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FUNDAMENTAL CHARACTERIZATION OF ALTERNATE FUEL
EFFECTS IN CONTINUOUS COMBUSTION SYSTEMS

Summary Technical Progress Report for August 15, 1978–
January 31, 1980

By
W. S. Blazowski
R. B. Edelman
E. Wong

DIST-68
NTIS-25

February 27, 1980

Work Performed Under Contract No. AC03-77ET11313

Exxon Research and Engineering Company
Corporate Research-Technology Feasibility Center
Linden, New Jersey

and

Science Applications, Incorporated
Canoga Park, California

U. S. DEPARTMENT OF ENERGY

R162

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FOR PERIOD AUGUST 15, 1978-JANUARY 31, 1980

by

W. S. Blazowski
Exxon Research and Engineering Company
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Linden, New Jersey 07036

and

R. B. Edelman
E. Wong
Science Applications, Inc.
Canoga Park, California

EXXON/CR.2EBA.80

February 27, 1980

Prepared for

the Department of Energy

Under Contract DE-AC03-77-ET-11313

This report has been released by

N. R. WERTHAMER
CONTRACT RESEARCH DIVISION

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

GAS PHASE ELEMENTS

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

THERMODYNAMIC AND HEAT TRANSFER ELEMENTS

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

SOLUTION SCHEME

- Simplification of Equations
- Solution Procedure
- 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

W. S. Blazowski
Exxon Research and Engineering Company
P. O. Box 45
Linden, New Jersey 07036

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 O_2/N_2 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 $\text{CHO}^+ + \text{e}^-$. 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 H_2 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 $150^\circ C$. 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 N_2 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 N_2 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 N_2 are held constant, a constant, repeatable dilution results.

The system is calibrated with a C_2H_4/N_2 mixture prepared on-line with metered quantities of C_2H_4 and N_2 . This mixture is preheated in a coil within the oven as was the N_2 , 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 NH_3 Measurements

Experiments concerning the fate of fuel nitrogen during combustion must be concerned with total fixed nitrogen, $TFN = NO + NO_2 + HCN + NH_3$. Large quantities of HCN and NH_3 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 ($NO + HCN + NH_3$) 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 O_3 produced within the instrument and fed to the chamber. The NO and O_3 produce an activated NO_2 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. NO_2 is usually determined using the same procedure, but after the sample has been passed through a stainless steel tube at about $900^\circ C$ which converts NO_2

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 O_2/N_2 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 O_2/N_2 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 O_2/N_2 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

Equivalence Ratio	Hydrocarbon Concentration (% as Methane)			
	T = 1700 K	1800 K	1900 K	2000 K
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 ($\sim 80\%$) 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

<u>Equivalence Ratio</u>	<u>Hydrocarbon Concentration</u> (% as Methane)		<u>Soot Production</u> (mg/l)	
	<u>T = 1900 K</u>	<u>2000 K</u>	<u>T = 1900 K</u>	<u>2000 K</u>
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

<u>Residence Time (ms)</u>	<u>Hydrocarbons (% as Methane)</u>		
	<u>$\phi = 1.4$</u>	<u>$\phi = 1.6$</u>	<u>$\phi = 1.8$</u>
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 NH_3 is not added to the inlet mixture as well as that where 1300 ppmv is introduced. HCN and NH_3 were not determined at equivalence ratios less than 1.2 because previous experience had indicated that values at these conditions are negligible. NH_3 and HCN were not determined for any of the baseline fuel (undoped with NH_3) experiments. The fuel nitrogen conversion listed in the last column of Table 5 is calculated as the total fixed nitrogen present ($\text{NO} + \text{NH}_3 + \text{HCN}$) 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 NH_3 measurements.

Conversion is high ($\sim 80\%$) 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 CH_4 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 NH_3 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 NH_3 was added to the inlet mixture but, as with methane as the fuel, HCN and NH_3 measurements were not made for the undoped case. NO, HCN, and NH_3 were determined for runs where NH_3 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 ($\text{TFN} = \text{NO} + \text{HCN} + \text{NH}_3$) 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 CH_4 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, $\text{C}_5\text{H}_5\text{N}$. 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 CH_4 and C_2H_4 experiments. Data were obtained with an inlet temperature of 300°C and residence time of 4 ms. NO, HCN, and NH_3 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 C_2H_4/NH_3 /AIR MIXTURES*

ϕ	T(K) (Measured)	HC (ppm as CH_4)		NO (ppm) Without NH_3	NO (ppm) With NH_3	HCN (ppm) With NH_3	NH_3 (ppm) With NH_3	Fuel N Conversion (%)
		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 NH_3 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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PART B: ANALYTICAL PROGRAM PROGRESS

R. B. Edelman, E. Y. Wong
Science Applications, Inc.
Combustion Science and
Advanced Technology Department
21133 Victory Boulevard, Suite 216
Canoga Park, California 91303

1. INTRODUCTION

The objective of the model development effort is to provide user-oriented tools to aid in accelerating the implementation of alternative fuels in stationary gas turbines. Fundamental information is being translated into a form that relates the important performance criteria to the flame structure with emphasis on fuel property effects. The practical results are models that will relate efficiency and emissions to controllable design parameters. At the same time the models will provide important information on fuel/air distribution, aerodynamic flow patterns and heat transfer.

The approach of relating fundamental combustion phenomena to fuel properties involves the application of analytical models developed with and ultimately verified by data obtained from specially designed experiments. The models are being developed through the integration of chemical and fuel related elements, thermodynamic and heat transfer elements, and aerodynamic elements. The physical processes include droplet and spray combustion, heat transfer by convection and radiation, aerodynamic flow patterns, and turbulent mixing.

The work reported upon here emphasizes the approach to the model development for fuel related elements. The engineering model for this element is based on extending the quasiglobal kinetics model. The concept of this sub-model involves the coupling of a set of subglobal reaction steps to a set of detailed steps for those reaction chains for which substantial information already exists for their kinetics and mechanism. While the original quasiglobal kinetics model consisted of a single global partial oxidation step coupled to the detailed "wet CO mechanism", the extended model includes fuel pyrolysis, soot formation and oxidation and fuel-bound nitrogen conversion steps.

The effort during this phase of the program has concentrated on the development of the extended quasiglobal kinetics model with particular emphasis on soot emissions.

2. EXTENDED QUASIGLOBAL KINETICS MODEL*

The details of the kinetics and mechanism of the combustion of most hydrocarbon fuels, particularly heavy hydrocarbons, is not fully understood at this time. The quasiglobal kinetics model represents an intermediate level of detail and involves the essential features of the coupling of a set of subglobal steps to a set of detailed steps for which sufficient information to accurately describe their kinetics and mechanism exists. The original quasiglobal kinetics model, however, consists of a single subglobal partial oxidation step coupled to the detailed wet CO mechanism.

That model has been used with reasonable success in accounting for the variation in fuel type, i.e. aliphatic versus cyclic in fuel lean systems. Consistent with the general quasiglobal concept, the current model has been extended to include important combustion characteristics in fuel rich systems. The extended model, illustrated in Table 1, includes subglobal steps for fuel pyrolysis, fuel bound nitrogen conversion, partial oxidation, soot formation and oxidation. Furthermore, the products of partial oxidation, CO and H₂, are allowed to react toward completion through a set of elementary steps. In addition, detailed NO_x formation steps are included. Many of these detailed steps, together with their rate constants have been recently compiled and updated in an SAI report published by Gelinas, et al, (Ref. 1).

For the fuel nitrogen conversion step, it is assumed that a nitrogen-containing intermediate (NX) is released through hydrocarbon pyrolysis. The intermediate might be NH₂, N, or even HCN, as Fenimore, et al, (Ref. 2), and Corrett, et al, (Ref. 3) have suggested. As the intermediate is formed, it may further react to produce other nitrogen containing compound(s) (e.g. NCH and NH₃), or nitric oxide, or a stable nitrogen compound (e.g. N₂). The kinetic steps under "NO_x Formation" in Table 1 illustrate our approach to the fuel nitrogen conversion process. Foster (Ref. 4) has proposed a rather detailed mechanism for the fate of fuel bound nitrogen and these results will be included in our model. In addition, nitric oxide can also form through a direct thermal process and is accounted for by the extended Zeldovich mechanism given by the last three reactions in Table 1.

Finally, the rate constants for the subglobal steps are expressed in modified Arrhenius form and the rate of production (consumption) is given by expressions of this type:

$$R = AT^b C_1^a C_2^c \exp (-E/RT)$$

where the constants A, b, a, c and E are the rate parameters for the particular subglobal reaction. For the partial oxidation steps, C₁ and C₂ are the concentrations of the particular hydrocarbons and oxygen, respectively. For pure pyrolysis, c is zero and a is unity for first order decomposition. The rate parameters are being determined from literature values, but mainly in conjunction with ER&E data.

During this period emphasis was on the analysis of the net soot emissions data measured in the jet stirred combustor described in Part A of this report. In terms of the quasiglobal scheme, the work concentrated on the two steps comprising soot formation and soot oxidation given in Table 1.

* This section is drawn from the AGARD paper written jointly by R. B. Edelman, A. Turan, P. T. Harsha, and E. Wong of SAI and W. S. Blazowski (Exxon) which is included in the Appendix to this report.

TABLE 1 - SKELETAL SYSTEM FOR THE EXTENDED QUASI-GLOBAL MODEL

Hydrocarbon Pyrolysis

Hydrocarbon Partial Oxidation

Soot Formation

Soot Oxidation

Elementary Steps for CO/O₂ Reaction Mechanism

Elementary Steps for H₂/O₂ Reaction Mechanism

⋮

⋮

NO_x Formation

⋮

⋮

3. EXISTING SOOT FORMATION MODELS

Many studies on soot formation have been carried out but few lead to quantitative predictions of soot production. Furthermore, there is little agreement as to the details of the intermediate steps involved in the production of soot. Nevertheless, there seems to be general agreement that the overall soot formation reaction is triggered by hydrocarbon pyrolysis and involves subsequent soot nuclei formation, soot particle formation, and particle growth and coagulation. A model that treats these in some detail has been considered by Jensen (Ref. 5). Application of the model to a methane flame has led to qualitative agreement with experimental observations. Although this approach represents an attempt to deal with the problem at a mechanistic level the uncertainty of intermediate species, reactions and rates requires long term development to provide quantitative predictions. Tesner, et al (Ref. 6) have proposed a model in which soot formation is characterized by three rate-limited steps. The feature of the model is that all the complex elementary steps associated with pyrolysis, nuclei formation and soot formation are grouped into three subglobal steps. The model includes a first order (with respect to hydrocarbon concentration) pyrolysis rate, a chain branching and chain termination rate, and a soot formation rate:

$$\begin{array}{lll} \text{Pyrolysis} & n_0 = 10^{13} C_{HC} \exp (-170,000/RT) & 2 \\ \text{Nuclei Formation} & \frac{dn}{dt} = n_0 + (f-g)n - g_0 Nn & 3 \\ \text{Soot Formation} & \frac{dN}{dt} = (a-bN)n \text{ [particle/cm}^3\text{sec]} & 4 \end{array}$$

The values of the kinetic parameters (f, g, g_0 , a, b) for Toluene (Ref. 7) are:

$$\begin{array}{ll} (f-g) & = 500.0 \\ y_0 & = 10^{-8} \\ a & = 10^5 \\ b & = 3 \times 10^{-6} \end{array}$$

In contrast to this three-step scheme, Greeves, et al, (Ref. 8) proposed a single step soot formation rate,

$$\frac{dC_s}{dt} = 0.468 p_{HC} \phi_u^3 \exp (-40,000/RT) \text{ [gm/cm}^3\text{sec]} \quad 5$$

where p_{HC} and ϕ_u represent the partial pressure of unburnt hydrocarbon and the unburnt equivalence ratio. The rate parameters given in this equation were selected by Greeves to fit data obtained under conditions designed to simulate typical diesel operation. The fuel was an unspecified diesel fuel.

Comparisons between computations using the Tesner and Greeves models and a set of ER&E soot measurements are shown in Fig. 1. Soot emissions become detectable at $\phi = 1.3$ and the soot concentration level increases as the equivalence ratio increases. The relatively horizontal curve obtained using the Tesner model shows no discernible trend. In contrast to the experimental observation, the Tesner model appears to be insensitive to the equivalence ratio. Fig. 1 also shows the predictions based upon the Greeves model. In this case the predicted soot concentration appears to be overly sensitive to the equivalence ratio and the predictions are generally one order of magnitude higher than the experimental data.

Figure 1. Comparison of Predicted with Measured Soot Concentrations, Toluene

The disparity between the ER&E data and Tesner model has not been fully reconciled. However, an examination of the method used in obtaining the rate constants suggests that they may have been influenced by aerodynamic effects including turbulent mixing. Furthermore, the Tesner model has treated the kinetic parameters (a , b , f , g , g_0) as constants throughout the range of conditions covered in their experiments. However, in studies on explosion limits, Semenov and coworkers (Ref. 9) have shown that these parameters are, in fact, functions of local conditions, such as temperature and radical concentrations, suggesting that for this model to have practical use considerably more information is required concerning these dependencies.

Furthermore, a significant deficiency of these models is that they do not account for the effect of soot oxidation. In high temperature combustion systems where soot burnout is expected to be significant and might possibly be controlled, it is important that the formation and the oxidation reactions be considered simultaneously in the prediction of net soot emission.

4. NET SOOT EMISSIONS

As a result of the above investigation, a somewhat more general two step model comprised of a formation and an oxidation step has been developed. For the prediction of net soot emissions under well-stirred environments, however, these reaction steps are coupled into the species conservation equations in order to provide the desired net soot emissions relationship. The species conservation equation for soot can be expressed as follows:

$$\frac{\dot{m}}{\rho V} (C_s - C_{s0}) = R_f - A_t R_{ox} \quad [\text{gm/cm}^3 \text{sec}] \quad 6$$

where $\dot{m}$, ρ , V , C_s , C_{s0} , are total mass flow rate, exhaust gas density, reactor volume, outlet and inlet soot concentrations. As a whole, $\dot{m}/\rho V$ represents the reciprocal of residence time. A_t which can be expressed in terms of C_s , soot density (ρ_s) and soot particle diameter (D) is the total surface area available for oxidation. Finally, R_f and R_{ox} are the reaction rates for the soot formation and oxidation steps.

The formation step assumes the following form:

$$R_f = A T^\alpha C_{HC}^a C_{O_2}^b \exp(-E/RT) \quad [\text{gm/cm}^3 \text{sec}] \quad 7$$

where C_{HC} and C_{O_2} are concentrations of unburnt hydrocarbon and oxygen, and A , α , a , b , E are rate constants. Tentative values for these constants have been determined by using ER&E jet-stirred reactor data (Ref. 10). These data comprise three residence times, i.e. three mass flow rates corresponding to 112.5, 80.0 and 50.0 gm/min. The set of data having air flow rates of 112.5 gm/min was used to determine these rate constants. These data comprising the unburnt hydrocarbon and oxygen concentrations are illustrated on Figs. 2 and 3. Because the nature of the data does not allow a direct determination of these rate constants, a series of Arrhenius type plots were constructed by systematically varying the value of these rate parameters. This procedure produced the following set of rate constants:

$$\begin{aligned} A &= 1.33 \times 10^{14} \\ \alpha &= -1.94 \\ a &= 1.81 \\ b &= -0.5 \\ E &= 32,000 \end{aligned}$$

Regarding the oxidation step, various oxidation models have been reviewed. In particular, models developed by Lee, Thring, and Beer (Ref. 11) and Nagle, Strickland-Constable (Ref. 12) have been examined in some detail. These models were of particular interest because the rate constants were determined using data obtained from soot or soot-like combustion experiments. Since the model of Lee, et al, can be deduced from that of Nagle and Strickland-Constable when the oxygen concentration is small, the more general model of Nagle and Strickland-Constable has been tentatively adopted. This model gives the rate of soot consumption as follows:

Figure 2: Measured Unburnt Hydrocarbon Concentration in Jet Stirred Reactor,
Air Flow = 112.5 gm/min, Toluene

Figure 3: Measured Unconsumed Oxygen Concentration in Jet Stirred Reactor,
Air Flow = 112.5 gm/min, Toluene

$$R_{ox} = 12 \left[\left(\frac{k_Z P_{O_2}}{1 + k_Z P_{O_2}} \right) \chi + k_B P_{O_2} (1 - \chi) \right] [\text{gm}/\text{cm}^2 \cdot \text{sec}] \quad 8$$

$$\text{where } \chi = \left[1 + k_T / (k_B P_{O_2}) \right]^{-1} \quad 9$$

$$k_A = 20 \exp (-30,000/RT)$$

$$k_B = 4.46 \times 10^{-3} \exp (-15,200/RT)$$

$$k_Z = 1.51 \times 10^5 \exp (-97,000/RT)$$

$$k_T = 21.3 \times \exp (4100/RT)$$

Substitution of the formation and oxidation rates into equation 6 gives the desired result for the concentration of the soot emission

$$C_s = \frac{\left(\frac{V}{\rho m} \right) \times 1.33 \times 10^{14} T^{-1.94} C_{HC}^{1.81} C_{O_2}^{-0.5} \exp (32,000/RT)}{1 + \left(\frac{\rho V}{\dot{m}} \right) \left(\frac{6}{\rho_s D} \right) R_{ox}} [\text{gm}/\text{cm}^3] \quad 10$$

The relationship was used in the prediction of the soot emission data obtained from ER&E JSC experiments. For this purpose, a single soot particle size of 250 Å was assumed. The results of our calculations are shown in Fig. 4. It can be seen that the predictions based upon the above equation generally agree with the data over the range of operating conditions covered. In addition, Figs. 5 thru 7 show the comparison between predictions and data recently obtained from ER&E isothermal experiments. These data were obtained for constant reactor temperatures at various inlet equivalence ratios. Even for these cases the agreement is good for soot concentrations above 0.1 mg/l. Below this level the trend in the data is generally predicted but the scatter suggests the desirability of obtaining additional data at these low emissions level conditions. Finally, Fig. 8 shows a comparison of computed and measured soot concentration as a function of residence time. Again, the predictions follow the trend of the data very well.

Figure 4. Comparison of Predicted with Measured Soot Concentrations, Toluene

Figure 5: Comparison of Predicted with Measured Soot Concentrations,
Controlled Reactor Temperature = 1700°K, toluene

Figure 6: Comparison of Predicted with Measured Soot Concentrations,
Controlled Reactor Temperature = 1800°K, Toluene

Figure 7: Comparison of Predicted with Measured Soot Concentrations, Controlled Reactor Temperature = 1900°K, Toluene

Figure 8: Comparison of Predicted with Measured Soot Concentrations, Controlled Reactor Temperature = 1900°K, Toluene

5. DISCUSSION OF RESULTS

The results of the investigations conducted to date on toluene show that a relatively simple engineering model for net soot emissions is feasible. Furthermore, the iterative procedure used in developing the model in conjunction with the ER&E jet-stirred combustor experiments is providing the basis for the establishment of guidelines for the control of sooting characteristics from combustor primary zones characterized by intense backmixing under kinetically controlled conditions. Although the rate parameters have been determined for a limited range of conditions the results are applicable to certain of the important operating characteristics encountered in gas turbine combustors. Residence times span the range from 2-7 milliseconds for fuel/air equivalence ratios in the range of from 1 to 2. The temperature levels covered were predominantly in the 1800-2000°K range and much of this data was obtained by independently varying the equivalence ratio and residence times under isothermal conditions.

While a broad base of information has been established it represents only part of the modeling required in the development of the overall engineering model for gas turbine combustors. The work required includes expanding the chemical kinetics modeling to cover fuel property variations, through the investigation of other fuels and fuel blends and NO_x emissions. Of particular importance is the effect of pressure on net soot emissions as well as the physical processes of spray combustion and the aerodynamics of the combustion process including flow patterns and turbulence.

6. FUTURE WORK

This section summarizes work to be conducted in the next phase of the program. Technical data required to accomplish the work will be provided by ER&E jet-stirred reactor and continuous flow reactor facilities. In cases where the type of experiment required for model development is still uncertain, particularly for soot emission in fuel blend systems and fuel nitrogen conversion to NO_x , some preliminary analytical work will be performed in advance, and guidance in experimental design will be provided. In general, work related to the following technical areas will be performed.

A. Quasiglobal Model Development

- (1) Soot emissions for the methylnaphthalene system
- (2) Soot emissions from fuel blend systems
- (3) Fuel nitrogen conversion to NO_x
- (4) Pressure effect on soot emissions
- (5) Fuel pyrolysis
- (6) Soot oxidation

B. Other Submodel Development

- (1) Gas dynamics
- (2) Spray interaction
- (3) Flame radiation

C. Modular Model Development

It should be noted that the order of tasks identified above does not necessarily constitute the actual priority of work.

Soot production for toluene systems has been studied extensively in the last phase of the program; as a result we have successfully developed a tentative model capable of predicting the soot emissions under typical ER&E JSC conditions. However, for the methylnaphthalene systems, experimental data have shown that soot emissions in such systems is much heavier than those of toluene under similar conditions. This suggests that methylnaphthalene, being structurally different from toluene in terms of the number of aromatic rings, is likely to follow a different route to produce soot. Therefore, independent modeling for this fuel is required and this probably will involve the determination of an independent set of rate constants.

Soot emissions for fuel blends will be studied in order to provide a broad base of modeling capability for a range of possible practical fuels to be encountered in the future. It is expected that experience gained from the modeling of each parent fuel will provide guidance on modeling the blends. In addition, the effect of mixture ratio on unburnt hydrocarbon emissions, as well as soot formation will be determined.

Fuel nitrogen conversion to NO_x will be studied, as the practical fuels of interest in the future will have high nitrogen content. The

currently available JSC data on fuel bound nitrogen conversion will be analyzed and data requirements for further model development will be established.

As observed by various researchers, soot emission is enhanced as the total pressure increases. Therefore, the effect of pressure on unburnt hydrocarbon, oxygen emission and soot production will be determined. Work related to fuel pyrolysis and soot oxidation has already been initiated and this work will continue with some parametric studies on pyrolysis. However, when experimental data becomes available, models for these reactions will be developed. Finally, the structure of the products of pyrolysis will also be determined.

Under the Other Submodel Development, work related to gas dynamics, spray interaction and flame radiation will be studied in parallel with other model developments.

The modular model for the overall gas turbine combustion system constitutes the framework for the coupling of the chemical and physical submodels. Work on the development of this modular model will be initiated during the next phase of the program.

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PART C: TECHNICAL PAPERS DURING REPORTING PERIOD

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FUNDAMENTAL CHARACTERIZATION OF ALTERNATIVE
FUEL EFFECTS IN CONTINUOUS COMBUSTION SYSTEMS

by

R. B. Edelman, A. Turan, P. T. Harsha, and E. Wong
Science Applications, Inc.
Combustion Dynamics and Propulsion Technology Division
20335 Ventura Blvd/Suite 423
Woodland Hills, California 91364

W. S. Blazowski
Exxon Research and Engineering Company
Government Research Laboratories
P.O. Box 8
Linden, New Jersey 07036

SUMMARY

Increased interest in alternative fuels use in gas turbines has prompted questions related to the impact of fuel property variability on the combustion process. Reduced hydrogen content is characteristic of syncrudes that have been identified as probable alternate fuel sources. An interrelated analytical and experimental program is being conducted in which chemical and aerodynamic interactions are being investigated in order to provide a technology base to aid in dealing with problems of burning alternative fuels. One element of this effort is devoted to characterizing the kinetics of the oxidation of alternative fuels. This paper is concerned principally with the problem of net soot generation which is aggravated by the reduced hydrogen content. The kinetics of the process is being modeled using the quasiglobal concept while experimental data is being developed primarily from a laboratory jet stirred combustor. Results are presented showing that soot emissions can be characterized in terms of major species and that soot oxidation must be included in the prediction of net soot generation. In addition, the techniques being employed for coupling the chemical and aerodynamic processes are outlined.

INTRODUCTION

Until recently the development of gas turbine combustors as well as the development of combustion chambers for most other applications has been based largely upon empirical methods. While reliable systems have been produced by this approach the cost is becoming prohibitive. Furthermore, time constraints for the development of new systems by this approach are not necessarily compatible with meeting near term requirements for cleaner burning and more efficient systems. Not only do the near term needs blunt purely empirical approaches but we are in a critical period where the development of new technology bases must be initiated and sustained to meet the long term requirements dictated by the increasingly changing fuel availability picture. Although economics and supply are primarily responsible for this recent interest in new fuel sources, projections of available worldwide petroleum resources also indicate the necessity for seeking non-petroleum based fuels.

Fuel variability has not been a factor commonly accounted for in empirically based design procedures. Because of the uncertainty in future fuels as well as the need to use less conventional petroleum based fuels, the requirement to develop fuel flexible systems is well established. The design of fuel flexible combustors that burn cleanly and efficiently requires a more precise understanding of the mechanisms that control flame structure than has been needed in the past.

The practical goal in understanding the combustion process is to relate the parameters in the control of the designer to the performance of the system. By performance we include in a general sense combustion efficiency and emissions characteristics.

In this paper emphasis is given to the effects of fuel properties on combustion but the relationship between the fuel and the aerodynamics of the gas turbine combustion process is also addressed.

FUEL EFFECTS ON GAS TURBINE COMBUSTION

Fuel characteristics which are most likely to affect the design of future gas turbines are fuel hydrogen content, viscosity, volatility, nitrogen content and thermal stability, Ref. 1.

The impacts of reduced fuel hydrogen content are associated with increased rates of carbon particle formation. Increased levels of carbon particle concentrations formed in fuel rich regions of the primary zone lead to higher liner temperatures and higher smoke emissions. Reduced volatility and increased viscosity affect droplet life times and atomization, respectively. Volatility affects the rate at which liquid fuel introduced into the combustor can vaporize. Since important heat release processes do not occur until gas phase reactions take place, a reduction of volatility reduces the time available for chemical reaction within the combustion system. In the aircraft engine this can result in difficulty in ground or altitude ignition capability, reduced combustor stability, increased emissions of carbon monoxide (CO) and hydrocarbons (HC), and the associated loss in combustion efficiency. Moreover, carbon particle formation is aided by the formation and maintenance of fuel-rich pockets in the hot combustion zone, Ref. 2. Low volatility allows rich pockets to

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persist because of the reduced vaporization rate. Again, increased soot can cause additional radiative loading to combustor liners.

The desired formation of a finely dispersed spray of small fuel droplets is adversely affected by viscosity. Consequently, the shortened time for gas phase combustion reactions and prolonging of fuel-rich pockets experienced with low volatility can also occur with increased viscosity. Ignition, stability, emissions, and smoke problems also increase for higher viscosity fuels.

Increased fuel bound nitrogen levels can lead to increased NO_x emissions. Indications are that bound nitrogen conversion to NO_x can be minimized in fuel rich combustion, Ref. 3. Apparently, this will occur if sufficient time under fuel rich conditions is allowed for direct conversion of the bound nitrogen to N₂. Problems of fuel stability are aggravated with increased bound nitrogen and undersirable levels of carbon deposit buildup in fuel management systems and on combustor components can occur.

While our investigations are addressing all of these fuel related problems it has become apparent that to characterize net soot generation requires a broader description of the kinetics of pyrolysis and partial oxidation.

While both carbon formation and carbon consumption processes occur in continuous combustion systems, the latter are very much slower. The optimum approach for preventing hardware distress and avoiding serious environmental consequences is to develop technology to avoid carbon formation while satisfying other system requirements (efficiency, gaseous emissions, hardware reliability, etc.).

NET SOOT GENERATION

The predominance of fundamental research activity has involved laminar premixed flames. Street and Thomas' work published in 1955 is extremely thorough in experimental detail and breadth of hydrocarbons examined, Ref. 4; it has become the classical paper in the field. Other publications are References 5-16. These investigations have universally confirmed that soot formation is a kinetically controlled process. Equilibrium calculations indicate that soot should not be present at fuel-air mixture conditions where the oxygen-to-carbon atomic ratio (O/C) is greater than one. That is, the general chemical equation

should define a soot formation threshold. All experimental results have shown soot formation at O/C substantially in excess of unity.

Another very important premixed flame experiment conducted at the British National Gas Turbine Establishment (NGTE) attempted to evaluate the effect of pressure on soot formation, Ref. 11. All previously mentioned work with premixed flames concerned atmospheric or sub-atmospheric conditions. The combustion system employed took special precautions to avoid flashing back to upstream locations, an additional difficulty associated with the high pressure operation. In addition to sooting limits, the amount of soot formed was determined and expressed as a "soot formation ratio" (the percent of fuel carbon evident as soot). The index of the soot quantity was found to increase with the cube of pressure. Very useful plots of pressure versus equivalence ratio for various values of soot formation ratio were presented. Examples are shown in Figure 1 for cyclohexane, cyclohexene, and benzene. Gas phase species were also determined during this testing and it was concluded that H₂O and CO₂ (oxygenated compounds not predicted by equilibrium for the system $C_xH_y + \frac{x}{2} O_2 \rightarrow xCO + \frac{y}{2} H_2$) are formed in substantial quantities and deplete the system of oxygen prior to consumption of all fuel.

Soot formation in laminar diffusion flames has also been studied, Refs. 17-20. The direct utility of this information for the gas turbine combustion application has been questioned, as the mixing rates and characteristic times for chemical reaction are very much different than those in the typical combustor. Shirmer, Ref. 21, has discussed the significant differences between such experiments and the actual combustion process. He is particularly critical of the use of the smoke point test as an index of fuel tendency to form carbon particulates. Turbulent diffusion flame results would appear to be more applicable, Ref. 22. Wright, Ref. 20, has examined soot formation in a diffusion flame burner and has published results of soot measured when the fuel side of the flame is supplemented with oxygen at concentrations well below O/C = 1. Surprisingly, it was found that the addition of oxygen increases soot formation up to an optimal rate at which the influence abruptly reverses and soot suppression is accomplished at higher O₂ concentrations.

Wright's work involving soot formation in the jet stirred reactor, Refs. 23, 24, is perhaps of most interest to this discussion -- it is a combustion process similar to that at which soot forms in the primary zone of an actual continuous combustion system. As in the previously mentioned studies, it was determined that soot forms at O/C > 1 but the strong backmixing of the jet stirred reactor did afford some broadening of the soot-free O/C ratio. In addition to the establishment of sooting limits, as determined by the color of the flame (luminous yellow versus blue), Wright determined the concentrations of soot formed for some limited conditions of O/C below the soot limit. No analysis of this "yield" data to determine soot formation kinetics was undertaken but it is recognized that more such data might provide the basis for global carbon formation chemical model.

MODELS OF SOOT FORMATION

Many studies on soot formation have been carried out, but few lead to quantitative

predictions of soot production, and there is little agreement as to the details of the mechanism. Nevertheless, there seems to be general agreement that the overall soot formation reaction is triggered by hydrocarbon pyrolysis and involves subsequent soot nuclei formation, soot particle formation, and particle growth and coagulation. A model that treats these in some detail has been considered by Jensen, Ref. 25. Application of the model to a methane flame has led to qualitative agreement with experimental observations. Although this approach represents an attempt to deal with the problem at a mechanistic level the uncertainty of intermediate species, reactions and rates requires long term development to provide quantitative predictions. Tesner, et al., Ref. 26, have proposed a model in which soot formation is characterized by three rate equations. The feature of the model is that all the complex elementary steps associated with pyrolysis, nuclei formation and soot formation are grouped into three subglobal steps which are characterized by three separate equations. The model includes a first order (with respect to hydrocarbon concentration) pyrolysis rate, a chain branching and chain termination rate, and a soot formation rate:

Values of the kinetic parameters (f, g, g_o, a, b) for acetylene and toluene are available, so that the model can be evaluated through comparison with experimental data. Comparisons with data developed in this investigation are presented later in this paper. Greeves, et al., Ref. 27, developed a model using diesel engine data obtained under high pressures. The model consists of a single global Arrhenius type equation:

$$\frac{dS}{dt} = 4.68 \times 10^5 P_{HC} \phi_u^3 e^{-40,000/RT} \quad 4$$

Where P_{HC} and ϕ_u are the local partial pressure of the unburnt hydrocarbon and the local equivalence ratio, respectively. This type of one-step model lumps all intermediate reactions associated with nuclei formation and soot formation into one rate equation, and the application of the model requires knowledge of the local hydrocarbon concentration and the unburnt equivalence ratio.

Attempts to correlate data developed in this investigation with Greeve's model, Equation 4, are presented in this paper.

The Greeves and Tesner models represent the essential state-of-the-art of practical soot prediction methods. However, the process requires information on certain intermediates that must be assumed in order to implement these models in a strictly predictive mode. This information includes, for example, the local hydrocarbon and oxygen concentrations as well as the temperature. In addition, net soot generation requires not only consideration of soot formation but its oxidation as well. These factors are included in the current model development.

QUASIGLOBAL MODEL

The essential feature of the quasiglobal concept is the coupling of a set of subglobal steps to a set of detailed steps for those reaction chains for which sufficient information to accurately describe their kinetics and mechanisms exists. The basic quasiglobal model is described in Ref. 28. In addition to having demonstrated the ability of the quasiglobal model to predict experimental observations it has been shown to be ideally structured to account for the variation in fuel type, i.e. aliphatic vs. cyclic, etc. Of particular interest here is the current work on fuel rich systems for which this basic model is being extended. The new model includes the following additional subglobal finite rate reaction steps given below in skeleton form:

Where BN represents the bound nitrogen. Reactions 5 through 10 are coupled to detailed mechanisms describing the rate at which H₂, CO and BN are converted to H₂O, CO₂ and NO_x. The rate constants for the subglobal steps are expressed in modified Arrhenius form and the rate of production (or consumption) is given by expression of the type:

$$\dot{C}_1 = A T^a C_1^b \exp(-E/RT) \quad 11$$

where the constants A, a, b, c and E are determined through controlled experiments. The

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reactions and rates associated with the detailed steps are based upon available literature values.

The quasiglobal model has been used successfully for high energy fuels, such as shell-dyne-H and H-methylcyclopentadiene, as well as for conventional fuels such as propane and JP-types. The versatility of this approach has been demonstrated by comparisons with experimentally determined combustion characteristics including ignition delay times for both long chain and cyclic type hydrocarbons reacting in air. For example, Figure 2 shows some typical results of such a comparison between predictions and data obtained from a steady flow reactor; Figures 3, 4, 5, and 6 show comparisons of predictions with current data obtained in a reactor described later. Figures 3 and 4 compare data with predictions for O_2 and CO concentrations. The agreement between the predictions and the data is very good. Of particular interest are the CO and hydrocarbon concentrations since they both relate to efficiency and emissions, while the hydrocarbon concentration relates to soot formation. Figure 5 shows the CO concentration comparison where data for three fuel types is given; a paraffin (isooctane), an aromatic (toluene), and an olefin (ethylene). While there are measurable differences amongst the fuel types the prediction for the CO concentration is reasonable, noting that the concentration levels are in percent. What is significant to note is the minimum in CO at equivalence ratios between .4 and .6 depending on the fuel. This minimum is reproduced by the prediction and is associated with the approach to blow-out at the low equivalence ratios where low temperatures (reduced reaction rates) enhance incomplete combustion, while at the higher equivalence ratios reaction rates increase since temperature is increasing, and although the system is out of equilibrium, the tendency toward equilibrium is consistent with the water gas shift reaction tending to increase CO (and H_2O). The ability of the quasiglobal model to predict this type of detail is relevant to the determination of "optimum" operating conditions and to scaling to other operating conditions. Of equal importance to the CO concentration is the fuel conversion and Figure 6 shows the hydrocarbon concentration as measured and compared with predictions. The comparison is favorable considering the low concentration levels of fuel existing in the system under the particular operating conditions. The rapid rise in the hydrocarbon concentration corresponds to the approach to blow out and is consistent with the increase in CO previously cited.

The examples cited above were used to illustrate some of the features of the quasiglobal model. For the prediction of net soot generation additional information related to reactions 8, 9 and 10 is required. The soot model is constructed in terms of two steps reflecting the dependence of net soot generation on the simultaneous formation and oxidation of soot particles. The soot formation rate is assumed to be a function of the hydrocarbon concentration, the oxygen concentration and the temperature, viz.

$$\dot{R}_{C(s)}^+ = A T^a C_{HC}^b C_{O_2}^{-a} e^{-E/RT} \quad 12$$

where A, b, a and E are constants. The oxidation step is based upon data involving the consumption of soot (and carbon) particles in oxidizing environments, from, for example the work of Lee, Thring and Beer, Ref. 29, and the work of Nagle and Strickland-Constable Refs. 30 and 31. For the Lee, Thring and Beer model the rate of consumption per unit surface area is given by

$$\dot{R}_{C(s)}^- = 1.085 \times 10^4 \frac{P_{O_2}}{T^3} \exp \left(- \frac{39,300}{RT} \right), \quad 13$$

where P_{O_2} is the partial pressure of oxygen in the mixture. Reactions 12 and 13 are combined to yield the net rate of soot production as a function of hydrocarbon and oxygen concentrations and temperature. The constants A, a, b, a and E have been determined from experimental data and it is interesting to note that net soot production is more strongly dependent upon the hydrocarbon concentrations than on the temperature. It is also important to note, as will be discussed later, that as much as 20-25 percent of the soot formed can be consumed by oxidation.

EXPERIMENTAL METHOD

The experimental program focused on a study of the soot formation process using the Jet-Stirred Combustor (JSC), shown schematically in Figure 7. This device is a modification of the Longwell-Weiss reactor, Ref. 32, with hemispherical geometry. The JSC has been used extensively in fluid mechanic and combustion modeling because combustion rates are limited by chemical kinetics as opposed to transport effects. A key advantage of the JSC for the work described here is that the strongly backmixed nature of this combustion process provides a simulation of the recirculating characteristics of the gas turbine primary zone. It is in this zone where mixture conditions are sufficiently rich to produce soot. Consequently, the JSC allows study of soot formation in an aerodynamic situation relevant to gas turbine systems. Another advantage of the stirred combustor is that the reactor is homogeneous in species concentration as well as temperature; each operating condition is characterized by a single set of temperature and concentration data rather than profiles of these parameters. This simplifies the tasks of obtaining and interpreting the data.

Details of the experimental apparatus and measurement techniques used have been reported by Blazowski, Ref. 38. The measurements include fuel and air mass flow rates and fuel/air mixture injection temperature, reactor gas samples and reactor internal and wall temperatures. Both gas-phase and particulate sampling systems are used, providing data on the incipient soot formation equivalence ratio and quantitative data on soot production (mg soot/liter).

EXPERIMENTAL RESULTS

Detailed experiments were conducted using the Jet Stirred Combustor to determine the soot formation characteristics of ethylene, a hydrocarbon thought to produce combustion information representative of aliphatics, and toluene, a condensed-ring aromatic. Substantial differences in the behavior of these two hydrocarbons were noted and a number of other hydrocarbons were studied to determine whether they behaved as C_2H_4 or as $C_6H_5CH_3$. Finally, the soot formation characteristics of two-component fuel blends and practical petroleum-derived fuels have been investigated.

Characteristics of Ethylene and Toluene

Jet Stirred Combustor experiments with ethylene showed that CO was the major carbon-containing species and remained at a concentration of about twelve mole percent for all equivalence ratios tested. Total hydrocarbons increased significantly with equivalence ratio but CO_2 decreased. Oxygen concentration was very low at an equivalence ratio of 1.77 but steadily increased at higher equivalence ratios--an indication of poor reactiveness as the mixture was further enriched. Further, THC concentrations were found to be very significant at the even below the incipient soot formation limit.

For toluene, CO was again found to be the predominant species. However, a substantial difference between the data for toluene and that for ethylene was observed: whereas with toluene, incipient soot occurred as hydrocarbons begin to "break through" under rich operating conditions, the soot limit for ethylene occurred at conditions where hydrocarbon concentration is high - a factor of 36 times that for toluene.

Results for these two fuels, described in detail in Ref. 33, indicate significant differences between the soot formation process for ethylene and toluene:

1. Toluene soots at a much lower equivalence ratio (1.35) than ethylene (1.95), and the amount of soot formed with increasing equivalence ratio beyond the incipient limit is much larger.
2. In the case of ethylene, significant amounts of hydrocarbons (~3-8% as CH_4) were present at equivalence ratios leaner than the soot limit, but with toluene the incipient soot limit corresponded approximately to the equivalence ratio for the initial presence of hydrocarbons in the combustion products.

Sooting Characteristics of Other Hydrocarbon Types

The observations for ethylene and toluene indicate that there is a fundamental difference in the soot formation mechanisms for these two fuels under the strongly backmixed conditions of the Jet Stirred Combustor. These findings lend support to the possibility of developing useful simplified overall chemical kinetic models of the soot formation process (quasi-global models) based on hydrocarbon type. In order to further develop this concept a large number of other fuel types were screened to determine whether their sooting characteristics were similar to ethylene or toluene, or if they showed characteristics distinctly different from either of these fuels.

It was found that all hydrocarbons tested might be grouped into three categories as follows:

Like C_2H_4	Like $C_6H_5CH_3$	Unlike C_2H_4 or $C_6H_5CH_3$
Hexane	O-xylene	1-methyl-naphthalene
Cyclo-hexane	M-xylene	
N-octane	P-xylene	
Iso-Octane	Cumene	
1-octene	Tetralin	
Cyclo-octane	Dicyclopentadiene	
Decalin		

The first group produced large amounts of exhaust hydrocarbons without sooting as did ethylene and in no case was significant soot observed. The second group produced soot at the mixture ratio which corresponded to hydrocarbon breakthrough. In all cases the measured hydrocarbon composition was less than one percent at the incipient limit. Another commonality in the second group is that the amount of soot produced as equivalence ratio was increased beyond the incipient limit was similar for all the hydrocarbons. 1-methyl-naphthalene was significantly different in this respect producing much higher soot quantities than those in the second category.

Sooting Characteristics of Fuel Blends

Blends of iso-octane and toluene were tested to determine the behavior of a two-component mixture with Group 1 (like- C_2H_4) and Group 2 (like- $C_6H_5CH_3$) hydrocarbons. These results are shown in Figure 8. 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. With less toluene in the blend, the concentration of hydrocarbons at the incipient limit tended to increase. These results indicate a combination of Group 1 and 2 behaviors; thus a combination of the analytical descriptions for toluene and iso-octane might be a reasonable approach for prediction of the sooting characteristics of fuel blends. An excellent correlation is obtained between soot concentration and hydrogen content, Fig. 9. This is in direct compliance

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with actual gas turbine tests, Ref. 1. The similarity between sooting characteristics in the JSC and those in an actual combustor is evident.

Mechanisms of Soot Formation

Many mechanistic models for soot formation have been proposed. Generally, it is recognized that condensed ring aromatic hydrocarbons can produce soot via a different mechanism than do aliphatic hydrocarbons. A simplified mechanism following Graham, et al., Refs. 34 and 35, is as shown schematically in Fig. 10.

Aromatic hydrocarbons can produce soot via two mechanisms: a) condensation of the aromatic rings into a graphite-like structure, or b) breakup to small hydrocarbon fragments which then polymerize to form larger, hydrogen deficient molecules which eventually nucleate and produce soot. Based on his shock tube studies of soot formation, Graham concludes that the condensation route is much faster than the fragmentation/polymerization route. Further, he has found that the mechanism by which an aromatic forms soot changes with temperature; below 1800 K the condensation path is favored while above this temperature the fragmentation/polymerization route is followed.

According to this simple model, aliphatics produce soot via the fragmentation/polymerization mechanism only. As a result, these hydrocarbons do not form the quantities of soot produced by the aromatics. Indeed, during the fuel rich combustion of a fuel blend composed of aromatics and aliphatics at a temperature less than 1800 K, the aromatic hydrocarbons would produce the major portion of soot. Combustion of the aliphatic portions of the fuel would influence temperature and hydrocarbon fragment concentration but soot formation via fragmentation/polymerization would be minimal. Above 1800 K, however, both the aliphatic and aromatic hydrocarbons would produce soot via the fragmentation /polymerization route.

The experimental results obtained in the present work are consistent with this model. It has been observed that soot formation with the condensed-ring aromatic fuels commences with the initial presence of hydrocarbons in the exhaust. If it is assumed that these breakthrough hydrocarbons maintain their aromatic character, this observation reflects the fast kinetics of the ring-building or condensation reactions. On the other hand, the aromatic molecule may be an effective source of C_2H_2 and high concentrations of acetylene as fuel pyrolysis occurs may be responsible for extensive soot production. Further, the results for 1-methyl-naphthalene indicate that a double-ring aromatic provides the most rapid soot formation of the hydrocarbons studied. This observation is also consistent with either the ring building view (i.e., the first ring-joining has already occurred) or the polymerization mechanism (i.e., even higher amounts of C_2H_2 are present in the pyrolysis zone).

These comparisons are not intended to establish the validity of any theory, but are noted to illustrate that the results obtained in this work complement existing simplified views of the soot formation process. Most importantly, the current results lend support to the utility of the approach of quasi global modeling of the soot formation process for various categories of hydrocarbons.

COMPARISON OF DATA WITH PREDICTIONS

The majority of the soot data obtained to date has been on fuel rich combustion of toluene/air mixtures. Initially, predictions based upon the models of Tesner and Greeves were made and compared with the measured soot concentration data, Fig. 11. Although the Greeves model exhibits the sensitivity to inlet equivalence ratio shown by the data neither of the two models adequately represents the experimental observations. The disparity between the current data and Greeves and Tesner models has not been fully reconciled. However, an examination of their methods for obtaining rate constants suggests that they may have been influenced by aerodynamic effects.

The current model is based upon a broader base of data than the previous models had available and is structured to separately account for pyrolysis and partial oxidation of the fuel as well as oxidation of the soot. For the present purposes Eqs. 12 and 13 are combined into a model for net soot emission from a perfectly stirred reactor, viz.

$$s = \frac{A T^a [HC]^b [O_2]^{-a} e^{-E/RT}}{\frac{\dot{m}}{\rho V} + \frac{6}{\rho_s d} \cdot \frac{1.085 \times 10^4 P_{O_2}}{T^2} e^{-39,300/RT} \cdot \left(\frac{K_m}{cm}\right)} \quad 14$$

where $[HC]$ and $[O_2]$ are the molar concentrations of the hydrocarbon and molecular oxygen, ρ is the mixture density, ρ_s is the soot density, $\dot{m}$ is input flow rate, V is the reactor volume and d is the soot particle diameter. Tentative values for the remaining rate parameters are:

$$\begin{aligned} A &= 5.0 \times 10^{13} & a &= 0.5 \\ a &= -2 & E &= 32,000 \text{ cal./mole} \\ b &= 1.75 \end{aligned}$$

Figure 12 shows the comparison of the present model predictions with data, based upon a soot particle size of 250μ . The air flow rate range covered by the data corresponds to a residence time range of from about 3 to 7 milliseconds. It should be noted that large scale unmixedness effects are the probable cause for the discrepancy observed at $\phi=1.9$ for the air mass flow rate of 50 gm/min. This point corresponds to incipient blowout where unsteadiness is observed. However, the results in general are very encouraging and seem to support the concept of modeling soot emissions in terms of the major species

present in the flame. Furthermore, the effect of soot oxidation can be significant. The predicted reduction in soot emissions ranges from 20-25% at the high air flow rate (short residence time) down to 9-13% at the lowest air flow rate (longest residence time). These results represent the first known attempt to characterize net soot generation from a stirred combustor. Work in progress is designed to provide information for validation of the models over wider ranges of operating conditions including above atmospheric pressure levels and on mixtures of fuel types. Development of the overall quasiglobal model represents the major goal of this chemically related element of the program.

PHYSICAL PROCESSES

Combustor modeling provides a means to obtain a quantitative understanding of primary combustion phenomena, such as liquid fuel droplet vaporization and burning, solid particle burning, gas phase chemical reaction kinetics, radiation heat transfer from combustion products, and mixing of reactants and combustion products. These processes are defined by the interaction of a number of mechanisms which are conveniently described in terms of physically or chemically related processes. The physical processes are:

1. Liquid fuel injection and atomization
2. Spray penetration and spreading
3. Droplet breakup
4. Droplet evaporation
5. Heat transfer by radiation and convection
6. Aerodynamic flow patterns
7. Turbulent mixing

and the chemical processes include:

1. Pyrolysis
2. Bound nitrogen conversion
3. Dropwise combustion
4. Gas phase oxidation
5. Particulate formation
6. Particulate oxidation

In this paper we have emphasized the modeling of the chemical processes listed above, but although we have grouped these processes separately they are mutually coupled in the combustion process. It is the treatment of this coupling that is the task of combustor modeling.

The concept of modular modeling provides a rational framework for the development of engineering models of combustor flowfields, and it is this concept that is being used in the work outlined in this paper. Fundamentally, modular modeling involves delineating characteristic regions of a combustor flowfield, treating each region in detail using a technique appropriate to its characteristics, and coupling these treatments together through their boundary conditions (Refs., 36, 37, 38). The characteristic regions may be defined by their scale, for example, in the treatment of fuel injection phenomena for which an appropriate scale is related to the size of the injector orifice, or by their fluid dynamics, as in the representation of recirculation zones as opposed to regions in which there is a characteristic flow direction.

Gas turbine combustors involve fuel and dilution air injection regions, recirculation regions, and regions in which a single characteristic velocity field exists. In early modular model formulations, Refs., 39 and 40, these combustors were represented by a combination of plug-flow reactors, well-stirred reactors, or both, with the interconnection between model elements supplied by empirical information. The modular model used in this work differs in two major ways from these early formulations: detailed flowfield modeling replaces the one-dimensional plug flow reactors of the early models, and the coupling between model elements is computed rather than empirically specified. Thus far more detail can be obtained from the model results, providing a greater quantitative understanding of the primary combustion phenomena described at the beginning of this section.

In the modular formulation described in Refs. 36, 37, 38, the combustor flowfield characteristic regions are regions of recirculating flow and regions in which a characteristic flow direction can be assigned: directed flow regions. The recirculating flow is characterized as a well-stirred reactor, while the directed flow is described using a detailed solution of the boundary-layer form of the governing equation. This is not, however, the only way in which the model formulation can be carried out. For example, a detailed calculation of the overall combustor flowfield can be carried out, using simple overall reaction models to characterize the combustor heat release, and then coupled to a detailed chemical kinetics treatment in regions of the combustor in which the flowfield solution shows a detailed treatment is required. In this way, a modular formulation based on reaction kinetics is obtained. This type of modular model is described by Swithenbank, A. Turan, and P. G. Felton in paper No. 2 of this meeting; a similar approach is being used in the work outlined here to assist in the development of the modular formulation described in Refs. 36, 37, 38.

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CLOSURE

The information being generated in this program provides an improved understanding of the processes important to alternate fuels utilization. The "end item" is an analytical model which allows prediction of fuel effects in various types of continuous combustion devices, particularly gas turbines. Such a development will provide combustor designers with a tool to develop fuel flexible combustion systems which can utilize synfuels which are produced with minimum refining/upgrading and, hence, minimum cost and energy consumption during refining.

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ACKNOWLEDGEMENT

This work was supported by the U.S. Department of Energy, Division of Fossil Fuel Utilization (Contract No. EC-77-C-03-1543). Dr. J. Birkeland of DOE is the responsible Program Manager and Dr. J. Fisher of Argonne National Laboratory is the Technical Program Monitor.

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Figure 1. Effect of Pressure and Mixture Strength On Soot Formation
(S denotes flame stability limit, T the soot formation threshold, and numbers indicate conditions producing a constant "soot formation ratio") From Reference 37.

Figure 2. Experimental Ignition Delay Time Data Comparison with Quasiglobal Kinetics Predictions for Aliphatic and Cyclic Type Hydrocarbons

Figure 3. Comparison of Predicted and Measured O_2 Concentration, Isooctane.

Figure 4. Comparison of Predicted and Measured CO_2 Concentration, Isooctane.

Figure 5. Comparison of Predicted with Measured CO Concentrations.

Figure 6. Comparison of Predicted and Measured Hydrocarbon Concentration, Isooctane.

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Figure 7. Schematic of Jet Stirred Combustor.

Figure 8. Soot Production vs. Equivalence Ratio for Toluene and Toluene/Iso-Octane Blends at 300 C Inlet Temperature and 112.5 gm/min Air Flow.

Figure 9. Dependence of Soot Production on Hydrogen Content of Toluene/Iso-Octane Blends.

Figure 10. Simplified Soot Formation Mechanism. ...

Figure 11. Comparison of Greeves and Tesner Model with Soot Production Data.

Figure 12. Comparison of Present Model Prediction with Soot Production Data For Toluene/Air Mixtures.

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W. S. Blazowski
Exxon Research and Engineering Company,
London, NJ

**A. F. Sarofim
J. C. Keck**
Massachusetts Institute of Technology,
Cambridge, MA

The Interrelationship between Soot and Fuel NO_x Control in Gas Turbine Combustors

The decreased hydrogen content of future fuels will lead to increased formation of soot, while increased organically bound nitrogen in the fuel can result in excessive NO_x emission. Control concepts for these two problems are in conflict: prevention of soot requires leaner operation while control of emissions from fuel nitrogen requires fuel-rich operation. However, recent results of two DOE research programs point to both processes having a major dependence on "hydrocarbon breakthrough." Control of both fuel nitrogen conversion and soot formation can be achieved by primary zone operation at equivalence ratios just below that for hydrocarbon breakthrough. This paper reviews the evidence for the importance of hydrocarbon breakthrough, explains our current understanding of why hydrocarbon breakthrough is important, and offers suggestions of how these results might be applied.

Introduction

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 [1-3]. 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. Originally-bound nitrogen is effectively converted to NO_x¹ in conventional combustion systems. NO_x is also formed thermally by fixation of N₂ and O₂ 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 [4], 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.

It is well known that soot production is reduced by operating combustion systems leaner (i.e., with more excess air) in the soot formation zone. In premixed systems or other processes not significantly influenced by droplet burning, the equivalence ratio² at which soot begins to form is greater than 1.0. Since the gas turbine combustion system operates with a low overall equivalence ratio ($\phi \sim 0.3$) it would seem that soot-free operation is routinely achievable. Unfortunately, stabilization of the combustion process requires a portion of the combustor, the primary zone, to be operated at stoichiometric or fuel rich mixture ratios. Further, reduction of fuel nitrogen-to-NO_x conversion requires fuel-rich operation (i.e., $\phi > 1.0$) in the first stage of the combustion process. Consequently, a working knowledge of the interrelationships between the soot formation and fuel nitrogen conversion processes during fuel-rich operation is vital to the development of future combustion systems capable of utilizing the lower hydrogen, higher nitrogen fuels of the future.

This paper presents research results of two organizations conducting independent programs for the U.S. Department of Energy which together provide important practical insight into the interrelationships between the soot formation and fuel nitrogen conversion problems. It has been found that both processes have a major dependence on the presence of hydrocarbons in the combustion process. The sooting limit corresponds to mixture conditions at which hydrocarbons are first observed in the first stage combustion products (the hydrocarbon breakthrough point) and the minimum fuel nitrogen conversion to NO_x occurs at the highest fuel-air ratio prior to the hydrocarbon breakthrough point. Strategies to prevent both soot formation and fuel nitrogen conversion should account for these important phenomena and control concepts might be based on this information.

² Equivalence ratio, ϕ , is the actual fuel-air ratio divided by the stoichiometrically correct fuel-air ratio. Values less than one correspond to lean operation while values greater than one indicate fuel-rich operation.

¹ NO_x is the general symbol which represents the sum of NO and NO₂ emission from a source.

Contributed by the Gas Turbine Division for presentation at the Gas Turbine Conference and Products Show, New Orleans, La., March 10-13, 1980 of THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS. Manuscript received at ASME Headquarters December 13, 1979. Paper No. 80-GT-76.

Copies will be available until November 1980.

Fig. 1(a) Fraction of fuel carbon converted to each exhaust product for ethylene-air combustion [19]

The balance of this paper is organized into three major sections. The first addresses current evidence that hydrocarbon breakthrough is critical to the soot formation and fuel nitrogen conversion processes. In general, the background work on soot formation was performed at Exxon Research while the fuel nitrogen conversion results were obtained at MIT. The second major section provides our current understanding of why hydrocarbon breakthrough is important to these processes. The third provides some insight on how these results might be applied in a gas turbine system. Use of the information could take the form of guidance for design, explanation of available results, or development of control concepts.

Evidence of Hydrocarbon Importance

Soot Formation. While both carbon formation and carbon consumption processes occur in continuous combustion systems, the latter are very much slower. The optimum approach for preventing hardware distress and avoiding serious environmental consequences is to develop combustion systems which avoid carbon formation while satisfying other system requirements (efficiency, gaseous emissions, hardware reliability, etc.).

The predominance of fundamental research activity has involved laminar premixed flames. Street and Thomas' work published in 1955 is extremely thorough in experimental detail and breadth of hydrocarbons examined [5]; it has become the classic paper in the field. Other publications are references [6-17]. Equilibrium calculations indicate that soot should not be present at fuel-air mixture conditions where the oxygen-to-carbon atomic ratio (O/C) is greater than one. That is, the general chemical equation:

should define a soot formation threshold. However, all experimental results have shown soot formation at O/C substantially in excess of unity, thus proving that the process is kinetically controlled.

The most relevant work to the present interest—soot formation in gas turbine systems—has been recently conducted using a highly-backmixed, experimental combustor [18-20]. As noted above, most previous soot formation research had employed laminar premixed flames. The laminar aerodynamic situation is very different than that in the soot-forming region of continuous combustion devices like the gas turbine where combustion products are usually backmixed with incoming fuel and air in a strong, highly-turbulent recirculation zone. Therefore, soot formation experiments conducted in a highly-backmixed combustion environment are the most relevant here.

The highly backmixed combustion studies of soot formation have been conducted using the Jet Stirred Combustor. The device used was a modification of the Longwell-Weiss reactor [21] with hemispherical geometry. The reaction zone was 5.08 cm in diameter and had 25 radial exhaust ports of 3.2 mm dia. Combustion experiments were conducted

Fig. 1(b) Fraction of fuel carbon converted to each exhaust product for toluene-air combustion (air mass flow = 112.5 gm/min, inlet temperature = 300 °C) [19]

at atmospheric pressure with a range of residence times of 0.6 to 4 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, CO₂, THC³, O₂), the incipient soot equivalence ratio, and soot production (mg/l). A complete description of the experiment can be found in references [18-20].

The previously reported Jet Stirred Combustor results [18-20] included an evaluation of the fuel-rich combustion and soot formation characteristics of a number of pure hydrocarbons. Groups of the hydrocarbons tested were found to behave similarly and three categories of hydrocarbons were defined. The groupings were as follows:

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

The first group produced large amounts of exhaust hydrocarbons (i.e., many percent based on equivalent flame ionization detector response to methane) without sooting and in no case was significant (i.e., measurable at the mg/l level) soot observed.

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 limit. Figure 1 compares the behavior of ethylene (from Group 1) and toluene (from Group 2). The illustration presents the portions of fuel carbon converted to CO, CO₂ and THC. Hydrocarbon concentrations are very significant at and even below the incipient soot limit in the case of ethylene combustion, but for toluene the soot limit corresponds to the hydrocarbon breakthrough equivalence ratio.

Another commonality in the second group is that the incipient soot limit of these fuels was 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

³ THC = Total hydrocarbons present in the exhaust products; expressed in volumetric concentration as if their composition was entirely methane.

Fig. 2 Soot production for various pure hydrocarbons at 300°C inlet temperature and 112.5 gms/min air flow [19]

Fig. 3 Soot production versus equivalence ratio for toluene and toluene/iso-octane blends [20]

and having an even lower soot formation equivalence ratio (see Fig. 2). Consequently, this double-ring aromatic represents a third category of hydrocarbon soot forming characteristic.

Blends of iso-octane and toluene were tested to determine the behavior of a two-component mixture with Group 1 and Group 2 hydrocarbons. Results are shown in Fig. 3. Mixtures with 50 or more percent toluene produced soot while a 25 percent 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.

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 (see Table 1). For example, with 50 percent toluene, the hydrocarbon concentration was 2.4 percent at the incipient soot limit, while with 100 percent toluene this value was 0.2 percent. 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.

Taken together, these results allow us to develop the following conclusions concerning soot formation in gas turbines utilizing synthetic liquids:

- Future synfuels having low H-content due to high concentrations of single ring (Group 2) and double ring (Group 3) aromatics are capable of producing substantial quantities of soot.
- The amount of soot produced will be related to the amount of

FUEL COMPOSITION = $\text{CH}_{1.7}$

TEMPERATURE = 2000 K

$$\sum X_{\text{NO}_x} = X_{\text{NO}_2} + X_{\text{NO}} + X_{\text{HNO}} + X_{\text{HNO}_2}$$

$$\sum X_{\text{NH}_i} = X_{\text{N}} + X_{\text{NH}} + X_{\text{NH}_2} + X_{\text{NH}_3}$$

$$\sum X_{\text{CN}} = X_{\text{CN}} + X_{\text{HCN}} + X_{\text{HNCO}} + X_{\text{NCO}} + 2X_{\text{C}_2\text{N}_2} + 2X_{\text{C}_2\text{N}} + X_{\text{C}_2\text{N}}$$

$$\sum = \sum X_{\text{NO}_x} + \sum X_{\text{NH}_i} + \sum X_{\text{CN}}$$

Fig. 4 Equilibrium fixed nitrogen species mole fractions as a function of fuel equivalence ratio. Fuel composition = $\text{CH}_{1.7}$, $T = 2000 \text{ K}$ [22]

Table 1 Combustion product hydrocarbon concentrations in jet stirred combustor experiments

	At Incipient Soot Limit		At Blow-out Point	
	ϕ	% HC	ϕ	% HC
100% Toluene	1.39	0.2	—	—
87.5% Toluene/ 12.5% Isooctane	1.41	0.15	—	—
75% Toluene/ 25% Isooctane	1.40	1.21	—	—
62.5% Toluene/ 37.5% Isooctane	1.49	0.82	—	—
50% Toluene/ 50% Isooctane	1.5	2.4	—	—
25% Toluene/ 75% Isooctane	—	—	1.61	7.12
10% Toluene/ 90% Isooctane	—	—	1.51	7.0

Group 2 and (especially) Group 3 compounds present in the fuel.

- Most importantly, in the case of highly aromatic fuels, the soot limit will correspond to the equivalence ratio at which hydrocarbons become a significant (~1 percent) combustion product.

As stated in the introductory section, the prevention of significant soot production should be accomplished in a combustion process which also minimizes fuel nitrogen conversion. The following subsection presents the evidence of the important influence of hydrocarbon breakthrough on this other process.

Fuel Nitrogen Conversion. It is well recognized that the production of nitric oxide by the combustion of fuels containing organically bound nitrogen can be suppressed by operating the first stage of the combustor fuel rich. The questions of what is the maximum attainable reduction in bound nitrogen conversion and what is the optimum first-stage equivalence ratio needed to achieve the maximum reduction are closely related to the presence of hydrocarbon species during the combustion process, that is, hydrocarbon breakthrough.

Consideration of the effect of increasing equivalence ratio on the equilibrium concentration of bound nitrogen species provides a measure of the constraints on the use of a staged combustion process to reduce NO_x emissions [22]. Representative calculations summarized in Fig. 4 for a flame temperature of 2000K and a fuel with an atomic hydrogen/carbon ratio of 1.7 show that increasing equivalence ratio decreases the concentration of nitrogen oxides ($\sum X_{\text{NO}_x}$) but increases that of amines ($\sum X_{\text{NH}_i}$) and cyanides (X_{CN}). It is vital to design the first stage of the combustion process to minimize amines and cyanides as well as NO_x because, if formed, these species will al-

Fig. 5 Joint plot of laminar and turbulence diffusion flame data. (a) flat flame data for $C_2H_2/O_2/He/Ar$ flame at $\phi = 1.6$ with 2.5 percent N as NH_3 . $T < 2120$ K (b) turbulent diffusion flame data for kerosene/air flame at $\phi = 1.5$ with 1.0 percent N as pyridine. $T \sim 1900$ K [23]

most completely convert to NO_x in the fuel lean second stage. The emission of total fixed or bound nitrogen ($\Sigma X_{NO_x} + \Sigma X_{NH_3} + \Sigma X_{CN}$) passes through a minimum at a ϕ of about 2.4.

The equilibrium concentration of bound nitrogen species at the minimum (slightly more than 1 ppm) is, however, not attained in practice. The factors which prevent the attainment of the equilibrium concentration are: (1) the relatively slow rate at which fuel nitrogen species are converted to the thermodynamically-stable and environmentally-preferred molecular nitrogen, (2) the interaction of hydrocarbon species with nitric oxide at higher equivalence ratios to form HCN which reacts even more slowly to N_2 , thus providing an upper bound on the ϕ which can be used in practice, and (3) mixing constraints. Selected results from the program at MIT showing the importance of these three factors are presented below.

The kinetic constraints can be inferred from time-resolved measurement of HCN, NH_3 , and NO obtained in the combustion products of a laminar flat flame of ethylene doped with ammonia (Fig. 5(a)) and the spray combustion of kerosene doped with pyridine (Fig. 5(b)). Several points need to be made. First, although the fuel nitrogen in the premixed flame was added to the flame as NH_3 , most of the bound nitrogen at the first sampling point was in the form of HCN. It is only after the hydrocarbons decay that the ammonia concentration, that NH_3 to be found in the combustion products, begins to increase. Secondly, the rate of decay of the HCN and NO in the post flame gases shows the very slow rate of approach towards equilibrium. Finally, the behavior of the products of combustion for the pyridine-doped kerosene flame is qualitatively similar to that of the ethylene/ NH_3 system, but the time frame is stretched due to the critical additional constraint of mixing in the spray flame.

Examining the effect of equivalence ratio on bound nitrogen species concentrations measured in the premixed flame (Fig. 6) suggests that the optimum value of ϕ is about 1.8. The difference between the experimentally observed ϕ for minimum fixed nitrogen and that calculated from equilibrium considerations (i.e., 1.8 versus 2.4) is at-

Fig. 6 Residual nitrogen species (dry basis) and temperature profiles as a function of fuel equivalence ratio, at 30 mm above the burner surface. $C_2H_4/O_2/He$ flames doped with NH_3 , $He/O_2 = 6.02$ [28]

Fig. 7 HCN versus unburned hydrocarbons: $\phi = 1.5$; $T_{inlet} = 600$ K; $\circ$ Kerosene doped with Pyridine to 1 percent N by mass; $\square$ kerosene; $X/D = 5.0$ [23]

tributable to the presence of hydrocarbons beyond $\phi = 1.8$ which allows substantial retention of fixed nitrogen as HCN. At these higher equivalence ratios HCN is by far the dominant species—the minima expresses a boundary where leaner operation is characterized by NO dominance and richer operation results in copious HCN. When at $\phi = 1.8$, this flame is still effective in consuming the initial fuel and no significant hydrocarbon concentrations are observed in the downstream portions of the flame system.

The equivalence ratio for minimum total fixed nitrogen is reduced to an even lower value in the spray flame where hydrocarbons persist at $\phi > 1.5$ due to unmixedness. The influence of hydrocarbons on the emission can be seen from the studies of reference [23] which concern the emissions from both kerosene and pyridine-doped kerosene flames. The values of HCN observed in the combustion products are plotted against the total hydrocarbon content (as measured by a flame ionization detector) in Fig. 7. It is clear that the levels of HCN for both doped and undoped fuels increased with increasing hydrocarbon content. Again it was found that the optimum ϕ for minimizing bound nitrogen emissions is determined by trade-offs between NO and HCN emissions; the optimum ϕ is close to the point at which hydrocarbons breakthrough and HCN shows a corresponding sharp increase at equivalence ratios beyond this point. For the kerosene spray combustor the ϕ for minimum emission of fixed nitrogen was in the range of 1.5.

Current Understanding

Soot Formation. Many mechanistic models for soot formation have been proposed and a number of references to these have been included. Generally, it is recognized that condensed ring aromatic hydrocarbons can produce soot via a different mechanism than do aliphatic hydrocarbons. A simplified mechanism following Graham, et al. [16,17] is shown in Fig. 8.

Aromatic hydrocarbons can produce soot via two mechanisms: (1) condensation of the aromatic rings into a graphite-like structure, or (2) breakup to small hydrocarbon fragments which then polymerize to form larger, hydrogen-deficient molecules which eventually nucleate and produce soot. Based on his shock tube studies of soot formation, Graham concludes that the condensation route is much faster than the fragmentation/polymerization mechanism. Further, he has proposed that the mechanism by which an aromatic forms soot changes with temperature, below 1800 K the condensation path is favored while above this temperature the fragmentation/polymerization route is followed.

While the aliphatic soot formation process also involves complex reactions of the polynuclear species [15], these influences are far less dominant than for the aromatics. Accordingly, this simple model shows aliphatics producing soot predominantly through the slower fragmentation/polymerization mechanism. As a result, these hydrocarbons do not form the quantities of soot produced by the aromatics. Indeed, during the fuel-rich combustion of a fuel blend composed of aromatics and aliphatics, the aromatic hydrocarbons would produce the major portion of soot. Combustion of the aliphatic portions of the fuel influence temperature and hydrocarbon fragment concentration but soot formation via fragmentation/polymerization is small relative to that of aromatics.

The experimental results are consistent with this model. It has been observed that soot formation with Group 2 fuels commences with the initial presence of hydrocarbons in the exhaust. If we assume that these breakthrough hydrocarbons maintain their aromatic character, this observation may reflect the fast kinetics of the ring-building or condensation reactions. On the other hand, the aromatic molecule may be an effective source of C_2H_2 and high concentrations of acetylene as fuel pyrolysis occurs may be responsible for extensive soot production. Further, the results for 1-methylnaphthalene indicate that a double-ring aromatic provides the most rapid soot formation of the hydrocarbons studied. This observation can also be viewed as consistent with either the ring building view (i.e., the first ring-joining has already occurred) or the polymerization mechanism (i.e., even higher amounts of C_2H_2 present in the pyrolysis zone).

Fuel Nitrogen Conversion. The importance of the reactions of NO and hydrocarbons to form HCN has long been recognized [24-26]. Two of the reactions cited for HCN formation from NO are

These radical fragments will be present during the pyrolysis of most hydrocarbons and the NO-hydrocarbon reaction is therefore expected to be less sensitive to hydrocarbon type than soot formation. More data are needed to establish the extent to which NO-hydrocarbon reaction may be affected by the fuel type.

The conclusions regarding the importance of THC concentrations previously drawn are reinforced by these mechanistic considerations and the message to the combustor designer continues to be to operate a combustor at conditions that minimize hydrocarbons breaking through with the combustion products, i.e., minimize the reactants responsible for soot and HCN formation.

Application of Findings

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. This paper proposes 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 compo-

Fig. 8 Equation (2)

sition. 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 [27]. 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 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 is minimized by operating the reaction zone as rich as possible without the presence of hydrocarbons. 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 which should be emphasized 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 con-

ditions approaching homogeneity 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 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.

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 THC 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.

Conclusion

The effective use of future synthetic fuels in gas turbines will require the development of two-stage combustion systems which minimize both soot formation and the conversion of fuel-bound nitrogen to NO_x . Recent results show that incipient sooting limits for highly aromatic fuels correspond to mixture conditions at which hydrocarbons are first observed in the combustion products (the hydrocarbon breakthrough point) and that minimization of fuel nitrogen conversion requires operating at the highest fuel-air ratio prior to the hydrocarbon breakthrough point. This paper concludes that the first stage of an advanced combustion system should be operated as a fuel rich stirred reactor. The design of such a system must insure that hydrocarbons are not present in substantial quantities in the first stage and measurements of first stage THC could be an important part of future combustor development programs. This paper also concludes that some form of THC measurement (physical probe, emission, absorption, or luminosity) might be employed as an effective control to maintain optimum combustor performance over the entire range of engine operation.

Acknowledgment

This work was supported by the U.S. Department of Energy under contracts EC-77-C-03-1543 (at Exxon) and AER75-15916 (at MIT). Dr. J. Birkeland of DOE was the responsible Program Manager and

Dr. J. Fischer of Argonne National Laboratory was the technical program monitor.

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Printed in U.S.A.

79-GT-155

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Dependence of Soot Production on Fuel Blend Characteristics and Combustion Conditions

W. S. BLAZOWSKI

Exxon Research and Engineering Co.,
Government Research Lab.,
Linden, N. J.

Liquid synthetic fuels derived from non-petroleum resources will play a major role in meeting future national energy demands. In the case of gas turbine applications, it is known that the different properties of these fuels can result in substantially altered combustion performance. Most importantly, decreased fuel hydrogen content resulting from an increased aromatic content has been observed to result in increased exhaust smoke and particulates as well as greater flame luminosity. This paper contributes empirical information and insight which allows the greater soot formation tendencies of low hydrogen content fuels to be better understood. A small-scale laboratory device which simulates the strongly back-mixed conditions present in the primary zone of a gas turbine combustor is utilized. The Jet Stirred Combustor provides for very rapid mixing between a premixture of vaporized fuel and air and the combustion products within a 5.08-cm-dia hemispherical reactor. Results to be presented are gaseous combustion product distributions, incipient soot limits, and soot production (mg/l) for a variety of fuels. The influences of combustor inlet temperature and reactor mass loading have been evaluated and the sooting characteristics of fuel blends have been studied. These results have been analyzed to develop useful correlations which are in general agreement with existing mechanistic concepts of the soot formation process.

Contributed by the Gas Turbine Division of The American Society of Mechanical Engineers for presentation at the Gas Turbine Conference & Exhibit & Solar Energy Conference, San Diego, Calif., March 12-15, 1979. Manuscript received at ASME Headquarters January 3, 1979.

Copies will be available until December 1, 1979.

Dependence of Soot Production on Fuel Blend Characteristics and Combustion Conditions

W. S. BLAZOWSKI

ABSTRACT

Liquid synthetic fuels derived from non-petroleum resources will play a major role in meeting future national energy demands. In the case of gas turbine applications, it is known that the different properties of these fuels can result in substantially altered combustion performance. Most importantly, decreased fuel hydrogen content resulting from an increased aromatic content has been observed to result in increased exhaust smoke and particulates as well as greater flame luminosity. This paper contributes empirical information and insight which allows the greater soot formation tendencies of low hydrogen content fuels to be better understood. A small-scale laboratory device which simulates the strongly back-mixed conditions present in the primary zone of a gas turbine combustor is utilized. The Jet Stirred Combustor provides for very rapid mixing between a premixture of vaporized fuel and air and the combustion products within a 5.08 cm diameter hemispherical reactor. Results to be presented are gaseous combustion product distributions, incipient soot limits, and soot production (mg/l) for a variety of fuels. The influences of combustor inlet temperature and reactor mass loading have been evaluated and the sooting characteristics of fuel blends have been studied. These results have been analyzed to develop useful correlations which are in general agreement with existing mechanistic concepts of the soot formation process.

INTRODUCTION

Characteristics of the basic feedstocks from which the future liquid fuels 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 significantly decreased hydrogen content. In the case of gas turbines these characteristics can be expected to result in increased soot formation, increased flame radiation (which can affect the integrity of combustor hardware), and increased deposit forming tendency, possibly resulting in plugging and fouling of equipment. Another significant difference between conventional petroleum and synthetic crudes is nitrogen content. Depending on the extent of refining performed, increased NO_x emission from fuel bound nitrogen may also be a problem. Finally, as a result of the generally lower volatility of synthetic crudes, synfuels might be expected to be less volatile than petroleum-derived fuels thereby causing problems associated with fuel evaporation or droplet burning.

In his plenary session paper "Synthetic Fuels and Combustion" at the 16th International Combustion Symposium, J. P. Longwell discussed the rationale for the utilization of synthetic liquid fuels without extensive refining (1). The incentives for following this route were shown to be very significant from the standpoints of energy conservation and cost. For combustion engineers and researchers, the task at hand is one of evaluating the impact of changes in fuel character and defining the range of fuel characteristics within which the system can operate. With this expanded insight, new fuel-flexible designs might be developed which allow operation with minimum cost and energy consumption.

The U.S. Air Force has initiated one such program for defining future military aircraft fuels (2). The combustion effects of future fuels are to be characterized along with other system factors (e.g., fuel tank design, pumps, handling requirements, etc.) and fuel processing information is to be acquired. A trade-off

analysis will then determine the characteristics (a future fuel specification) which will result in minimum total operating cost and adequate availability without significant sacrifice in safety, performance, or environmental impact. With respect to availability, geographic variability in the staple resource and in refining capability will cause combustion system flexibility to be an important asset.

In the case of gas turbines for future electric power generation, the potential for combined cycle operation makes it imperative that technology be developed to allow operation on liquid synfuels with minimum refining (3). 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.

An analysis of the combustion research requirements brought about by the need for development of fuel-flexible engines (4) indicates that the problem of soot formation resulting from utilization of low hydrogen content, highly-aromatic fuels should receive high priority. The present paper addresses this need. A small-scale combustion device, the Jet Stirred Combustor, has been used to study the soot formation process under strongly backmixed combustion conditions similar to that occurring in the primary zone of a gas turbine combustor. Most previous studies of soot formation involve laminar pre-mixed or diffusion flames--aerodynamic situations far removed from that occurring in the gas turbine combustor--and the present results are believed to be more applicable to gas turbine soot formation. Reference 4 contains an extensive listing of previous publications.

Previously reported Jet Stirred Combustor results (5) concerned the fuel rich combustion and soot formation characteristics of a number of pure hydrocarbons. It was found that all hydrocarbons tested might be grouped into three categories as follows:

Group 1	Group 2	Group 3
Ethylene	Toluene	1-methyl-napthalene
Hexane	O-xylene	
Cyclo-hexane	M-xylene	
N-octane	P-xylene	
Iso-octane	Cumene	
1-octane	Tetralin	
Cyclo-octane	Dicyclopentadiene	
Decalin		

The first group produced large amounts of exhaust hydrocarbons (i.e., many percent based on equivalent flame ionization detector response to methane) without sooting and in no case was significant (i.e., measurable in terms of mg/l) soot observed. 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 limit. Another commonality in the second group is that 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 the hydrocarbons. 1-methyl-napthalene was significantly different in this respect producing much higher soot quantities than those in the second category.

The purpose of this paper is to present additional experimental results which concern soot formation characteristics of fuel blends and the impact of operating conditions on soot formation. The fuel blend evaluation considered a two-component mixture composed of a Group 1 and a Group 2 hydrocarbon. Operating characteristics which were evaluated included reactor mass loading (mass flow into the reactor) and inlet temperature. Information presented below is organized into four further sections. Section II concerns the experimental system, Section III presents results, Section IV discusses the experimental findings, and Section V is a summary.

EXPERIMENTAL

The experimental program reported here focused on study of fuel-rich combustion and soot formation processes using the Jet-Stirred Combustor (JSC). This device is a modification of the Longwell-Weiss reactor (6) with hemispherical geometry. The JSC has been used extensively in fluid mechanic and combustion modeling because combustion rates are limited by chemical kinetics as opposed to transport effects. A key advantage of the JSC for the present program is that the strongly backmixed nature of this combustion process provides a simulation of the recirculating characteristics of the gas turbine primary zone. It is in this zone where mixture conditions are sufficiently rich to produce soot. Consequently, the JSC allows study of soot formation in an aerodynamic situation relevant to gas turbine systems. Another advantage of the stirred combustor is that the reactor is homogeneous in species concentration as well as temperature; each operating condition is characterized by a single set of temperature and concentration data rather than profiles of these parameters. This simplifies the tasks of obtaining and interpreting data.

The reactor (Figure 1) consists of an outer shell of castable refractory shaped as two halves of a sphere, 15.2 cm in diameter. Materials used in fabricating these reactors are Super Castable 3200, Fractocrete 3400, or Castable 141A, all products of Combustion Engineering Refractories. The upper hemisphere is solid with the exception of the hole through which the reactants are brought to the injector. The lower portion is hollowed out to a hemispherical reaction zone of 5.08 cm diameter and has twenty-five holes of 3.2 mm diameter through which the burned mixture exhausts. Combustion experiments are conducted at atmospheric pressure with a range of residence times from 0.6 to 4 ms.

FIGURE 1

The Jet Stirred Combustor

Fuel and air are metered separately through calibrated rotameters, preheated to the desired inlet temperature and then mixed before entering the combustor. Air and fuel heating to temperatures of 350 C (and fuel prevaporization in the case of liquids) is accomplished in an aluminum block heater. Separate coils for fuel and air are embedded in the solid aluminum block which is wrapped with electrical resistance heaters. In the case of liquid fuels, a small flow of N₂ is maintained through the fuel coil to atomize the fuel and provide for smooth vaporization. Atomization is achieved at the entrance to the heater with a Spraying Systems Company 1/4 JSS air atomizing nozzle. In this configuration, a central jet (0.2 mm diameter) of fuel is atomized by the strong shearing forces caused by a co-axial jet (between diameters of 1.2 and 1.6 mm) of N₂.

The temperature of the fuel/air stream is determined immediately before injection. This measurement is input to a digital controller which provides power to the block heater to maintain injector inlet temperature within ± 10 C of the set point. The fuel-air mixture enters the reaction zone through an Inconel injector which is a hemisphere of 1.27 cm diameter into which are drilled forty radial holes of 0.5 mm diameter. Reactants enter the reaction zone as small sonic jets which stir the reactor contents and produce a mixture of essentially uniform temperature and composition in a characteristic time which is very short compared with the average residence time.

A probe is inserted through one of the twenty-five exhaust ports to extract a sample. Special care has been taken to prevent condensation of water or unburned hydrocarbons within the probe and sample lines, as high concentrations of these constituents are expected at mixture ratios of interest in this study. The sampling probe is hot-water (~ 80 C) cooled and has a constant-area cross section two mm in diameter. Sample flow is 1-2 l/min. The gas sample is transferred through electrically-heated sample lines to a sample conditioning oven containing all filters, valves, and pumps. The lines and oven are maintained at 150 C.

Gas analysis is accomplished with conventional process instrumentation. A filter within the oven removed particulates from the sample stream sent to the gas analysis instrumentation. A first gas stream leaving the oven is transferred through hot (~ 150 C), electrically-heated lines to a Beckman Model 402 flame ionization detector for total hydrocarbon (THC) measurement. This instrument has a vast dynamic range allowing determination of hydrocarbon concentrations ranging from the parts-per-million level through tens of mole percent. The hydrocarbon instrument was calibrated with a mixture containing CH₄ and all reported THC results are "as methane". A second sample gas stream leaving the oven is chilled to eliminate condensable water (to a dew point of about 10 C) and hydrocarbons prior to introduction into NDIR analyzers for CO and CO₂ measurements.

The particulate sampling system uses different filters located within the sample-conditioning oven. Two 47 mm filters sealed in a stainless steel holder were used in "series". The first was a Millipore Mitex (Teflon) filter with a 5 μ m pore size; the second was a Gellman Type AE with a 0.3 μ m pore size. The Teflon filter was found to be necessary to prevent the glass fiber material from sticking to the Viton O-Ring sealing the filter holder. Nearly all the soot collected was found on the first (Teflon) filter.

The incipient soot formation equivalence ratio was the simplest determination of sooting characteristics pursued during this program. For this information, data are taken at increasing equivalence ratio¹ increments of 0.1 until a filter deposit is observed. Results presented will, therefore, represent an equivalence ratio value midway between test points at which soot was observed.

Soot production (mg soot/liter) was determined by a differential weighing procedure. The Teflon filters were not preconditioned to drive off moisture--it was experimentally found that this is not necessary. The glass-fiber filters were conditioned by overnight drying in an oven at 150 C followed by at least four hours in a desiccator. The Teflon and dried glass-fiber filters were then pre-weighed together and stored in the desiccator until actual use. After soot collection the samples were kept in a desiccator overnight to drive-off moisture remaining from the combustion gases which had passed through. Final weighing was then performed on a Mettler H20 balance. In general, 10 standard liters of gas passed through each filter produced a collection of soot sufficient for weighing. A wet test meter was used to determine this total volume throughput which usually required less than ten minutes to accomplish.

Under many conditions it was evident that significant soot had deposited along the inner wall at the probe tip during sampling. In these cases the deposited soot was limited to a few mm of the probe tip and was removed with a fine wire to be included with the filters in the differential weighing procedure. Under lightly-sooting conditions the fraction of the total soot determination attributed to the deposit was a small fraction of that on the filters. However, at highly-sooting conditions, the deposit weight could be equivalent to the filter contribution.

RESULTS

The previously reported results of this program (5) concerned detailed soot formation information for ethylene and toluene and the conclusion that these fuels behave in distinctly different ways. Data to be discussed below concern the dependence of sooting characteristics for these two fuels on reactor mass flow and inlet temperature. In addition, results will be presented which provide new information regarding the soot formation characteristics of fuel blends. Mixtures of iso-octane and toluene (from Groups 1 and 2 as described in the Introduction) were evaluated as was a commercial Jet A fuel.

Sooting Dependence On Operating Conditions

Ethylene was the first fuel studied under fuel-rich conditions at which soot may form. However, the amount of soot produced with ethylene is very small and no measurements of soot production were made. Experimental observations are limited to the incipient soot mixture ratio and the gas species concentrations in the neighborhood of the incipient soot limit.

The dependence of the incipient soot formation limit on reactor inlet mixture flow rate and inlet temperature was determined. Figure 2 illustrates

¹ Equivalence ratio, ϕ , is the actual fuel-air ratio divided by the stoichiometrically correct fuel-air ratio. Values less than one correspond to lean operation while values greater than one indicate fuel rich operation.

the dependence of the incipient soot formation limit on inlet mass flow rate for ethylene-air combustion at an inlet temperature of 25 C. The flow rate effect appears to be significant with soot limit equivalence ratio increasing from 1.85 to 2.25 over the flow range tested (70-160 gm air/min). It can be postulated that residence time effects--particularly the effect of reduced burnedness as JSC loading is increased--are important to ethylene's soot formation process in the well mixed situation. This will be discussed further in Section IV.

FIGURE 2

Incipient Soot Limit Equivalence Ratio
Dependence on Mass Flow for
Ethylene-Air Combustion (Inlet Temperature = 25 C)

Data presented in Table 1 indicate that the temperature effect on the incipient soot limit is not measurable over the range of ethylene air combustion conditions investigated (25-300 C). Wright (7,8) reported a continuous increase in incipient soot equivalence ratio with increasing temperature in a JSC experiment but considered a broader range of temperatures and identified the critical O/C by observing flame color.

Table 1

Incipient Soot Limit Dependence on Inlet
Temperature for Ethylene-Air Combustion

(m _{air} = 110 g/min)		
Temp.	ϕ	% HC
25 C	1.95	5.0
100 C	1.85	3.2
200 C	1.95	4.3
300 C	1.95	3.4

A notable temperature effect observed during this testing was that the darkness of the filter observed at the lowest sooting equivalence ratio increased with mixture inlet temperature. At 25 C the darkness of the soot deposit was very light with increased darkness as temperature was elevated. Another observation was that at mixture ratios richer than the soot limit the soot deposit on the filter first became darker but then lighter as the blowout mixture ratio was approached.

The incipient soot limit behavior of toluene was determined as a function of inlet mass flow and inlet mixture temperature (at 200, 250, and 300 C). No distinct relationship between the incipient soot limit and these parameters was uncovered. Using the same technique used in evaluating C₂H₄--leanest operation at which a soiled filter was observed--the limit was consistently found to be 1.35.

Figure 3 illustrates the dependence of soot production on mixture inlet temperature for toluene-air mixtures. As has been noted previously, the incipient soot limit was not substantially influenced by inlet temperature. However, these data illustrate that mixture inlet temperature (and flame temperature) increases result in greater soot production at the higher equivalence ratios.

FIGURE 3

The influence of reactor loading on toluene soot production is shown in Figure 4. These data correspond to operation at air mass flows of 50, 80, and 112.5 gm/min and at an inlet mixture temperature of 300 C. Note that while the incipient soot limit was not significantly affected by mass flow, soot production was substantially less at the lower air mass flow condition. An explanation of this behavior and interpretation of the practical implications of these findings is reserved for the discussion section which follows. The results of Figure 4 also indicate that soot production increases very significantly as the mixture equivalence ratio increases. However, translation of the data to fraction of fuel carbon as soot indicates that, even at the worst condition, less than 1% of the fuel carbon is converted to soot.

These results for toluene and ethylene indicate a number of potentially important differences between the effects of operating conditions on the soot formation processes of the Group 1 and Group 2 hydrocarbons:

- Toluene soots at a much lower equivalence ratio (1.35) than ethylene (1.95) and the amount of soot formed with ϕ beyond the incipient limit is much larger.
- The incipient soot limit for ethylene was found to vary with mass flow, but this was not the case for toluene.

Results presented previously (5) provide a third important difference between Groups 1 and 2 which complements those above. Namely, in the case of Group 1 hydrocarbon combustion, significant amounts of hydrocarbons ($\sim 3\text{--}8\%$ as CH_4) were present at equivalence ratios leaner than the soot limit but with the Group 2 hydrocarbons the incipient soot limit corresponded approximately to the equivalence ratio for the initial presence of hydrocarbons in the combustion products.

FIGURE 4
Dependence of Toluene Soot Production
on Mass Loading (Inlet Temperature = 300 C)

Sooting Characteristics Of Fuel Blends

Blends of iso-octane and toluene were tested to determine the behavior of a two-components mixture with like- C_2H_4 and like- $\text{C}_6\text{H}_5\text{CH}_3$ hydrocarbons. These results are shown in Figure 5 and Table 2. 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. It was also determined that with less toluene in the blend, the concentration of hydrocarbons at the incipient limit tended to increase. For example, with 50% toluene, the hydrocarbon concentration was 2.4%, while with 100% toluene this value was 0.20%. 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.

A commercial aviation turbine fuel, Jet A, was also tested. This fuel produced soot, but in amounts less than the 50% toluene/50% iso-octane blend discussed above. Further, the incipient soot limit equivalence ratio was found to be greater than that of the 50% blend ($\phi = 1.7$ vs 1.5). These results are consistent with the previous observations in that the Jet A has a hydrogen content of about 13.9%, midway between the 50% toluene blend (11.9%) and the 25% toluene blend (14.6%) which did not soot.

Attempts to test two coal liquids were made. These were both COED samples supplied by FMC of Princeton, New Jersey. The first was produced from Utah Coal while the second utilized a Western Kentucky coal. Both tests failed as these fuels were found to plug the atomizing nozzle utilized in the fuel pre-vaporizer. The 0.008 inch diameter fuel orifice became plugged with a gum-like substance which prevented fuel flow.

/ FIGURE 5

Soot Production vs Equivalence Ratio for
Toluene and Toluene/Iso-Octane Blends, at 300 C
Inlet Temperature and 112.5 gm/min Air Flow

DISCUSSION

The discussion below provides further interpretation of these results. Key items addressed are:

- Correlation of fuel blend soot production results with blend overall hydrogen content
- Assessment of soot production trends with exhaust product THC
- Comparison of current results with soot formation theories.

Hydrogen Content Correlation

The toluene/iso-octane soot production data illustrated in Figure 5 may also be examined to evaluate the effect of fuel hydrogen content, a parameter often reported as useful in correlating sooting characteristics. At constant equivalence ratios of 1.6 and 1.8, an excellent correlation implying a linear relationship is evident (see Figure 6). Actual gas turbine combustor testing has also found an approximately linear relationship between fuel hydrogen content and soot production (9) and the results discussed here indicate an important similarity between sooting in the well-characterized JSC and that in an actual combustor.

Another interesting implication of the Figure 6 correlation is that the JSC might be a tool useful in better relating fundamental fuel characteristics to combustion behavior. In this context, it will be useful to examine the Figure 6 correlation for other two component blends and for three and four component blends. This should provide the means of combining semi-or quasi-global models of the soot formation process for various hydrocarbon types to describe a fuel blend (see References 3 and 4 for a description of this approach). For example, it may be that in iso-octane/1-methyl-naphthalene blend will produce a steeper soot production/hydrocarbon content trend than is evident for the toluene/iso-octane blend. Work of this type might result in new insight regarding the ranking of the soot production potential of various continuous combustion system fuels.

Trends With THC

Throughout this paper and Reference 5 the concept that exhaust total hydrocarbon content is a key

Table 2

Fuel Blend Screening Results

Fuel	Incipient Soot Limit ⁽¹⁾		S _T ⁽²⁾ @ ISL + 0.2φ		S _T @ ISL + 0.4φ	
	φ	% HC	mg/l	% HC	mg/l	% HC
100% Toluene	1.39	0.20	0.118	1.72	0.765	5.88
87.5% Toluene/12.5% Iso-octane	1.41	0.15	.160	2.2	0.63	5.25
75% Toluene/25% Iso-octane	1.40	1.21	.122	4.88	(4)	
62.5% Toluene/37.5% Iso-octane	1.49	0.82	.165	3.85	(4)	
50% Toluene/50% Iso-octane	1.50	2.4	.060	6.75	(4)	
25% Toluene/75% Iso-octane	1.61 ⁽³⁾	7.12				
10% Toluene/90% Iso-octane	1.51 ⁽³⁾					

- (1) For screening purposes. Incipient soot limit (ISL) is condition at which soot was first noted on a clean filter.
 (2) S_T = Total soot combination of soot on filter and in probe.
 (3) Does not soot--highest equivalence ratio value obtained prior to blowout.
 (4) Rich blowout occurred before condition could be reached.

FIGURE 6

Dependence of Soot Production in Hydrogen Content of Toluene/Iso-Octane Blends

parameter in soot formation has been proposed. In analyzing the data obtained it has been found that useful correlations can be developed. Before presentation of this information, however, it is necessary to more closely examine the data which has been produced very near the rich blowout point. It will be concluded below that some of the data corresponded to operation beyond the rich blowout point. In these cases, the reactor operated sporadically with fuel passing through uncombusted at times and the system behaving as a pyrolysis or coker system.

Data for which this situation existed have been identified by close examination of the temperature information obtained. Close review of the results indicate that in many cases the measured and/or calculated reactor temperature is less than that of the thermocouple embedded furthest within the castable refractory. That is, the reactor is hotter than the combustion products and, therefore, must be supplying heat to the reactants. Naturally, this is an unstable process which leads to the sporadic combustion which was observed. These data must be considered as not directly relevant to the current study and have been discriminated against in the correlations which are to be discussed below.

The correlation involving THC as the key parameter involves the previously-reported results for toluene soot production variation with JSC mass load-

ing (Figure 4). It was determined that these data for 50, 80, and 112.5 gm air/min could be correlated with combustion product total hydrocarbon concentration. These results are illustrated in Figure 7. The shaded data points in this graph correspond to operating conditions believed to be beyond the rich blowout point and are not considered in developing the correlation. The implication of the trend pictured in Figure 7 is that regardless of residence time the factor most important to soot production is the reactor hydrocarbon concentration. Consequently, reduced reactor mass loading (longer residence time) causes increase reactedness (or combustion efficiency) and the decrease in hydrocarbon soot precursors results in less soot production. This information has the practical implication that soot production (and flame luminosity) in gas turbines can be minimized by reducing primary zone mass loading.

Comparison With Theory

Many mechanistic models for soot formation have been proposed (10-28). Generally, it is recognized that condensed ring aromatic hydrocarbons can produce soot via a different mechanism than do aliphatic hydrocarbons. A simplified mechanism following Graham, et al (18, 19) is as follows:

Aromatic hydrocarbons can produce soot via two mechanisms: a) condensation of the aromatic rings into a graphite-like structure, or b) breakup to small hydrocarbon fragments which then polymerize to form larger,

FIGURE 7

Correlation of Figure 4 Soot Production Data with Hydrocarbon Concentration (Shaded data points indicate operation beyond rich blowout.)

hydrogen deficient molecules which eventually nucleate and produce soot. Based on his shock tube studies, Graham concludes that the condensation route is much faster than the fragmentation/polymerization route. According to this simple model, aliphatics produce soot via the fragmentation/polymerization mechanism only. As a result, these hydrocarbons do not form the quantities of soot produced by the aromatics. Indeed, during the fuel rich combustion of a fuel blend composed of aromatics and aliphatics, the aromatic hydrocarbons would produce the major quantity of soot. Combustion of the aliphatic portions of the fuel would influence temperature and hydrocarbon fragment concentration but soot formation via fragmentation/polymerization would be minimal.

The experimental results presented here are consistent with this model. As the amount of toluene in the toluene/iso-octane fuel blends increased, more soot was formed and the incipient limit equivalence ratio decreased with increasing percent toluene. Moreover, the quantity of hydrocarbons present at the soot limit increased as the amount of iso-octane in the blend increased. This implies that exhaust hydrocarbons produced by breakdown or pyrolysis of iso-octane produce soot by the slow polymerization route while the breakthrough hydrocarbons with toluene produce soot much more effectively by the ring condensation route. Furthermore, the presence Group 1 and Group 2 behavior evident here indicates that a combination of the analytical descriptions for the two categories might be a reasonable approach for predictions involving fuel blends.

In the variable air flow experiments with toluene (Figure 7) soot production is closely related to hydrocarbon presence in the exhaust. If we assume that these hydrocarbons maintain their aromatic character, this observation reflects the fast kinetics of the ring-building or condensation reactions. Unfortunately, the present results involve flame ionization detector measurements of total hydrocarbons only. Future efforts to determine the nature of these hydrocarbons are necessary to evaluate this important assumption.

These experimental/mechanism comparisons are not intended to firmly establish the validity of any theory. For example, an equally suitable mechanism can be postulated where the aromatic pyrolysis process supplies very large C_2H_2 concentrations which then can result in substantial soot formation. The observations are presented to illustrate that the results do complement existing simplified views of the soot formation process. Most importantly, the current results lend optimism to the simple engineering approach of quasi-global modeling of the soot formation process.

SUMMARY

Liquid synthetic fuels of the future will be substantially lower in hydrogen content than those currently utilized. Optimal utilization of this resource will involve devising means of altering combustion systems to allow the use of these resources with minimum processing for upgrading. This paper presents results concerning soot formation in a strongly back-mixed combustion device which is representative of gas turbine primary zones.

The influences of combustor inlet temperature and reactor mass loading have been evaluated and the sooting characteristics of fuel blends have been studied. It was shown that toluene (representative of aromatic constituents in fuels) has an incipient soot formation limit which is not dependent on mass flow while that for ethylene (representative of the aliphatic constituents of fuel) was a function of this parameter. Incipient sooting limits did not vary with inlet temperature, but soot production (at equivalence ratios beyond the limit) for toluene did increase with inlet temperature. Toluene soot production does depend on reactor mass loading in a manner which implies that minimization of soot formation within the primary zone of a gas turbine requires that the zone not be highly loaded.

Fuel blend investigations involved study of toluene/iso-octane blends, Group 1 and Group 2 mixtures; Reference 5 established the distinctly different sooting characteristics of these two hydrocarbon categories. Soot production increased and incipient soot limit equivalence ratio decreased with more toluene in the blend. A correlation between fuel hydrogen content and soot production was established and testing of a commercial Jet A proved consistent with these results. Collectively, these results strongly support the use of the Jet Stirred Combustor for fundamental studies of soot formation in continuous combustion systems. The findings also imply that the JSC may be a useful tool in assessing the soot production potential of various fuels.

All results described here were found to be consistent with a simple soot formation mechanism. While these comments do not prove or confirm the validity of the mechanism, confidence that simple, quasi-global soot formation mechanisms might be developed for use in analytical models of combustion systems is gained by the agreement.

Finally, a note of caution must be expressed. The present results involve a very well mixed system with a vapor fuel. Complications arising from droplets within the combustion zone and turbulence/chemistry coupling via unmixedness which are present in real systems must be taken into account. Future experiments in this program are oriented towards obtaining information to address these questions.

ACKNOWLEDGEMENT

This work was supported by the U.S. Department of Energy, Power Systems Division (Contract No. 77-C-03-1543). Dr. J. Birkeland of DOE is the responsible Program Manager and Drs. R. Dean Pierce and J. Fisher of Argonne National Laboratory are the technical program monitors. The author is grateful to Mr. Robert Schroeder of Exxon Research and Engineering Company for his contributions to the design of the experimental system and performance of the experimental program.

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DEPENDENCE OF SOOT PRODUCTION ON FUEL STRUCTURE
IN BACKMIXED COMBUSTION

By

W. S. Blazowski

Exxon Research and Engineering Company
Government Research Laboratories
Linden, New Jersey 07036

Submitted to

Combustion Science and Technology

Revised Jan. 25, 1979

ABSTRACT

Experimental results are described which identify the dependence of soot production on fuel molecular structure in strongly backmixed combustion. This type of aerodynamic process simulates that occurring within the primary zone of many continuous combustion devices (e.g. the gas turbine) where fuel-air ratio conditions are sufficiently rich to form appreciable quantities of soot. Results to be presented are gaseous combustion product distributions, incipient soot limits, and soot production. These parameters have been developed for a variety of hydrocarbons which represent constituents of practical fuels--normal and cyclic paraffins, olefins, single-ring aromatics, and double-ring aromatics. Substantial differences in sooting behavior between the aromatic and aliphatic hydrocarbons have been found and important observations regarding the presence of unburned hydrocarbons at and near the soot limit have been made.

I. INTRODUCTION

With increased emphasis on the utilization of U.S. energy resources for national self-reliance, coal and alternate (synthetic) fuels are expected to play an important role in future energy developments. This paper reports important experimental results obtained as part of a U.S. Department of Energy program to develop an improved understanding of alternate fuel effects in continuous combustion systems. The work is limited to investigation of alternate liquid fuels used in continuous combustion systems, with gas turbine systems receiving special attention. Future electric power generation with combined cycle gas turbines makes it highly desirable that technology be developed to allow operation on liquid synfuels with minimum refining (Cooper and Duncan, 1978). 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. The results of this program will also benefit the second important gas turbine application, aircraft propulsion. In this case, the future use of lower hydrogen content fuels can improve availability (a vital consideration for military applications) and reduce cost (Churchill et.al., 1978).

Characteristics of the basic feedstocks from which the future liquid fuels 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 significantly decreased hydrogen content. These characteristics can be expected to result in increased soot formation, increased flame radiation (which can affect the integrity of combustor hardware), and increased deposit forming tendency, possibly resulting in plugging and fouling of equipment. Another significant difference between conventional petroleum and synthetic crudes is nitrogen content. Depending on the extent of refining performed, increased NO_x emission from fuel bound nitrogen may also be a

problem. Finally, as a result of the generally lower volatility of synthetic crudes, snyfuels might be expected to be less volatile than petroleum-derived fuels thereby causing problems associated with fuel droplet burning.

Experimental findings reported here relate to the problems associated with the increased sooting characteristics of lower hydrogen content non-petroleum liquids. This reduced hydrogen content is due to the increased presence of aromatic hydrocarbons which are known to be very effective soot producers. While both carbon formation and consumption processes occur within continuous combustion systems like the gas turbine, the latter process is very much slower. Therefore, prevention of the luminous flame radiation and smoke/particulate emissions problems will require minimization of soot formation.

It is well known that soot production is reduced by operating combustion systems leaner (i.e. with more excess air) in the soot formation zone. However, there are two important complications associated with the lean combustion approach. First, the stability and ignition capabilities of the combustion process are compromised, an especially important consideration for aircraft turbine applications. Secondly, control of fuel nitrogen-to- NO_x conversion, an important consideration for future ground based turbines, requires fuel-rich operation as a first stage of the combustion process. Consequently, a working knowledge of the soot formation process and the influences of various hydrocarbon types is vital to the development of future combustion systems capable of utilizing the lower-hydrogen, higher nitrogen fuels of the future.

Present results concern the impact of fuel structure on the soot production process in highly backmixed combustion. Most previous experimental studies have been conducted using laminar premixed and diffusion flames. These aerodynamic situations are very different from that found

in the soot forming region of many continuous combustion devices, especially the gas turbine. In the actual hardware, combustion products are backmixed with the incoming fuel and air in a strong recirculation zone and, therefore, experiments conducted in a well-stirred combustion reactor are much more meaningful.

Wright (1968 and 1970) evaluated the sooting characteristics of various hydrocarbons with such an experimental device. These results were compared with pre-mixed laminar flame data much of which was obtained by Street and Thomas (1955). It was found that the incipient soot limit mixture ratios for various hydrocarbons in the JSC were in the same relative order as determined in pre-mixed laminar flames but that the incipient limits in the JSC occurred at somewhat richer mixture conditions. This paper expands upon previous investigations of sooting under strongly backmixed conditions by presenting information which describes temperature and species concentrations at sooting conditions and defines critical differences in the soot production characteristics of various hydrocarbons. The effects of inlet mixture temperature, residence time, and fuel blending have also been investigated and are the subject of a separate paper (Blazowski, 1979).

The paper is organized into four further sections. A description of the experimental procedures employed is offered in Section II while results are presented in Section III. Discussion of the results is included in Section IV and Section V provides a summary.

II. EXPERIMENTAL

The experimental program focused on study on the soot formation process using the Jet-Stirred Combustor (JSC). This device is a modification of the Longwell-Weiss reactor (Longwell and Weiss, 1955) with hemispherical geometry. The JSC has been used extensively in fluid mechanic and combustion modeling because combustion rates are limited by chemical kinetics as opposed to transport effects. A key advantage of the JSC for the present program is that the strongly backmixed nature of this combustion process provides a simulation of the recirculating characteristics of the gas turbine primary zone. It is in this zone where mixture conditions are sufficiently rich to produce soot. Consequently, the JSC allows study of soot formation in an aerodynamic situation relevant to gas turbine systems. Another advantage of the stirred combustor is that the reactor is homogeneous in species concentration as well as temperature; each operating condition is characterized by a single set of temperature and concentration data rather than profiles of these parameters. This simplifies the tasks of obtaining and interpreting the data.

The reactor (Figure 1) consists of an outer shell of castable refractory shaped as two halves of a sphere, 15.2 cm in diameter. Materials used in fabricating these reactors are Super Castable 3200, Fractocrete 3400, or Castable 141A, all products of Combustion Engineering Refractories. The upper hemisphere is solid with the exception of the hole through which the reactants are brought to the injector. The lower portion is hollowed out to a hemispherical reaction zone of 5.08 cm diameter and has twenty-five holes of 3.2 mm diameter through which the burned mixture exhausts. Combustion experiments are conducted at atmospheric pressure with a range of residence times from 0.6 to 4 ms.

FIGURE 1

The Jet Stirred Combustor

Fuel and air are metered separately through calibrated rotameters, preheated to the desired inlet temperature and then mixed before entering the combustor. Air and fuel heating to temperatures of 350°C (and fuel prevaporization in the case of liquids) is accomplished in an aluminum block heater. Separate coils for fuel and air are embedded in the solid aluminum block which is wrapped with electrical resistance heaters. In the case of liquid fuels, a small flow of N_2 is maintained through the fuel coil to atomize the fuel and provide for smooth vaporization.

The temperature of the fuel/air stream is determined immediately before injection. This measurement is input to a digital controller which provides power to the block heater to maintain injector inlet temperature within $\pm 10^\circ C$ of the set point. The fuel-air mixture enters the reaction zone through an Inconel injector which is a hemisphere of 1.27 cm diameter into which are drilled forty radial holes of 0.5 mm diameter. Reactants enter the reaction zone as small sonic jets which stir the reactor contents and produce a mixture of essentially uniform temperature and composition in a characteristic time which is very short compared with the average residence time.

The temperature within the reactor was determined with a platinum/platinum-13% rodium thermocouple positioned such that the thermocouple bead was continuously exposed to the highly turbulent flow within the reactor. Six other thermocouples positioned with the refractory material and on the outside shell were used to determine condition heat loss from the JSC.

A probe is inserted through one of the twenty-five exhaust ports to extract a sample. Special care has been taken to prevent condensation of water or unburned hydrocarbons within the probe and sample lines, as high concentrations of these constituents are expected at mixture ratios of interest in this study. The sampling probe is hot-water cooled and sample transfer is accomplished using electrically heated sample lines.

Gas analysis is accomplished with conventional process instrumentation. A filter within the oven removes particulates from gases passing to the instrumentation. A first gas stream leaving the oven is transferred through hot ($\sim 150^{\circ}\text{C}$), electrically-heated lines to a Beckman Model 402 flame ionization detector for total hydrocarbon (THC) measurement. This instrument has a vast dynamic range allowing determination of hydrocarbon concentrations ranging from the parts-per-million level through tens of mole percent. The hydrocarbon instrument was calibrated with a mixture containing CH_4 and all reported THC results are "as methane". A second sample gas stream leaving the oven is chilled to eliminate condensable water (to a dew point of about 10°C) and hydrocarbons prior to introduction into NDIR analyzers for CO and CO_2 measurements.

The particulate sampling system uses different filters located within the sample-conditioning oven. Two 47 mm filters sealed in a stainless steel holder were used in "series". The first was a Millipore Mitex (Teflon) filter with a $5\text{ }\mu\text{m}$ pore size; the second was a Gellman Type AE with a $0.3\text{ }\mu\text{m}$ pore size. The Teflon filter was found to be necessary to prevent the glass fiber material from sticking to the Viton O-Ring sealing the filter holder. Nearly all the soot collected was found on the first (Teflon) filter.

The incipient soot formation equivalence ratio* was the simplest determination of sooting characteristics pursued during this program. For this information, data is taken at increasing equivalence ratio increments of 0.1 until a filter deposit is observed. Results presented will, therefore, represent an equivalence ratio value midway between test points at which soot was observed.

*Equivalence ratio, ϕ , is the actual fuel-air ratio divided by the stoichiometrically correct fuel-air ratio. Values less than one correspond to lean operation while values greater than one indicate fuel rich operation.

Soot production (mg soot/liter) was determined by a differential weighing procedure. The Teflon filters were not preconditioned to drive off moisture--it was experimentally found that this is not necessary. The glass-fiber filters were conditioned by overnight drying in an oven at 150°C followed by at least four hours in a desicator. The Teflon and dried glass-fiber filters were then pre-weighed together and stored in the desicator until actual use. After soot collection the samples were kept in a desicator overnight to drive-off moisture remaining from the combustion gases which had passed through. Final weighing was then performed on a Metler H20 balance. In general, 10 standard liters of gas passed through each filter produced a collection of soot sufficient for weighing. A wet test meter was used to determine this total volume throughput which usually required less than ten minutes to accomplish.

Under many conditions it was evident that significant soot had deposited at the tip of the probe during sampling. In these cases the deposited soot was limited to a few mm of the probe tip and was removed with a fine wire to be included with the filters in the differential weighing procedure. Under lightly-sooting conditions the fraction of the total soot determination attributed to the deposit was a small fraction of that on the filters. However, at highly-sooting conditions, the deposit weight could be equivalent to the filter contribution.

III. RESULTS

Detailed experiments were conducted to determine the soot formation characteristics of ethylene, a hydrocarbon thought to produce combustion information representative of aliphatics, and toluene, a condensed-ring aromatic. Substantial differences in the behavior of these two hydrocarbons were noted and a number of other hydrocarbons were studied to determine whether they behaved as C_2H_4 or as $C_6H_5CH_3$.

Ethylene Sooting Characteristics

Ethylene was the first fuel studied under fuel-rich conditions at which soot may form. However, the amount of soot produced with ethylene is very small and no measurements of soot production were made. Experimental observations are limited to the incipient soot mixture ratio and the gas species concentrations in the neighborhood of the incipient soot limit.

Gas species at the incipient limit were determined for ethylene-air mixtures at $25^\circ C$ and a number of air mass flows. Figure 2 illustrates typical results for the incipient soot limit behavior of ethylene air mixtures at an air flow rate of 160 gm/min at $25^\circ C$. CO was the major carbon-containing species and remained at a concentration of about twelve mole percent for all equivalence ratios tested. Total hydrocarbons increased significantly with equivalence ratio but CO_2 decreased. Oxygen concentration was very low at an equivalence ratio of 1.77 but steadily increased at higher equivalence ratios--an indication of poor reactedness as the mixture was further enriched.

The concentrations of H_2 and H_2O as well as the reactor temperature were calculated from these data. Inside reactor temperature was determined by an enthalpy balance between incoming total enthalpy, outgoing

FIGURE 2: Measured Combustion Product Concentrations for Rich Ethylene-Air Combustion
(Air Flow = 160 gm/min, Inlet Temperature = 25°C)

total enthalpy, conduction heat loss, and radiative heat loss. Note that since the radiative heat loss is a sensitive function of reactor temperature, iterative calculation between the enthalpy balance and radiative heat loss was necessary. The enthalpy balance required knowledge of H_2 and H_2O concentrations. Since these concentrations were not measured, they could be determined only with the assumption that the combustion products are in partial equilibrium where the water-gas equilibrium relationship is obeyed. In general, it was found that calculated and measured reactor temperatures agreed to within 10% at all operating conditions except those near blowout (Blazowski et.al. 1978).

Temperature, H_2 and H_2O concentration results are shown in Figure 3. Temperature varies from about 1900 to 1520 K over the 1.77 to 2.27 range of equivalence ratio studied. Calculated hydrogen concentration increases with equivalence ratio to about 9.6 mole percent at $\phi = 2.27$. H_2O decreases from about 9.2 at $\phi = 1.77$ to 4.7 mole percent.

Finally, it is of interest to examine the fraction of fuel carbon which is converted to each carbon-containing exhaust product, CO, CO_2 or THC. Figure 4 illustrates the portions of fuel carbon converted to CO, CO_2 , and total hydrocarbons for these same conditions of ethylene air combustion. As indicated, CO is by far the predominant species. It is important to note that THC concentrations are very significant at and even below the incipient soot formation limit in the case of C_2H_4 combustion--a sharp contrast to this behavior will be described below for toluene-air combustion.

Toluene Sooting Characteristics

Gas phase species concentrations at and beyond the incipient soot limit for toluene-air combustion were obtained and are presented in Figure 5. These data were obtained at an inlet temperature of 300°C with an inlet air flow rate of 112.5 gm/min. The plot illustrates typical gas

FIGURE 3: Calculated H₂ and H₂O Concentrations and Reactor Temperature for Rich Ethylene Air Combustion (Air Flow = 160 gm/min, Inlet Temperature = 25°C).

FIGURE 4: Fraction of Fuel Carbon Converted to Each Exhaust Product For Ethylene-Air Combustion (Data from Figure 2).

FIGURE 5: Fraction of Fuel Carbon Converted to Each Exhaust Product for Toluene-Air Combustion (Air Mass Flow = 112.5 gm/min, Inlet Temperature = 300°C).

phase behavior by displaying the portions of fuel carbon converted to CO, CO₂, and total hydrocarbons. These data have a lower bound on equivalence ratio of 1.29 because below this value, reactor temperature exceeds refractory material limitations (about 2033°K). As with ethylene, CO is the predominant species. However, a substantial difference between these data and C₂H₄ results was observed. Whereas with toluene incipient soot occurs as hydrocarbons begin to "break thru" under rich operating conditions, ethylene's soot limit occurs at conditions where hydrocarbon concentration is high (a factor of 36 times that for toluene).

Typical results for toluene soot production are shown in Figure 6. These data correspond to operation at an air mass flow of 112.5 gm/min and at an inlet mixture temperature of 300°C. These results indicate that soot production increases very significantly as the mixture equivalence ratio increases. However, translation of the data to fraction of fuel carbon or soot indicates that, even at the worst condition, less than 1% of the fuel carbon is converted to soot.

These results for toluene indicate a number of important differences between the soot formation processes of ethylene and toluene:

- a) Toluene soots at a much lower equivalence ratio (1.35) than ethylene (1.95) and the amount of soot formed with ϕ beyond the incipient limit is much larger.
- b) In the case of C₂H₄ combustion, significant amounts of hydrocarbons (~3-8% as CH₄) were present at equivalence ratios leaner than the soot limit but with toluene the incipient soot limit corresponded approximately to the equivalence ratio for the initial presence of hydrocarbons in the combustion products.

FIGURE 6: Dependence of Toluene Soot Production on Equivalence Ratio (Inlet Temperature = 300°C, Air Flow = 112.5 gm/min)

Sooting Characteristics of Other Hydrocarbon Types

The observations described above indicate a fundamental difference in the soot formation mechanisms for C_2H_4 and $C_6H_5CH_3$ under the strongly backmixed conditions of the Jet Stirred Combustor. These findings lend support to the possibility of developing useful simplified overall chemical kinetic models of the soot formation process (quasi-global models) based on hydrocarbon type. In order to further develop this concept it is necessary to screen a large number of other fuel types to determine whether they behave like C_2H_4 or like $C_6H_5CH_3$ or have soot formation characteristics distinctly different than C_2H_4 or $C_6H_5CH_3$.

Results are summarized in Table 1. Air flow was set at 112.5 gm/min and the fuel-air mixture entered the reactor at 300°C for these tests.* The first column lists the fuels tested. They are grouped into alkanes and alkenes, single-ring aromatics, and double-ring compounds. Incipient soot formation limit values of equivalence ratio, hydrocarbon concentration, and measured reaction temperature have been listed in the second column. In cases where rich blowout was achieved without observation of sooting, the values for the richest condition prior to blowout are recorded. Attempts to evaluate n-octane at equivalence ratios greater than one were unsuccessful. The rich blowout equivalence ratio for n-octane was unusually low (1.3) relative to the other alkanes tested and reactor temperatures at these conditions exceeded the limits of the castable refractory used in the JSC.

Table 1 illustrates that the alkanes and alkenes tested behave like ethylene--significant concentrations of hydrocarbons (>1%) are present

*Note that the ethylene results previously discussed were obtained at higher mass flow and lower inlet temperature and this accounts for the differences between Table 1 and Figure 2. Mass flow and inlet temperature effects are discussed elsewhere (Blazowski, 1979).

TABLE 1

Pure Fuels Screening Results

Fuel	Incipient Soot Limit (1)		S_T (2) @ ISL + 0.2 ϕ			S_T @ ISL + 0.4 ϕ	
	ϕ	% HC	Measured Temperature (K)	mg/l	% HC	mg/l	% HC
Ethylene	2.0	3.4	1550	(5)			
Hexane	1.61(3)	9.25	1478				
Cyclo-hexane	1.70(3)	8.88	1426				
N-octane	(4)	(4)	-				
Iso-octane	1.70(3)	7.5	1546				
1-Octene	1.89(3)	8.5	1530				
Cyclo-octene	1.70(3)	7.8	1615				
Toluence	1.39	0.20	1951	0.118	1.72	0.765	5.88
O-xylene	1.31	0.37	1889	0.152	5.88	(5)	
M-xylene	1.30	0.52	1846	0.189	3.88	(5)	9.0
P-xylene	1.30	0.62	1858	0.166	4.62	(5)	
Cumene	1.40	0.65	1855	0.178	3.62	0.455	7.38
Decalin	1.61(3)	7.25	1510				
Tetralin	1.31	0.62	1836	0.356	4.75	(5)	(5)
1-Methylnaphthalene	1.21	0.39	1905	0.926	2.5	(6)	(6)
Dicyclopentadiene	1.39	0.78	1890	0.255	3.62	1.485	7.62

(1) For screening purposes. Incipient soot limit (ISL) is condition at which soot was first noticed on a clean filter.

(2) S_T = Total soot combination of soot on filter and in probe.

(3) Does not soot--highest equivalence ratio value obtained prior to blowout.

(4) Too hot to burn.

(5) Rich blowout occurred before condition could be reached.

(6) Soot concentration very high; probe plugged before data could be taken.

at fuel rich conditions without soot formation. All of the single-ring aromatics tested were found to produce soot with incipient soot limit equivalence ratios ranging from 1.3 to 1.4. Reactor temperature at the soot limit ranged from 1800-1950 K. As with toluene, the soot limit occurs at an equivalence ratio when small amounts of hydrocarbons begin to appear in the exhaust. Not all of the double-ring compounds produced soot. Decalin, a completely saturated double-ring compound, did not soot and behaved like the alkanes/alkenes in terms of exhaust hydrocarbon concentration. Tetralin, 1-methyl-naphthalene, and dicyclopentadiene did produce soot at equivalence ratios ranging from 1.21 to 1.39.

The final two columns in Table 1 illustrate soot production at equivalence ratios above the incipient limit. These same results have been illustrated in Figure 7. One striking feature of the graph is the similarity in the initial slope of the plots for all of the unsaturated ring compounds. When the equivalence ratio is increased further, however, the soot production of these hydrocarbons varies substantially. It is believed that the data at higher equivalence ratios for each hydrocarbon are unreliable, as the Jet Stirred Combustor is operating very near rich blowout with some hydrocarbon passing through entirely unignited at times (sporadic operation is observed at the richest operating conditions). Consequently, the reactor may be behaving partially as a high temperature pyrolysis device or coker during operation at the very highest equivalence ratios. Very high THC concentrations at these equivalence ratios lends support to this explanation.

The behavior of 1-methyl-naphthalene cannot be rationalized in this manner. It produces large amounts of soot at relatively low equivalence ratios and the reactor temperature is much higher than encountered

FIGURE 7: Soot Production for Various Pure Hydrocarbons at 300°C
Inlet Temperature and 112.5 gms/min Air Flow

at rich blowout of the other hydrocarbons in Figure 7. Further, THC at these high sooting conditions was lower than that of the others implying that 1-methyl-napthalene is an especially strong soot producing hydrocarbon.

In summary, it was found that all hydrocarbons tested might be grouped into three categories as follows:

<u>Like C_2H_4</u>	<u>Like $C_6H_5CH_3$</u>	<u>Unlike C_2H_4 or $C_6H_5CH_3$</u>
Hexane	O-xylene	1-methyl-napthalene
Cyclo-hexane	M-xylene	
N-octane	P-xylene	
Iso-octane	Cumene	
1-octene	Tetralin	
Cyclo-octane	Dicyclopentadiene	
Decalin		

The first group produced large amounts of exhaust hydrocarbons without sooting as did ethylene and in no case was significant soot observed. The second group produced soot at the mixture ratio which corresponded to hydrocarbon breakthrough. In all cases the measured hydrocarbon composition was less than one percent at the incipient limit. Another commonality in the second group is that the amount of soot produced as equivalence ratio was increased beyond the incipient limit was similar (i.e. the initial slopes in Figure 7) for all they hydrocarbons. 1-methyl-napthalene was significantly different in this respect producing much higher soot quantities than those in the second category.

IV. DISCUSSION

Many mechanistic models for soot formation have been proposed and a number of references to these have been included. Generally, it is recognized that condensed ring aromatic hydrocarbons can produce soot via a different mechanism than do aliphatic hydrocarbons. A simplified mechanism following Graham, et al (1975 and 1978) is as follows:

Aromatic hydrocarbons can produce soot via two mechanisms: a) condensation of the aromatic rings into a graphite-like structure, or b) breakup to small hydrocarbon fragments which then polymerize to form larger, hydrogen deficient molecules which eventually nucleate and produce soot. Based on his shock tube studies of soot formation, Graham concludes that the condensation route is much faster than the fragmentation/polymerization route. Further, he has found that the mechanism by which an aromatic forms soot changes with temperature; below 1800 K the condensation path is favored

while above this temperature the fragmentation/polymerization route is followed.

According to this simple model, aliphatics produce soot via the fragmentation/polymerization mechanism only. As a result, these hydrocarbons do not form the quantities of soot produced by the aromatics. Indeed, during the fuel rich combustion of a fuel blend composed of aromatics and aliphatics at a temperature less than 1800 K, the aromatic hydrocarbons would produce the major portion of soot. Combustion of the aliphatic portions of the fuel would influence temperature and hydrocarbon fragment concentration but soot formation via fragmentation/polymerization would be minimal. Above 1800 K, however, the both aliphatic and aromatic hydrocarbons would produce soot via the fragmentation/polymerization route.

The experimental results are consistent with this model. It has been observed that soot formation with the condensed-ring aromatic fuels commences with the initial presence of hydrocarbons in the exhaust. If we assume that these breakthrough hydrocarbons maintain their aromatic character, this observation reflects the fast kinetics of the ring-building or condensation reactions. On the other hand, the aromatic molecule may be an effective source of C_2H_2 and high concentrations of acetylene as fuel pyrolysis occurs may be responsible for extensive soot production. Further, the results for 1-methylnaphthalene indicate that a double-ring aromatic provides the most rapid soot formation of the hydrocarbons studied. This observation is also consistent with either the ring building view (ie. the first ring-joining has already occurred) or the polymerization mechanism (ie. even higher amounts of C_2H_2 are present in the pyrolysis zone).

It was found that soot production with the aromatic fuels was more pronounced as equivalence ratio increased. This increase coincides with temperature decreases from an incipient soot value of 1850-1950 K. Graham's shock tube data would imply that the increase is due to a transition to the ring building mechanism. Despite the apparent consistency, the empirical results are not sufficient to establish such a mechanism change. In fact, higher C_2H_2 concentrations due to greater hydrocarbon concentrations may be the correct explanation. Resolution of this behavior would require constant ϕ /variable T data. Further experimental work of this nature will be given high priority, as the implication that soot production can be reduced at higher temperature is potentially very important. If soot production from aromatic hydrocarbons is minimized at higher temperatures, combustion systems might be designed to accomodate optimal conditions.

These experimental/mechanism comparisons are not intended to establish the validity of any theory. The observations are presented to illustrate that the results presented do complement existing simplified views of the soot formation process. Most importantly, the current results lend support to the utility of the approach of quasi-global modeling of the soot formation process for various categories of hydrocarbons.

V. SUMMARY

Alternate fuels derived from coal, oil shale, tar sands, or other non-petroleum resources will play a major role in meeting future national energy demands. In the case of continuous combustion systems, it is known that the different properties of these fuels can result in substantially altered combustion performance. Most importantly, decreased fuel hydrogen content resulting from an increased aromatic content has been observed to result in increased exhaust smoke and particulates as well as greater flame luminosity.

This paper contributes empirical information and new insight which allows the greater soot formation tendencies of the aromatic hydrocarbons to be better understood. A small-scale, one-atmosphere laboratory device which simulates the strongly backmixed conditions present in the primary zone of a gas turbine combustor has been utilized. This Jet Stirred Combustor provides for very rapid mixing between a premixture of vaporized fuel and air and the combustion products within a 5.08 cm diameter hemispherical reactor.

The following conclusions have been drawn from the current experimental effort.

- Ethylene and toluene have distinctly different soot formation characteristics in backmixed combustion.
- The hydrocarbon concentration at and beyond the incipient soot limit appears to be a dominant factor influencing sooting characteristics.

- Other hydrocarbons may be categorized as like- C_2H_4 or like- $C_6H_5CH_3$ with 1-methyl-napthalene being a more powerful soot-producing compound.
- Results are consistent with existing simple mechanisms of the soot formation process and provide encouragement that generating quasi-global soot formation models for categories of hydrocarbons may be feasible.

ACKNOWLEDGEMENT

This work was supported by the U.S. Department of Energy, Power Systems Division (Contract No. EC-77-C-03-1543). Dr. J. Birkeland of DOE is the responsible Program Manager and Drs. R. Dean Pierce and J. Fisher of Argonne National Laboratory are the technical program monitors. The author is grateful to Mr. Robert Schroeder of Exxon Research and Engineering Company for his contributions to the design of the experimental system and performance of the experimental program.

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