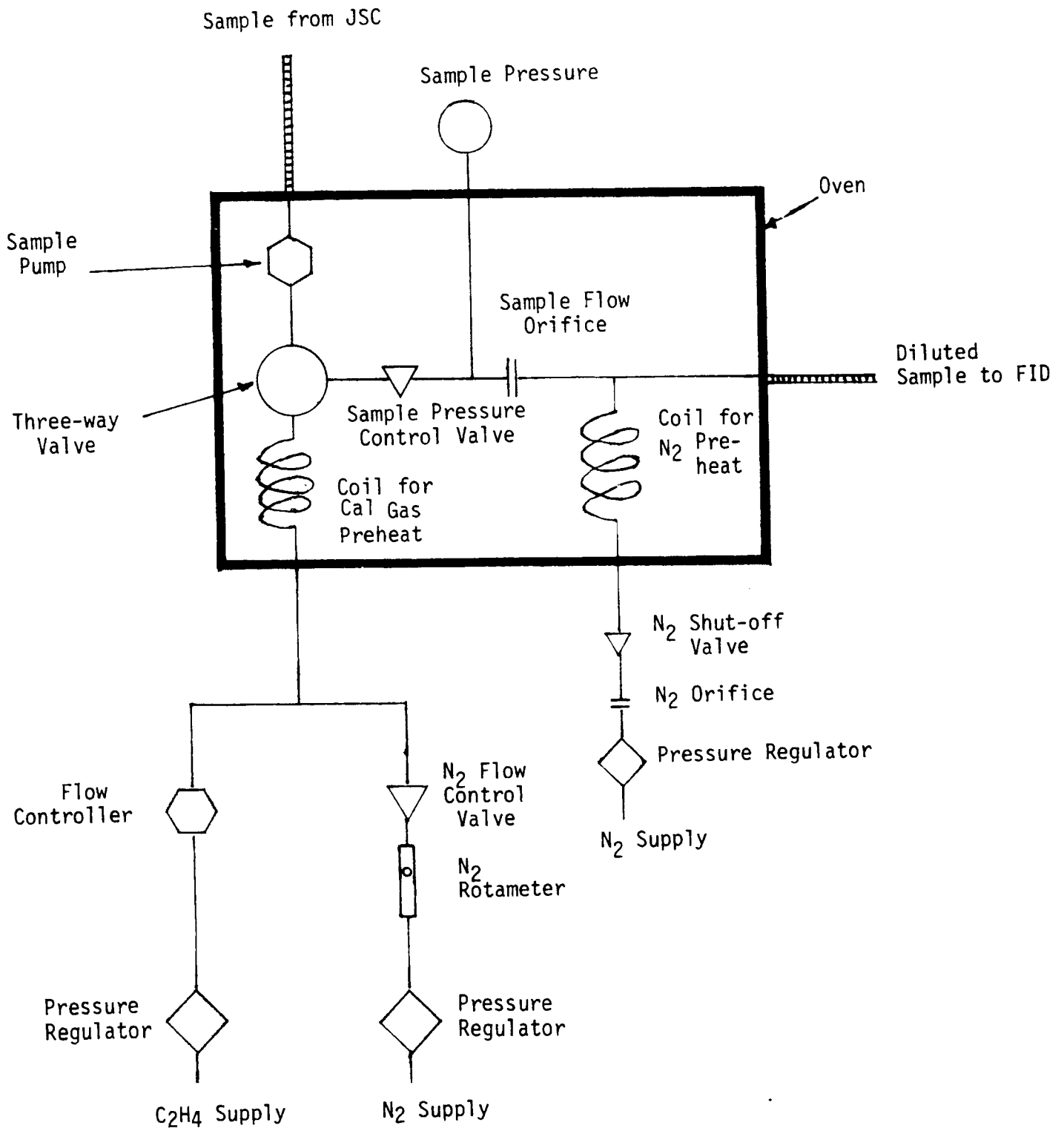


Figure 1: Schematic of Hydrocarbon Measurement Dilution Scheme

to NO. This allows $\text{NO}_x = \text{NO} + \text{NO}_2$ to be determined, NO_2 is then calculated as the difference between the two measurements. However, under fuel-rich operating conditions the NO_x measurement (and hence the implied NO_2 determination) is not valid because NO is reduced within the converter when substantial amounts of hydrocarbons are present. Consequently, under the fuel-rich conditions of interest in fuel-bound nitrogen investigations, only the NO measurement can be made. Fortunately, NO_2 is not likely to be produced at these fuel-rich operating conditions and the lack of a measurement is probably not a serious drawback.

HCN and NH_3 were determined using scrubbers and selective ion electrode analysis. Two sets of scrubbers were used in parallel, one set for HCN and one set for NH_3 . Each set consisted of two scrubbers in series, with the exhaust from the last scrubber passing through a rotameter-meter/valve combination, thence to an exhaust. The scrubbers consisted of Pyrex graduated cylinders (100 ml) fitted with sparge tubes and connecting fittings which were washed down with scrubbing solution into the appropriate scrubber. The solution volume in each scrubber was then brought to 100 ml by adding fresh solution. Scrubbing for NH_3 was done in 0.2% H_2SO_4 while that for HCN was done in 0.5 M NaOH.

Analysis for HCN was performed with an Orion model 94-06A electrode for CN^- and an Orion model 90-01 reference electrode. Analysis for NH_3 was performed with an Orion model 95-10-00 gas-sensing ammonia electrode. Both analyses used an Orion model 801A digital pH meter.

3.0 LIQUID FUEL JET STIRRED COMBUSTOR

As previously noted, prevaporizing the fuel and premixing it with the air, as has been done in all our previous JSC testing, represents a significant departure from practical continuous combustion systems. In the latter case, the fuel is usually injected as a liquid spray and the combustion process involves a great deal of unmixedness which significantly influences the sooting and fuel nitrogen conversion processes.

Our previous and continuing use of the JSC is necessary because it represents an idealized process which can be analyzed. It gives us a much better vehicle to unravel the key chemical processes without immediately encountering the complexities of unmixedness. Indeed, our success in identifying the importance of THC and the groupings of hydrocarbon fuel types may not have occurred without this useful tool.

Nevertheless, since our program intends to develop an engineering model in the short term, we must also look at the spray combustion process using an experimental system which is as well-characterized as possible. For this reason, our future studies will include investigations in the Liquid Fuel Jet Stirred Combustor (LFJSC) built this past year. The unit has a spherical stirred zone of 5.1 cm diameter into which fuel spray is injected followed by a turbulent plug flow section having a residence time roughly one-half that of the stirred zone. The two air atomizing spray nozzles can be removed and characterized in terms of droplet size distribution using a Malvern Spray Droplet Analyzer available to this program. A number of nozzle configurations can be utilized to vary spray characteristics. In this way the influence of spray parameters on the important findings uncovered using the vapor-fuel-fed JSC can be evaluated.

The LFJSC was constructed at Exxon expense during January-March of 1979. It has been operating since producing results for another government-sponsored program, Carbon Slurry Combustion (Air Force Aero Propulsion Laboratory Contract F33615-C-78-2025). Its future use in the subject DOE program will benefit greatly from the learning experiences of this past year.

While the LFJSC meets our needs to examine spray combustion, it is likely to create other problems. Most importantly, its undefined level of unmixedness may cause difficulties in fundamental interpretation of the data. The JSC was developed over an extended period of time to minimize unmixedness. Various tests over the years have implied (but not proven) that when operated at design conditions the reactor is very close to being perfectly stirred. Because of the design features necessary for introducing a liquid spray the LFJSC is not likely to be as well mixed and this may influence our ability to evaluate the results.

3.1 LFJSC Design

The LFJSC is composed of two sections, a spherical reactor and a cylindrical one (see Figures 2 and 3). The spherical portion of the LFJSC consists of two castable refractory halves housed within a 15.2 cm diameter metal shell. The refractory material is Castable 141A, a product of Combustion Engineering Refractories, capable of withstanding temperatures of up to 1870°C. Each section is cast separately with a 5.1 cm diameter hemispherical volume--the two sections together create the spherical reactor zone. The cylindrical plug-flow section is composed of a 7.6 cm long by 2.2 cm diameter alumina tube. Residence times of 2.4 to 6.0 and 1.6 to 4.0 msec can be

FIGURE 2

LIQUID FUEL JET STIRRED COMBUSTOR

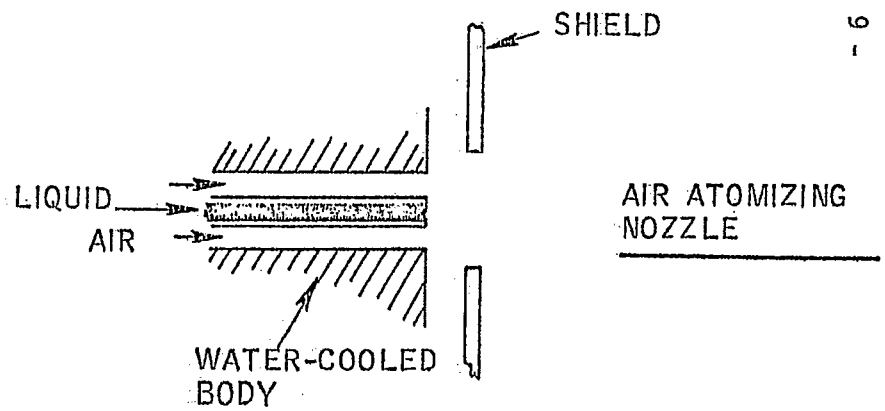
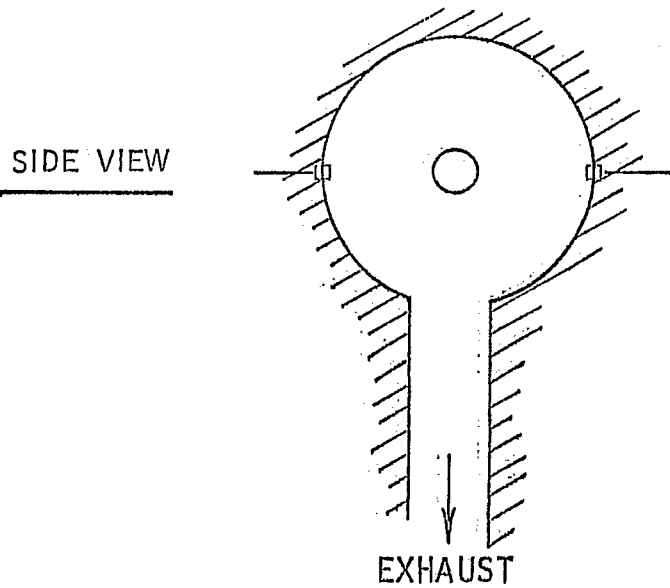
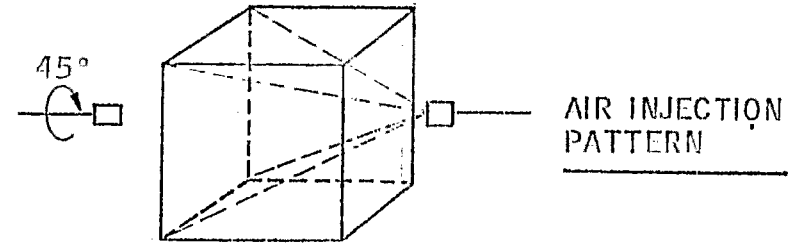
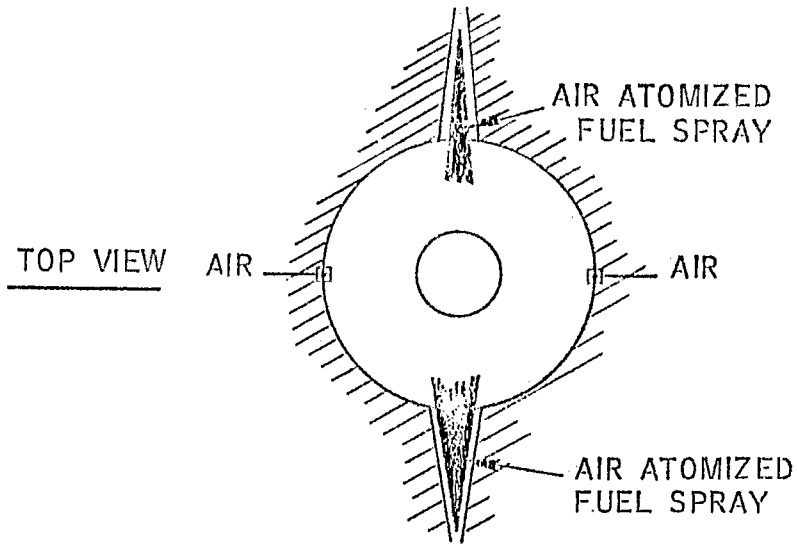
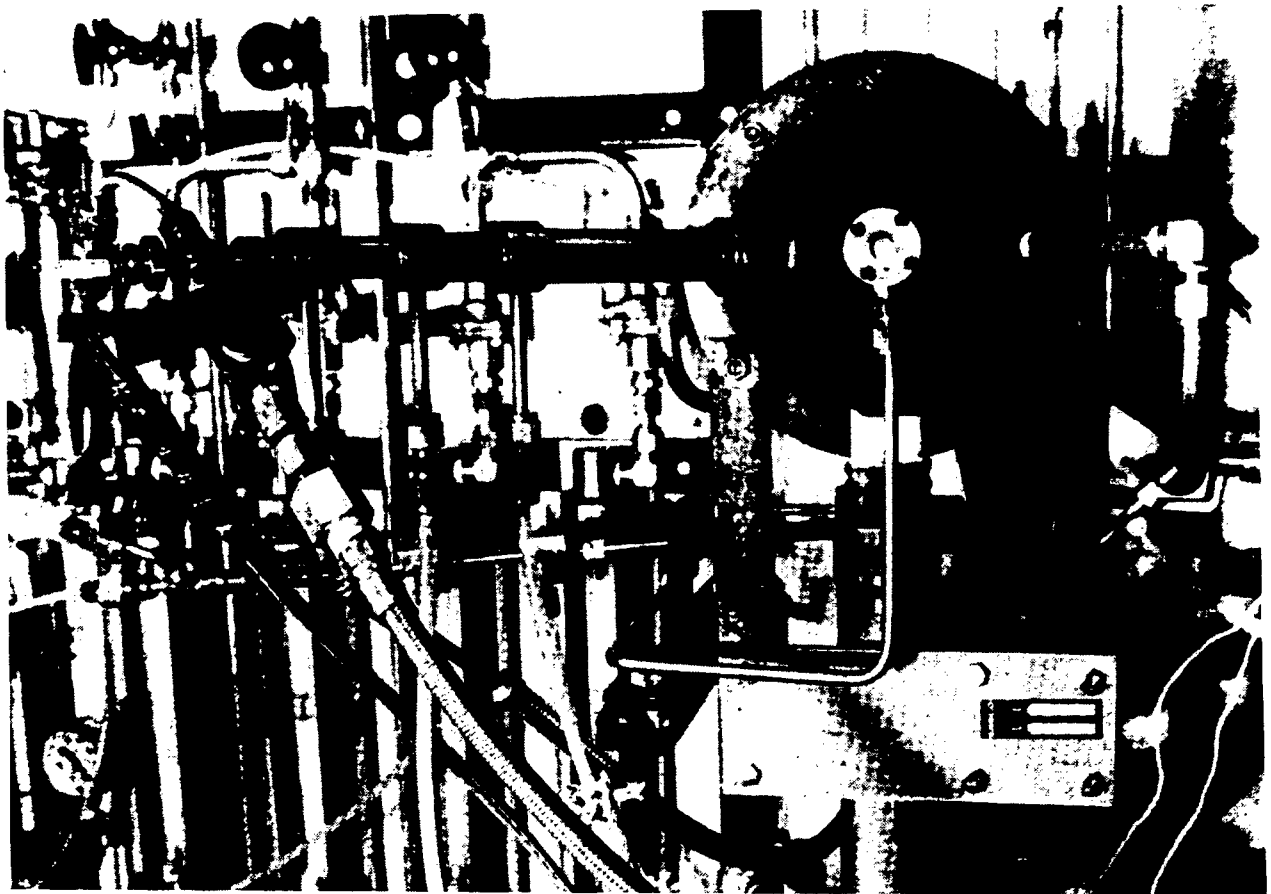


FIGURE 3
FRONT VIEW OF LIQUID FUEL JET STIRRED COMBUSTOR



achieved in the stirred and plug-flow sections. Scale-down or scale-up could allow expansion of these residence time ranges. Each of the following aspects of the facility will be discussed.

- Air Injection
- Fuel Injection
- Metering of Fuels and Air
- Oxygen Injection to Boost Temperature
- Exhaust System
- Temperature Measurement/Sight Port

Combustion air enters the spherical reaction zone through two air jets positioned 180° apart. Four air jets entering the reactor at each side (total of eight) are aimed towards the corners of a cube imagined to sit within the spherical reactor. See Figure 2. One set of air jets is rotated 45° with respect to the other to allow the opposing jets to mesh rather than collide. This approach provides for highly turbulent mixing and simulates the recirculating characteristics of gas turbine systems.*

Fuel enters the reactor at two positions 90° from each air jet. The fuel nozzle assemblies consist of 1/4J bodies, 0.030 cm fuel caps (Model 1250) and pressurizing air atomizing caps (Model 67147) all acquired from Spray Systems Co. This pressurizing cap provides for premixing of the fuel with the atomizing gas (air or nitrogen) prior to exiting the nozzle tip. Alternatively, a siphon air injection system can be used in which atomization takes place immediately downstream of the nozzle by shearing forces between the fuel and atomizing air. Schematic diagrams of the two nozzle types are shown in Figure 4. Metering of the combustion air, atomizing gases and liquid fuels is accomplished using calibrated rotameters.

The combustion products exit the well-stirred zone and enter the plug-flow region. A small sample of the exhaust gas is obtained by inserting a probe through the sample port at the base of this section. The remainder of the exhaust stream passes through a water cooled heat exchanger. Additional cooling is achieved by introducing into the exhaust stream a fine water mist produced by an atomizing nozzle. If, for any reason, the exhaust temperature is not reduced to below 200°C an audible alarm is sounded. The combustor will automatically be shut down if corrective action is not taken within 30 seconds.

Oxygen can be utilized to increase the combustion temperature at a given equivalence ratio. Its addition to the combustion air reduces the nitrogen content, which is a flame temperature diluent. The oxygen flow rate is determined using a calibrated rotameter and the flow is introduced to the air stream prior to its metering. This provides for a uniform air/O₂ mixture entering the reactor.

Temperature within the reactor is measured by utilizing a platinum-6% rhodium/platinum-30% rhodium thermocouple which enters the combustor through the ignition port. Addition of thermocouples in

* This reactor concept borrows from previous designs by Prof. R. Essenhigh (Ohio State) and A. Putnam (Battelle Columbus Laboratories). The Principal Investigator acknowledges their contribution to this development through discussions during late 1978.

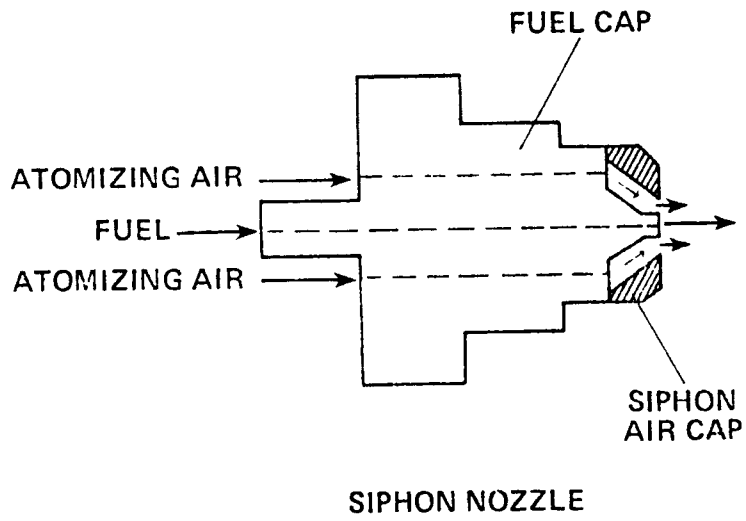
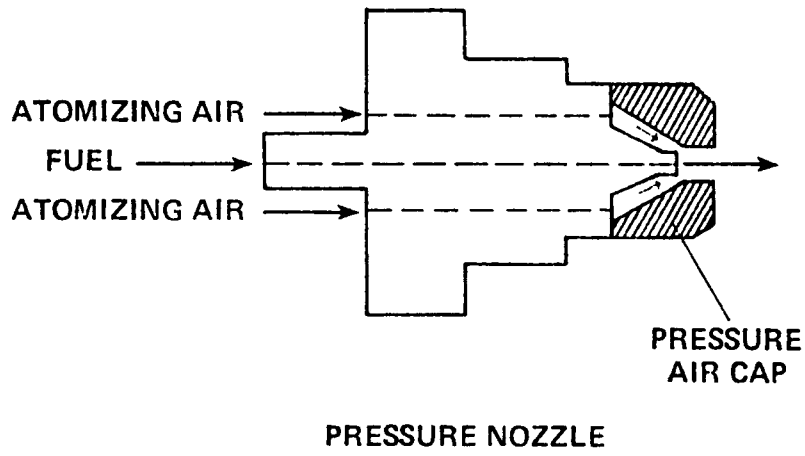


Figure 4: Fuel Nozzles

several key locations (inside the refractory and on the outer shell) is planned for the future. These will enable the refractory temperature gradient and heat losses to be calculated. A nitrogen-cooled sight port, positioned in the front of the reactor, provides optical access to the reactor interior and could also be used to determine temperature by pyrometry.

3.2 Combustion Product Sampling

A 30.5 cm long by 0.24 cm internal diameter sample probe will be used for obtaining gaseous emissions and soot measurements. Special care has been taken to prevent condensation of water or unburned hydrocarbons within the probe and sample lines. The sampling probe is hot-water cooled and sample transfer is accomplished using electrically heated sample lines. All sample conditioning (pumping, filtering, and valving) is accomplished within a Blue-M Model OV-18A oven maintained at 150°C. Valves have been selected which are rated for operation at temperatures up to at least 175°C and design characteristics are such that lubricated valve components are sealed from the gas path. The pump is a high temperature metal bellows type (Model MD-158 HT) driven by a 1/4 horsepower motor external to the oven. Gas analysis and particulate measurement are identical to that used with the JSC.

3.3 Operating Procedure and Data Reduction

The LFJSC has the capability of operating on gaseous, liquid or slurry fuels. A gaseous fuel, such as ethylene, is utilized for daily start-up of the reactor and is fed through the front nozzle. It is ignited by a flame from a small propane torch which enters the combustor through the ignition port. Liquid fuel and atomizing gas (air or nitrogen) are first introduced into the combustor through the rear fuel nozzle and then, once the ethylene flow is shut off, through the front nozzle.

A data reduction computer program was developed to convert measured gas analysis concentrations to wet values, calculate soot production and overall combustion efficiency, determine equivalence ratio, and perform redundant material balances to check the consistency of measured results. The program is similar to that developed for the JSC and discussed previously (Reference 1).

4. RESULTS

4.1 Soot Formation

The experimental program has concentrated on acquiring soot formation data at constant equivalence ratio and variable temperature. The data were acquired by adjusting O₂/N₂ ratios in the reactants--previous results had been acquired using air as the oxidant with each equivalence ratio producing a single operating temperature. Because of the need to monitor temperature and adjust O₂/N₂ ratio during the experiment, these data are difficult to obtain and very time consuming to acquire.

Following our previously-reported work in which hydrocarbons were categorized into three groups defining various soot formation characteristics, the following data have been acquired.

<u>Fuel</u>	<u>Equivalence Ratio</u>	<u>Temperature</u>
Iso-octane (representing Group 1)	1.0-1.7	1700
		1800
		1900
		2000
Toluene (representing Group 2)	1.0-1.8	1700
		1800
		1900
		2000
Methyl-Naphthalene (representing Group 3)	1.0-1.8	1900
		2000

These results are a large part of the basis from which we will develop quasiglobal soot formation models.

The effect of residence time on toluene soot production was also evaluated. These results were acquired at equivalence ratios of 1.4, 1.6 and 1.8 and again reactor temperature was held constant (at 1900 K) by varying O₂/N₂ ratio. These data can be used in two ways. First, they confirm the importance of hydrocarbon breakthrough by illustrating the dependence of soot formation on THC at constant temperature--a change in the chemical mechanism of soot formation is not involved. Secondly, they allow the development of key rate information--keeping the temperature effect constant the residence time influence is examined separately.

The iso-octane constant residence time data do not include soot production results--this Group 1 fuel does not produce measurable quantities of soot in the JSC. The main utility of the data concerns the future development of quasiglobal models for fuel decomposition and partial oxidation. While these processes do not directly impact on the soot production, portions of the overall model, this predictive capability is necessary to calculate correct values of species concentration and reaction temperature which, in turn, influence the soot prediction for the other hydrocarbon groups. Of particular importance is the behavior of THC under fuel-rich operating conditions. These results are shown

in Table 1. As expected, increases in ϕ or decreases in temperature resulted in higher hydrocarbon concentrations in the exhaust.

Toluene constant residence time data are shown in Table 2 and Figure 5. The table shows the expected behavior that increases in ϕ or decreases in temperature result in higher exhaust hydrocarbon concentrations. The table also illustrates the impact of increased reactor temperature on the range of soot-free equivalence ratios. As reactor temperatures are increased higher equivalence ratios can be achieved without sooting. The figure shows that soot production at a given equivalence ratio decreases with increasing temperature. The main reason for decreased soot production with temperature is evident from examination of the hydrocarbon concentration data in Table 2. As temperature increases the THC present at any given equivalence ratio decreases. Since soot production depends strongly on hydrocarbon concentration for these Group 2 fuels, the increased temperature results in less soot production. An alternative explanation of these temperature trends might be enhanced soot oxidation with increasing temperature. However, soot oxidation is not considered to be very temperature sensitive at 1700-2000 K (see discussion of Nagle-Strickland Constable model in Reference 1) and then the hydrocarbon explanation is much more likely. In a more general sense, these results re-emphasize our previous statements that the behavior of THC is the key to prediction of soot production in highly backmixed systems. Our quasiglobal models will clearly recognize this important point.

TABLE 1: BEHAVIOR OF HYDROCARBON CONCENTRATION AT CONTROLLED TEMPERATURES
FOR ISO-OCTANE/N₂/O₂ COMBUSTION AT FUEL-RICH CONDITIONS

<u>Equivalence Ratio</u>	<u>Hydrocarbon Concentration (% as Methane)</u>			
	<u>T = 1700 K</u>	<u>1800 K</u>	<u>1900 K</u>	<u>2000 K</u>
1.0	.15	.008	.016	.0012
1.2	.34	.25	.14	.08
1.3	.575	.40	.40	.115
1.4	.68	.8	.7	.27
1.5	1.77	1.45	1.25	.8
1.6	2.0	1.5	1.77	1.0
1.7	--	2.0	--	1.55

TABLE 2: BEHAVIOR OF HYDROCARBON CONCENTRATION AND SOOT PRODUCTION AT CONTROLLED TEMPERATURES FOR TOLUENE/N₂/O₂ COMBUSTION AT FUEL-RICH CONDITIONS

Equivalence Ratio	Hydrocarbon Concentration (% as Methane)				Soot Production (mg/l)			
	T = 1700 K	1800 K	1900 K	2000 K	T = 1700 K	1800 K	1900 K	2000 K
1.0	.0018	.0035	.0022	.0008	0	0	0	0
1.2	.01	.01	.0032	.001	.004	0	0	0
1.3	.03	.024	.0135	.0008	.04	0	0	0
1.4	.27	.03	.02	.0025	.037	.032	0	0
1.5	.32	.13	.076	.018	.074	.027	.035	.021
1.6	1.1	.6	.21	.031	.062	.055	.004	.018
1.7	2.4	2.9	.37	.015	.25	.35	.108	.039
1.8	--	--	3.1	.24	.503	.53	.203	--

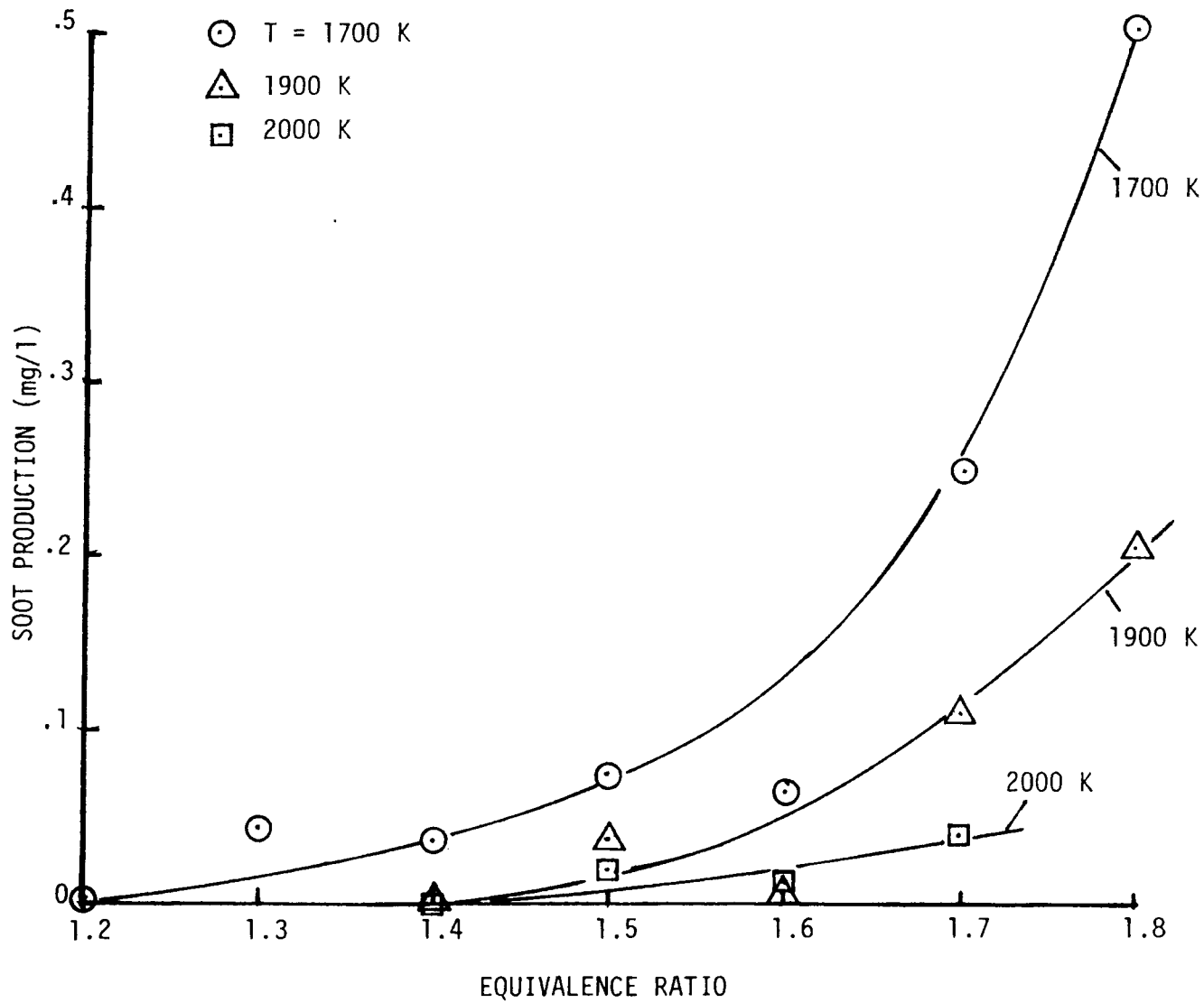


Figure 5: Dependence of Soot Production on Reactor Temperature for Toluene/N₂/O₂ Combustion

Methyl-naphthalene results are illustrated in Table 3. Again, the expected behavior that increases in ϕ or decreases in temperature result in higher exhaust hydrocarbon concentrations is observed. The temperature effect is so strong that soot forms only for $\phi = 1.6$ at 1900 K and $\phi = 1.8$ at 2000 K. The amount of soot produced is not much greater than in the case of toluene. This result is in conflict with earlier data (Reference 1), which suggested that methyl-naphthalene produced much more soot than toluene. The disagreement may be explained by a change in mechanism occurring as temperature is increased. As was noted in our first Annual Report (Reference 1), it has been postulated that two soot formation mechanisms are possible with Group 2 or 3 hydrocarbons: a direct condensation of aromatic rings or a ring fragmentation to smaller hydrocarbon fragments followed by "polymerization" which builds larger molecules. The condensation path is expected to be the much faster route; but, since the aromatic ring cannot survive above about 1800 K, this mechanism is not operative at high temperature. Therefore, in this case, only 1900 and 2000 K data are available and they may be entirely within a region where the ring condensation mechanism, which explained the excessive sooting of methyl-naphthalene, is not operative. Consequently, these results imply that above 1900 K, the Group 2/Group 3 distinction is not necessary.

The variable residence time results are shown in Figure 6 and Table 4. At a given equivalence ratio, soot emission increases as residence time is decreased. As expected, soot production is much greater at the higher equivalence ratio but the soot/residence time trend is similar at $\phi = 1.6$ and 1.8. The reason for the strong dependence on residence time is most likely the behavior of the THC within the reactor (see Table 4). At the shorter residence times, the hydrocarbons are not effectively consumed and the resulting high THC concentrations are responsible for greatly increasing soot production.

4.2 Fuel Nitrogen Conversion

Previous JSC studies of fuel nitrogen conversion (5) have shown that a high percentage (~80%) of fuel nitrogen is converted to NO_x under fuel-lean conditions but the amount of conversion at fuel-rich operation decreases sharply. While this observation is consistent with concepts involving rich/lean staged combustion, the fact that low conversion to NO_x is obtained at fuel-rich operation does not necessarily mean that low NO_x will be present after second stage combustion. HCN and NH_3 can be produced in large quantities in the first stage and if oxidized in the second stage, can result in high fuel nitrogen-to- NO_x conversion for the overall combustion system. Consequently, our new capability to determine HCN and NH_3 concentrations (Section 2.3) is necessary for thorough study of fuel nitrogen conversion.

Our experimental efforts have focused on acquiring information on fuel nitrogen behavior in the $\text{CH}_4/\text{NH}_3/\text{Air}$, $\text{C}_2\text{H}_4/\text{NH}_3/\text{Air}$, and Jet A/ $\text{C}_5\text{H}_5\text{N}/\text{Air}$ systems. NO , NH_3 , and HCN measurements were made over a range of equivalence ratios and the results give a perspective of the fuel nitrogen conversion process occurring during fuel-rich combustion in strongly backmixed systems.

Methane Results:

Table 5 illustrates the key results using methane as the fuel. These data were obtained with an inlet mixture temperature of 300°C, a residence time of 4 ms, and an inlet NH_3 concentration of 1300 ppmv

TABLE 3: BEHAVIOR OF HYDROCARBON CONCENTRATION AND SOOT PRODUCTION AT CONTROLLED TEMPERATURES FOR METHYL-NAPHTHALENE/N₂/O₂ COMBUSTION AT FUEL-RICH CONDITIONS

Equivalence Ratio	Hydrocarbon Concentration (% as Methane)		Soot Production (mg/l)	
	T = 1900 K	2000 K	T = 1900 K	2000 K
1.0	.0016	.0031	0	0
1.2	.030	.018	0	0
1.4	.58	.06	0	0
1.6	1.1	.32	.023	0
1.8	--	.6	--	.083

TABLE 4: BEHAVIOR OF HYDROCARBON CONCENTRATION WITH RESIDENCE TIME VARIATION FOR TOLUENE/N₂/O₂ COMBUSTION AT FUEL-RICH CONDITIONS

Residence Time (ms)	Hydrocarbons (% as Methane)		
	$\phi = 1.4$	$\phi = 1.6$	$\phi = 1.8$
2.5	.053	1.3	4.2
3.0	.015	.21	3.1
4.0	.0115	.057	1.14
5.0	.009	.0105	.24
6.0	.008	.0084	.06

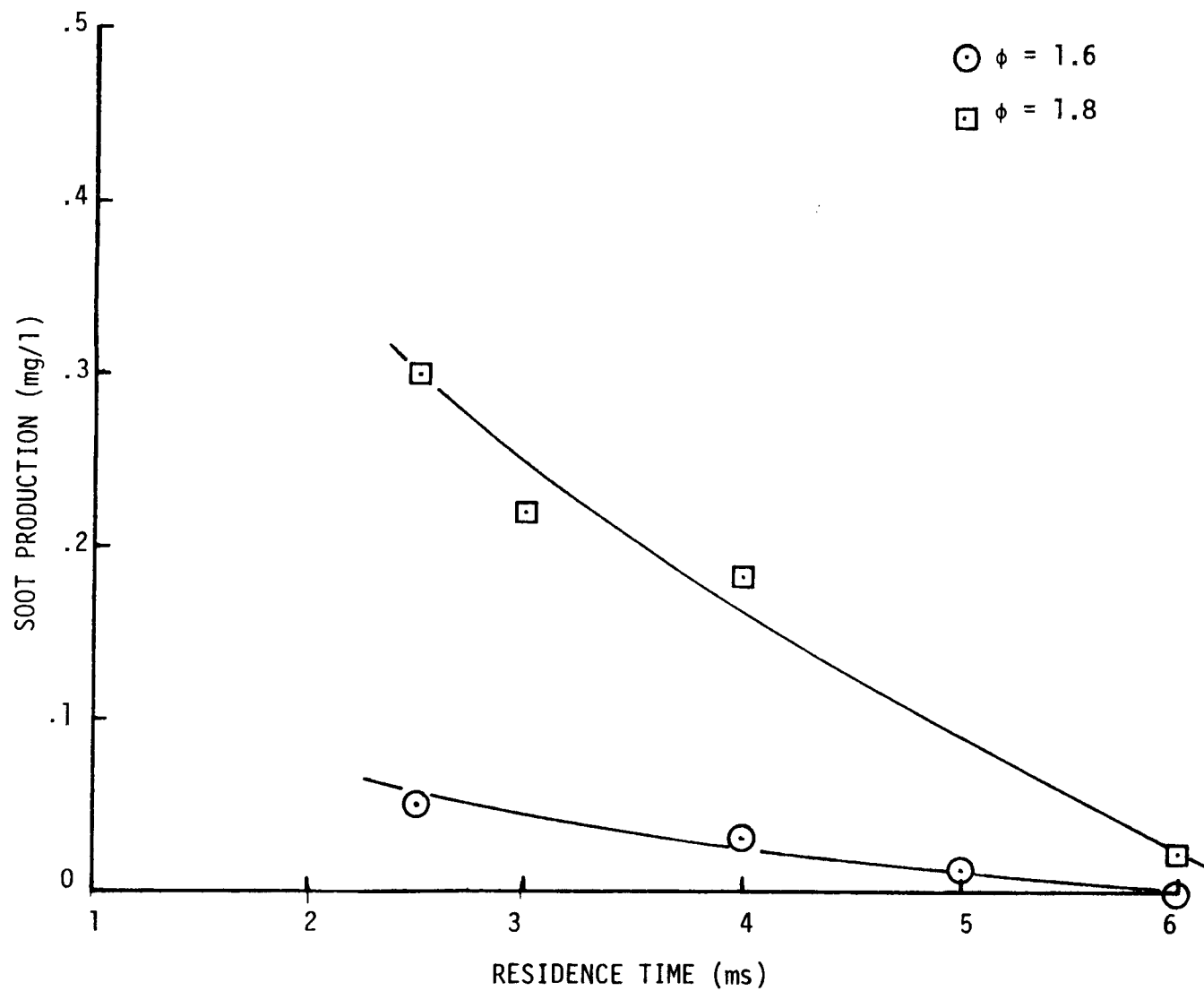


Figure 6: Dependence of Soot Production on Residence Time for Toluene/N₂/O₂ Combustion at 1900 K

in the mixture. NO concentrations are indicated for the case where NH₃ is not added to the inlet mixture as well as that where 1300 ppmv is introduced. HCN and NH₃ were not determined at equivalence ratios less than 1.2 because previous experience had indicated that values at these conditions are negligible. NH₃ and HCN were not determined for any of the baseline fuel (undoped with NH₃) experiments. The fuel nitrogen conversion listed in the last column of Table 5 is calculated as the total fixed nitrogen present (NO + NH₃ + HCN) less the NO present without fuel nitrogen in the inlet mixture, divided by an adjusted value of the inlet concentration of fuel nitrogen. The adjustment is necessary to account for a change in the number of moles between product and reactant and the knockout of water prior to the NO, HCN, and NH₃ measurements.

Conversion is high (~80%) at fuel-lean conditions, decreases to about 50% at $\phi = 1.4$, but then increases sharply as the blowout point is reached. Production of large amounts of HCN at the very fuel-rich conditions is responsible for this increase. These results emphasize the importance of considering TFN species other than NO in designing a rich/lean combustion system and illustrate that, in the case of CH₄ fuel, the equivalence ratio value giving reduced total fixed nitrogen is within a very narrow range about 1.4.

Ethylene Results:

Results for ethylene covering an equivalence ratio range of 1.4-2.2 are listed in Table 6. These data were obtained with an inlet mixture temperature of 25°C, a residence time of 4 ms, and an inlet NH₃ concentration of 1300 ppmv. The very high flame temperatures achieved with ethylene prevented examination at $\phi < 1.4$; the castable refractory reactor material limit was about 2000 K. NO concentrations are listed for the case where no NH₃ was added to the inlet mixture but, as with methane as the fuel, HCN and NH₃ measurements were not made for the undoped case. NO, HCN, and NH₃ were determined for runs where NH₃ was introduced at the inlet. The fuel nitrogen conversion listed in the last column of Table 6 is calculated as the total fixed nitrogen present (TFN=NO + HCN + NH₃) less the NO present without fuel nitrogen, divided by the properly adjusted value of the inlet fuel nitrogen concentration.

Conversion is about 54% at $\phi = 1.4$ but would have been near 80% with near-stoichiometric or lean mixtures. Fuel nitrogen conversion reaches a minimum of 43% at $\phi = 1.6$ and increases to higher values as the mixture is made more fuel-rich. As with CH₄ the total fixed nitrogen is dominated by HCN at the higher equivalence ratios. It should also be noted that the increase in HCN beyond the minimum coincides with the increase in total hydrocarbons in the combustion products beyond the level of about 1000 ppm at the TFN minimum.

Jet A Results:

Jet A experiments were conducted with nitrogen being added as pyridine, C₅H₅N. The natural Jet A nitrogen content is negligible (<10 ppm) and, therefore, testing of the undoped fuel provided our zero fuel nitrogen baseline. These experiments were conducted with a fixed fuel nitrogen concentration, 0.186% by weight. Consequently, the fuel nitrogen concentration of the mixture increased with equivalence ratio, unlike the CH₄ and C₂H₄ experiments. Data were obtained with an inlet temperature of 300°C and residence time of 4 ms. NO, HCN, and NH₃ were determined for both the undoped Jet A and the Jet A/pyridine blend.

TABLE 5: DEPENDENCE OF FIXED NITROGEN EMISSIONS ON ϕ
FOR CH₄/NH₃/Air Mixtures*

ϕ	T(K) (Measured)	CO(%)	CO ₂ (%)	H ₂ (%)	HC (ppm as CH ₄)	NO (ppm(%)) W/O NH ₃	NO (ppm w NH ₃)	HCN	NH ₃	Fuel N Conversion (%)
0.8	1885	0.35	7.4	0.075	17	59	940	-	-	80
1.0	1980	0.7	7.4	0.144	15	72	900	-	-	79
1.2	1950	4.7	5.6	2.57	12	84	780	62	0.6	69
1.3	1935	6.2	4.1	3.6	12	87	820	45	12.6	72
1.4	1850	7.0	4.0	4.5	40	59	510	103	9.5	50
1.5	1830	8.9	2.95	5.7	10	67	470	255	318	87
1.6	1775	9.75	2.4	10	4500	19	115	2626	32.8	232
1.7	blow out	-	-	-	-	-	-	-	-	-

* Combustor inlet temperature = 300± 15°C

Residence time = 4 ms

NH₃ concentration in inlet mixture \approx 1300 ppm

TABLE 6: DEPENDENCE OF FIXED NITROGEN EMISSIONS ON ϕ
FOR C₂H₄/NH₃/AIR MIXTURES*

ϕ	T(K) (Measured)	HC (ppm as CH ₄)		NO (ppm)		HCN (ppm) With NH ₃	NH ₃ (ppm) With NH ₃	Fuel N Conversion (%)
		Without NH ₃	With NH ₃	Without NH ₃	With NH ₃			
1.4	1854	260	330	81	610	147	1	54
1.5	1879	100	115	91	690	58	21	55
1.6	1824	1,300	1,000	64	415	130	33	43
1.7	1805	3,350	3,500	46	270	557	30	69
1.8	1757	11,250	13,250	10	105	963	33	95
1.9	1717	24,500	24,500	4	55	688	66	73
2.0	1685	29,000	29,000	4	44	673	51	70
2.2	1611	34,500	34,500	7	25	650	178	81

* 1300 ppm NH₃ in inlet mixture

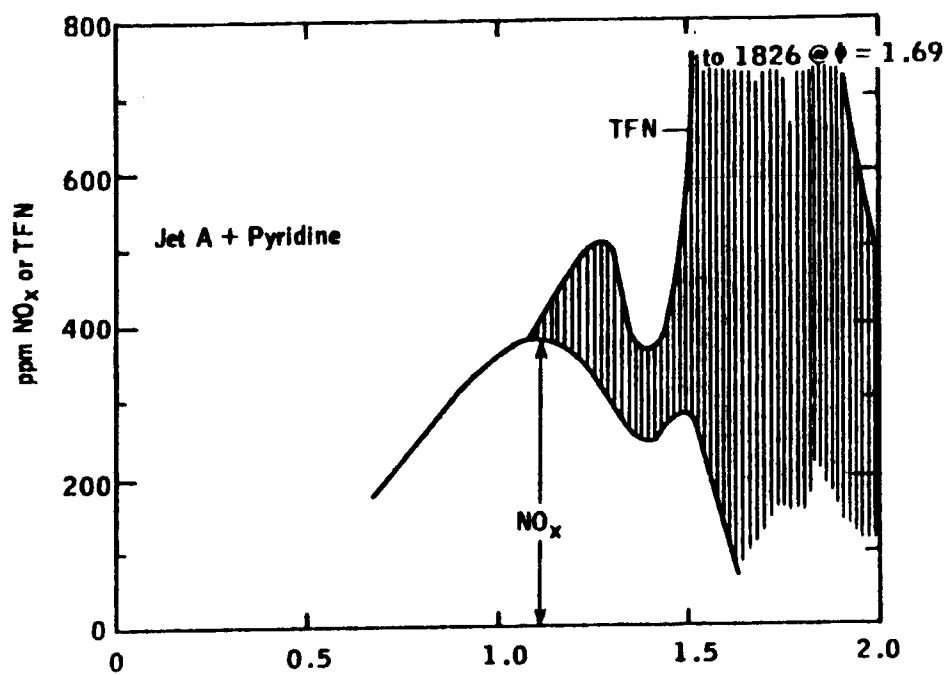
Results are shown in Table 7 and Figure 7. The table illustrates reactor temperature, total hydrocarbon concentrations, NO and TFN for both doped and undoped operation, and the percent of fuel nitrogen converted to TFN beyond the TFN found using undoped fuel. Note that this last parameter is different than that included in Tables 5 and 6. In that case HCN and NH₃ were not determined and conversion efficiency was calculated using the baseline fuel NO measurement only. Conversion of fuel nitrogen to TFN is about 80% at lean and near-stoichiometric conditions. It reaches a minimum at $\phi = 1.38$ where the total hydrocarbon concentration is about 600 ppm but then increases at higher equivalence ratios. Again, HCN is the predominant fixed nitrogen species. A drop in TFN at the highest equivalence ratios (1.69 and 1.94) is probably attributable to unreactedness of the initial fuel. That is, the pyrolysis of the initial fuel is not completed and fuel nitrogen remains as pyridine in the combustion products.

The Jet A case is the only one for which NH₃ and HCN were determined for the baseline or undoped fuel. These results show that while NO is maximized at near-stoichiometric conditions, TFN increases with ϕ once beyond the hydrocarbon breakthrough point in the JSC. The important TFN relationship is not a bell-shaped curve with a maximum at $\phi = 1$. When the process is under sufficiently fuel-rich conditions, hydrocarbon fragments apparently react with N₂ to produce HCN. This understanding is critical to successful development of staged combustion processes.

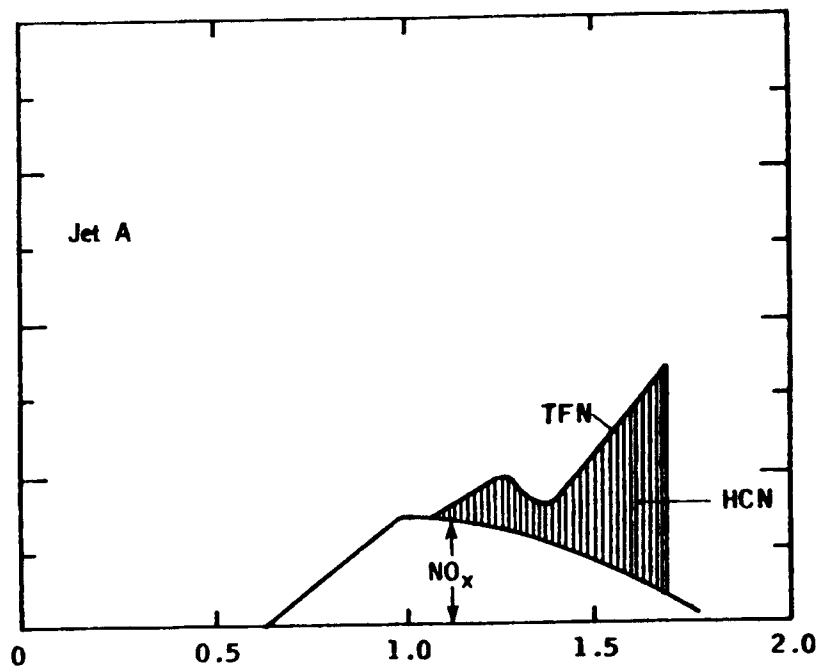
Another feature uncovered by these Jet A results is that a fuel nitrogen conversion efficiency greater than 100% is achievable, even when HCN and NH₃ are taken into account. This means that more N₂ is converted to TFN when fuel nitrogen is present than when a very low nitrogen fuel is used. That is, fuel nitrogen can accelerate the N₂ reaction with hydrocarbon fragments, to produce an apparent TFN conversion in excess of unity.

TABLE 7: DEPENDENCE OF FIXED NITROGEN EMISSIONS ON ϕ
FOR JET A AND JET A/PYRIDINE

ϕ	T(K) (Measured)	Jet A Without Pyridine			Jet A + 0.186% N as Pyridine			Conversion to TFN (%)
		HC (ppm as CH ₄)	NO (ppm)	TFN (ppm)	HC (ppm as CH ₄)	NO (ppm)	TFN (ppm)	
0.68	1740	575	15	23	2,000	175	180	82
0.87	1984	500	98	124	1,150	305	310	75
1.08	2014	400	145	148	0	375	379	82
1.26	1933	400	113	193	150	320	507	93
1.38	1871	210	108	160	650	245	370	58
1.5	1823	1,025	60	229	4,000	280	754	138
1.62	1749	8,500	37	301	11,250	74	1,052	187
1.69	1730	21,500	12	1,405	15,000	60	1,826	101
1.94	1513	28,000	27	497	30,000	27	621	26



a. Jet A With 0.186% Nitrogen as Pyridine



b. Jet A Without Pyridine

Figure 7: Fuel Nitrogen Conversion Results for Jet A-type Fuel

5. DISCUSSION

5.1 Implications for Quasiglobal Modeling

5.1.1 Soot Formation

The soot formation results presented in Section 4 have immediate utility for developing quasiglobal models of soot production. As will be discussed in Part B of this report, quasiglobal models based on a strong unburned hydrocarbon dependence are successful in characterizing soot production. Differences in the soot formation characteristics of aliphatics, single-ring aromatics, and multi-ring aromatics can be accommodated by employing distinctly different quasiglobal expressions for the three fuel groups.

A practical fuel may be represented as a three-component blend having appropriate amounts of each component. The total amount of unburned hydrocarbons must be determined using quasiglobal rate expressions for fuel disappearance which are specific to each of the hydrocarbon groups. Using such expressions, one could then account for the different nature of the unburned hydrocarbons present. These unburned hydrocarbon quantities can then be utilized in predicting soot formation using the quasiglobal expressions specific to each group.

While these results are very encouraging, a number of current serious limitations must be kept in perspective. As already noted, the prediction of soot requires knowledge of the unburned hydrocarbon concentrations and their origin. Quasiglobal expressions to make this prediction do not currently exist. Secondly, a full demonstration that quasiglobal models can be combined linearly or in some other simple manner is not in hand. The possibility of synergistic effects between the different types of unburned hydrocarbons has not been eliminated. Thirdly, the size of the soot particles formed is not currently predicted. This information will certainly be needed for calculations of soot burnout in the downstream portion of continuous combustion systems. Finally, the current model is based on atmospheric pressure experimental data. Pressure effects have not been evaluated.

There are additional problems to be encountered in applying the model to practical systems. Unmixedness within the backmixed primary zone must be considered. Soot production is very sensitive to mixture ratio and the more fuel-rich pockets will disproportionately contribute to soot formation. This problem does not invalidate quasiglobal expressions being developed in this program, but it does place a stringent requirement on the aerodynamic portion of the overall model to recognize and accommodate unmixedness. In this connection, the presence of droplets may be important in certain combustor configurations. Most likely, the droplets will not combust in the classical diffusion flame configuration, but their evaporation characteristics will dominate the overall unmixedness. Accommodation of spray combustion may require the primary zone to be analyzed as a stirred reactor simultaneously combusting an ensemble of mixture ratios.

5.1.2 Fuel Nitrogen Conversion

The current JSC data for fuel nitrogen conversion do not represent a set of information sufficient to develop a model of fuel nitrogen behavior. However, they do comprise a set of results with which other proposed models can be tested. The subject program has cooperated with a companion DOE program at MIT and their kinetic model will serve as a starting position for our efforts. The MIT model will be compared with the current JSC data during the coming year.

The data describe some interesting phenomena which a successful model should be able to predict. First, the results of Jet A combustion without a nitrogen dopant show that very high quantities of HCN and NH_3 are produced at fuel-rich conditions. This suggests that HCN is being produced by N_2 combination with hydrocarbon fragments present under fuel-rich conditions. The results provide new information on "prompt NO" which has been shown to be a strong function of equivalence ratio in flat flame studies (6). These JSC results characterize the process using a single known hydrocarbon concentration. This is not the case for the flat flame burner results which dominate the literature on this topic. Hopefully, the data will be of assistance in developing a better understanding of prompt NO.

Secondly, under fuel-rich conditions the addition of fuel nitrogen actually results in the production of more TFN (mainly HCN) than could be justified by 100% conversion of fuel nitrogen (note Jet A data at 1.5 and 1.62 in Table 7). That is, the addition of some fuel N results in additional N_2 being converted to TFN. The chemistry by which this occurs should prove very interesting and this phenomenon should provide an excellent test for future analytical models of the fuel nitrogen conversion process.

5.2 Application of Findings*

5.2.1 THC Importance

Acceptable gas turbine combustion performance using low hydrogen, high nitrogen content fuels will require a fuel-rich first stage which promotes conversion of fuel N to N_2 while preventing excessive soot formation. The current results imply that the first stage be thought of as a well-stirred reactor--a zone which is sufficiently mixed to be nearly homogeneous in temperature and composition. The incoming fuel-air mixture is assumed to be instantaneously mixed with the combustion products and the entire reaction zone is represented by one set of composition/temperature conditions. Soot and fuel nitrogen conversion in this system can be viewed as the products of the reaction between these components in the "well stirred pot" at rates determined by the existing temperature conditions.

The distinction between the first stage operating as a plug flow reactor or as a stirred reactor is important. First, previous work has shown that the incipient soot formation limit in the stirred reactor configuration is richer than the plug flow case (2). A further distinction is added through consideration of fuel nitrogen conversion. In the plug flow case, destruction of fuel nitrogen occurs where large concentrations of hydrocarbon fragments are present and formation of HCN can be extensive; low fixed nitrogen may be achieved by allowing the system to relax back towards equilibrium. On the other hand, at appropriate operating conditions the stirred reactor may allow fuel nitrogen

* This section draws heavily on an ASME paper written jointly by W. S. Blazowski (Exxon) and A. F. Sarofim and J. C. Keck (MIT). The paper is included in its entirety in Part C.

destruction to occur at low hydrocarbon concentrations and the initial formation of HCN may be limited.

Soot will form in this well-stirred combustion zone if the initial fuel contains a substantial amount of single or double-ring aromatics and if the zone is operated in a manner which allows a significant concentration of hydrocarbons (unburned fuel fragments) to be present. Fuel nitrogen conversion is minimized by operating the reaction zone as rich as possible without the presence of high hydrocarbon concentrations. More oxidizing conditions allow the conversion of fuel N to NO_x to be more effective and the presence of hydrocarbons at richer operating conditions allows the formation of HCN in the first stage which will subsequently be oxidized to NO_x in the second, fuel-lean stage of the combustor. Consequently, these results imply that minimization of both NO_x and soot in gas turbines utilizing future fuels will require a staged combustion process designed for the richest possible operation without substantial hydrocarbon breakthrough. It is recommended that combustor designers utilize this information by analyzing THC concentrations within the fuel-rich first stage during combustor development testing.

The ability to operate fuel rich without soot formation is also influenced by the type of fuel being combusted (i.e., composition in terms of Group 1, 2, or 3). Lesser quantities of single-ring and double-ring compounds in the fuel will increase the incipient sooting ϕ and allow the THC concentration at the limit to increase. However, fuel nitrogen conversion is not likely to be as sensitive to fuel type--fixation of fuel nitrogen as HCN will coincide with the THC breakthrough regardless of the type of hydrocarbons present in the fuel. Consequently, the maximum operating equivalence ratio for fuels with a predominance of Group 1 hydrocarbons may be dictated more by considerations of fuel nitrogen conversion than soot formation.

A point already mentioned which should be emphasized again is that the JSC experiments on which these conclusions are based involves a premixed prevaporized system. The presence of fuel droplets in the first stage would be expected to seriously influence the results. Successful operation will require the pockets of fuel-rich mixture resulting from droplets in the first stage be avoided--otherwise the consequence of hydrocarbon breakthrough (soot formation and fixation of fuel nitrogen) will occur locally. Fuel injection, droplet-air mixing, and droplet vaporization must be accomplished in a manner which allows homogeneous conditions to be achieved on a micro-scale within the first stage.

Finally, the second stage combustion process is also critical for achieving low levels of NO_x emission. Large quantities of thermal NO_x can be produced if the mixing process is too slow and allows regions of near-stoichiometric, high temperature reaction.

5.2.2 Control by THC or Radiative Characteristics

One important concern in the design of low NO_x combustion systems is the impact of load variation on operating characteristics. For example, a reduction in load causes a decrease in fuel-air ratio requirements and perhaps combustor inlet temperature. These changes can cause the system to operate in a manner substantially off the optimum operating point unless adjustments are made to key combustion parameters.

The evidence that THC is a critical indicator of optimum operation suggests that measurement of this parameter might be used to control conditions in the first stage. One can envision a flame ionization detector which monitors first stage gas composition to provide a signal proportional to first stage THC. This, in turn, could control air supplied to the first stage in a manner which assures optimum operation. In essence, this control scheme would attempt to have the combustor always operating at the "knee" of the THC versus equivalence ratio characteristic.

Alternative methods of monitoring THC which do not involve extraction of a physical sample might also be employed. Luminosity is a measure of soot formation but is more indicative of Group 2 and Group 3 hydrocarbon breakthrough than Group 1. It is therefore expected to be a useful measure of when HCN breakthrough occurs but could overlook situations in which fuels with a low sooting potential are utilized. Alternatively, a spectroscopic analysis of flame emission or adsorption in a spectral region characteristic of hydrocarbons could be employed as the control signal.

Establishing the best method of sensing hydrocarbon breakthrough and controlling key combustor variables will require additional research and development. The appropriate THC concentration to use as a set point is not known and the ability to design first stage zones with controllable flows must be developed.

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