PART C: TECHNICAL PAPERS DURING REPORTING PERIOD

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 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 N_2. Problems of fuel stability are aggravated with increased bound nitrogen and undersible 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

$$C_xH_y + \frac{x}{2} O_2 \rightarrow xCO + \frac{y}{2} H_2$$

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 quanity 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 persented. 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 H_2O and CO_2 (oxygenated compounds not predicted by equilibrium for the system ($C_xH_y + \frac{y}{2} O_2 \rightarrow xCO + \frac{y}{2} H_2$) 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 O_2 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 respresents 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:

Pyrolysis: $$N_o = 10^{13} N_o e^{-170,000/RT} \qquad 1$$

Nuclei Formation $$\frac{dn}{dt} = N_o + (f-g)n - g_o Nn \qquad 2$$

Soot Formation $$\frac{dN}{dt} = (a - bN)n \qquad 3$$

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:

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

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:

Pyrolysis: $$C_nH_mBN + M \rightarrow C_xH_y + M + BN \qquad (M \equiv \text{third body}) \qquad 5$$

Partial Oxidation: $$C_nH_m + O_2 \rightarrow CO + H_2 \qquad 6$$

$$C_xH_y + O_2 \rightarrow CO + H_2 \qquad 7$$

Soot Formation: $$C_nH_m \rightarrow C_{(s)} + H_2 \qquad 8$$

$$C_xH_y \rightarrow C_{(s)} + H_2 \qquad 9$$

Soot Oxidation: $$C_{(s)} + O_2 \rightarrow CO + CO_2 \qquad 10$$

Where BN represents the bound nitrogen. Reactions 5 through 10 are coupled to detailed mechanisms describing the rate at which H_2, CO and BN are converted to H_2O, CO_2 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:

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

where the constants A, a, b, c and E are determined through controlled experiments. The reactions and rates associated with the detailed steps are based upon available literature values.

The quasiglobal model has been used sucessfully for high energy fuels, such as shelldyne-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 comparisions 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 parafin (isooctane), an aromatic (toluene), and an olefin (ethylene). While there are measureable 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.

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

where A, b, α 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

$$\dot{R}^{-}_{c_{(s)}} = 1.085 \times 10^{4}\ \frac{P_{O_2}}{T^{\frac{1}{2}}}\ \exp\left(-\frac{39,300}{RT}\right), \qquad 13$$

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, α 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 that 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 interpretating 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 reactedness as the mixture was further enriched. Further, THC concentrations were found to be very significant at ~~the~~ [illegible], 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 occured as hydrocarbons begin to "break through" under rich operating conditions, the soot limit for ethylene occured 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 as 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 ehtylene, 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 distincly 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-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 for all the hydrocarbons. 1-methyl-napthalene 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 isooctane 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 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-napthalene 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 occured) 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 then 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.

$$s = \frac{A\ T^{a}\ |HC|^{b}\ |O_2|^{-\alpha}\ e^{-E/RT}}{\frac{\dot{m}}{\rho V} + \frac{6}{\rho_s d}\cdot\frac{1.085 \times 10^{4}\ P_{O_2}}{T^{2}}\ e^{-39,300/RT}}\ ,\ \left(\frac{gm}{cm^{3}}\right) \qquad 14$$

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:

$A = 5.0 \times 10^{13}$

$a = -2$

$b = 1.75$

$\alpha = 0.5$

$E = 32,000$ cal./mole

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 discrepency observed at ϕ=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 interconnectior 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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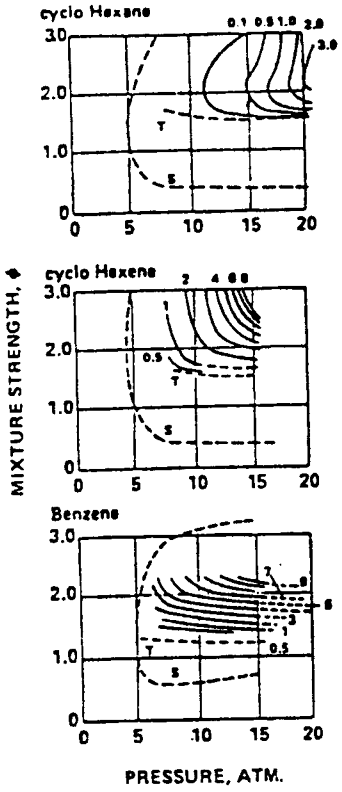

Figure 1. Effect of Pressure and Mixture Strength On Soot Formation

(S denotes flame stability limit, T the soot formation threshold, and numbers indicate conditions producing a constant "soot formation ratio") From Reference 37.

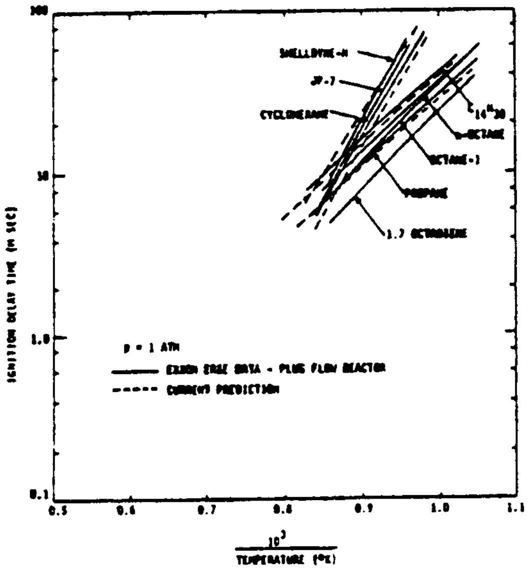

Figure 2. Experimental Ignition Delay Time Data Comparison with Quasiglobal Kinetics Predictions for Aliphatic and Cyclic Type Hydrocarbons

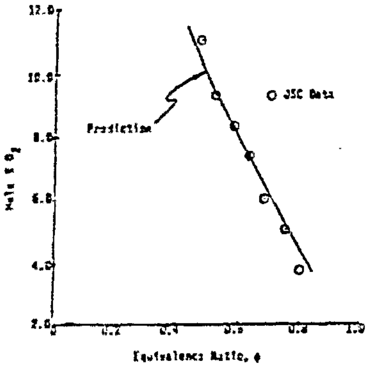

Figure 3. Comparison of Predicted and Measured O_2 Concentration, Isooctane.

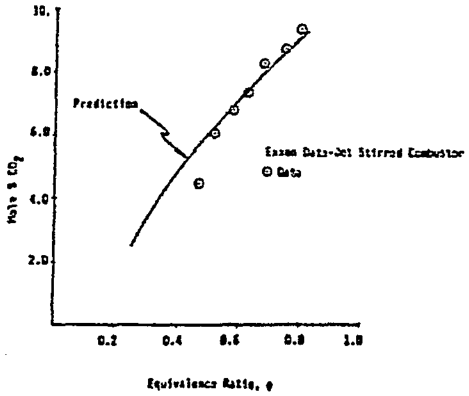

Figure 4. Comparison of Predicted and Measured CO_2 Concentration, Isooctane.

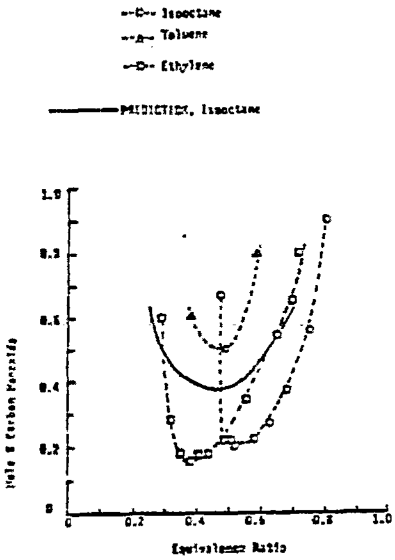

Figure 5. Comparison of Predicted with Measured CO Concentrations.

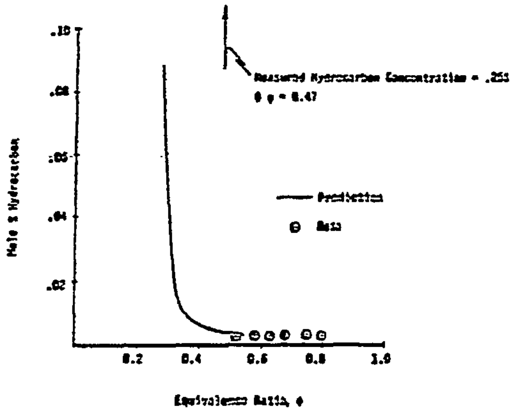

Figure 6. Comparison of Predicted and Measured Hydrocarbon Concentration, Isooctane.

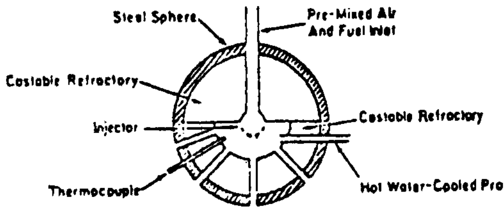

Figure 7. Schematic of Jet Stirred Combustor.

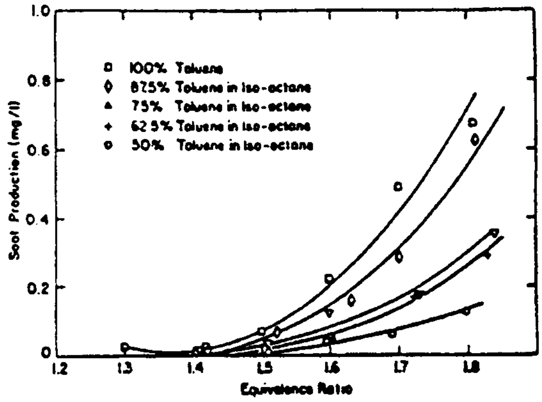

Figure 8. Soot Production vs. Equivalence Ratio for Toluene and Toluene/Iso-Octane Blends at 300 C Inlet Temperature and 112.5 gm/min Air Flow.

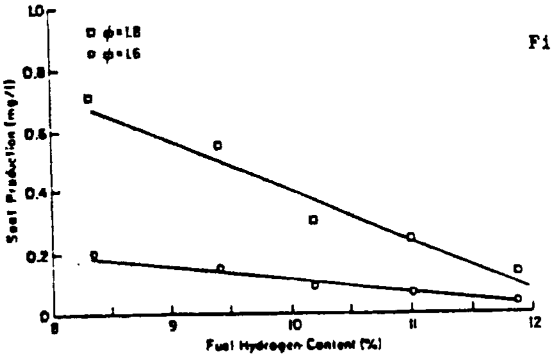

Figure 9. Dependence of Soot Production on Hydrogen Content of Toluene/Iso-Octane Blends.

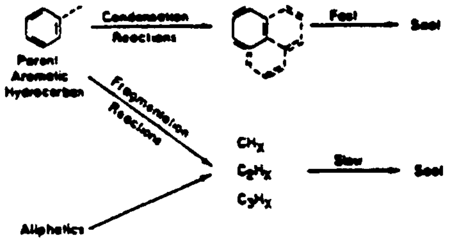

Figure 10. Simplified Soot Formation Mechanism.

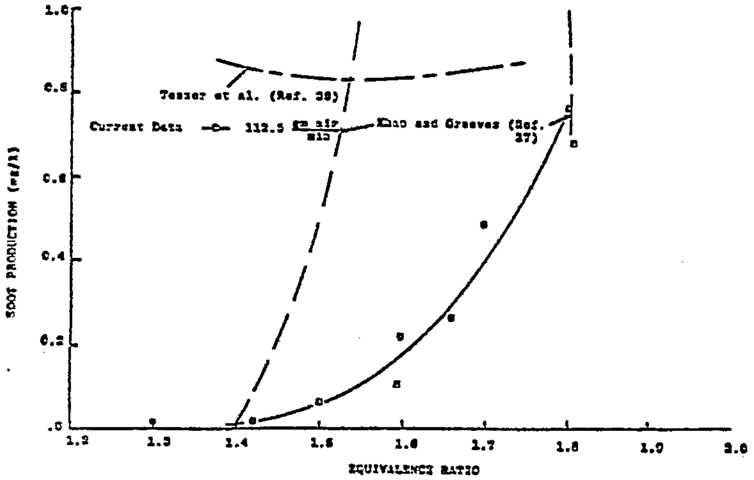

Figure 11. Comparison of Greeves and Tesner Model with Soot Production Data.

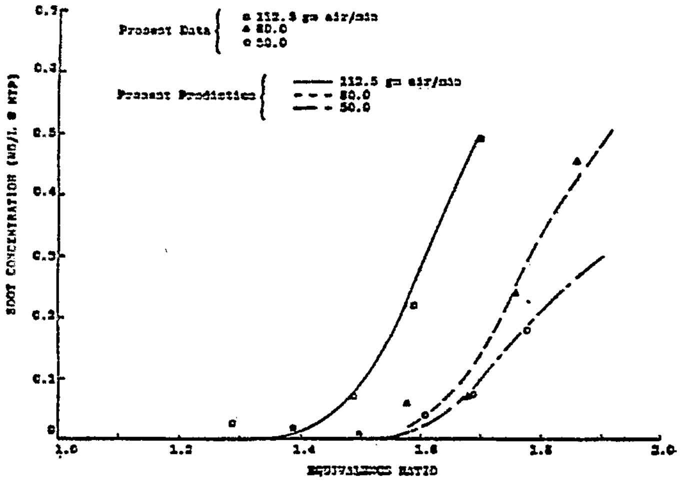

Figure 12. Comparison of Present Model Prediction with Soot Production Data For Toluene/Air Mixtures.

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345 E 47 St., New York, N.Y. 10017

W. S. Blazowski
Exxon Research and Engineering Company,
Linden, 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_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 [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 ratio[2] 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.

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

[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.

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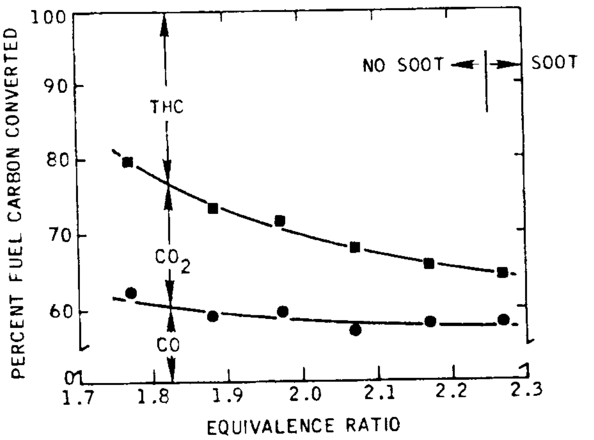

Fig. 1(a) Fraction of fuel carbon converted to each exhaust product for ethylene-air combustion [19]

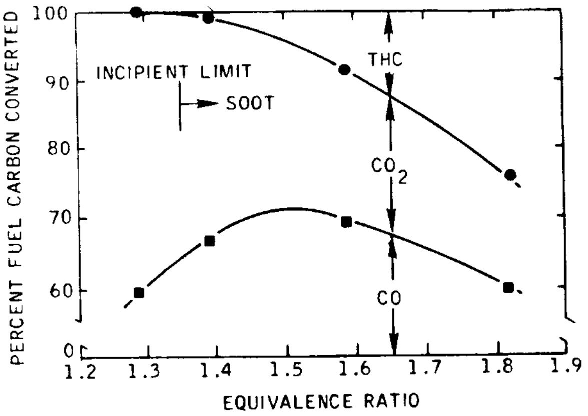

Fig. 1(b) Fraction of fuel carbon converted to each exhaust product for toluene-air combustion (air mass flow = 112.5 gm/min, inlet temperature = 300 °C) [19]

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:

$$C_xH_y + \frac{x}{2}O_2 \rightarrow xCO + \frac{y}{2}H_2 \qquad (1)$$

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 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, CO_2, THC[3], O_2), 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, CO_2 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

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

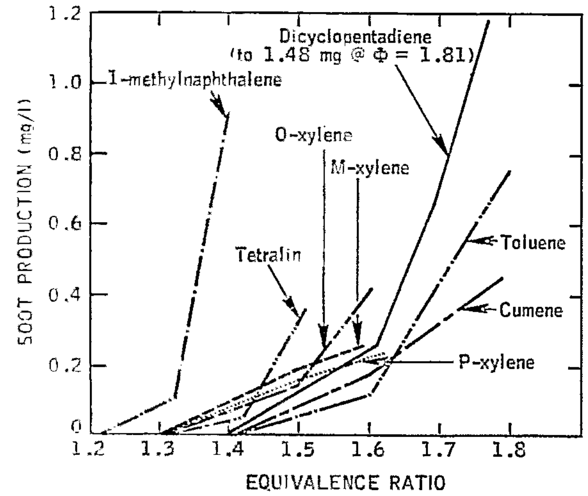


Fig. 2 Soot production for various pure hydrocarbons at 300°C inlet temperature and 112.5 gms/min air flow [19]

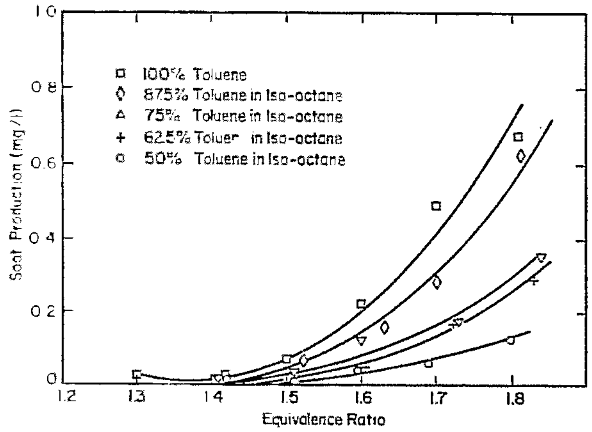


Fig. 3 Soot production versus equivalence ratio for toluene and toluene/iso-octane blends [20]

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 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.

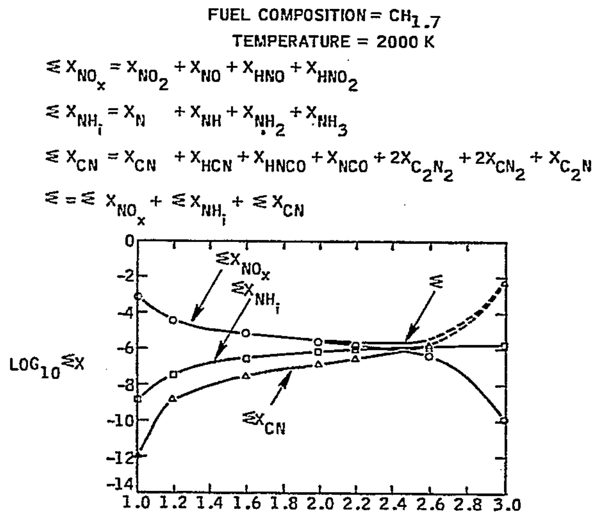


Fig. 4 Equilibrium fixed nitrogen species mole fractions as a function of fuel equivalence ratio. Fuel composition = $CH_{1.7}$, $T = 2000$ K [22]

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

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 combusion 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 (ΣX_{NO_x}) but increases that of amines (ΣX_{NHi}) 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-

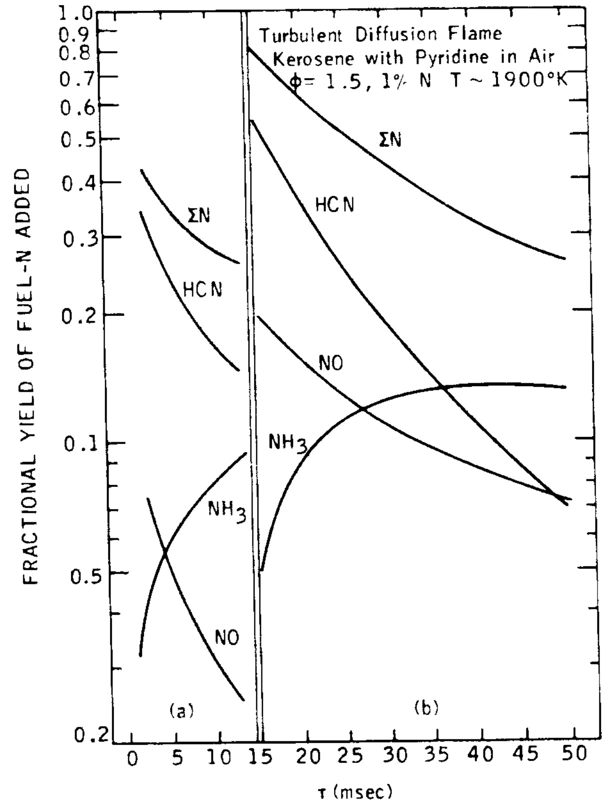


Fig. 5 Joint plot of laminar and turbulence diffusion flame data. (a) flat flame data for $C_2H_4/O_2/He/Ar$ flame at $\varphi = 1.6$ with 2.5 percent N as NH_3. $T < 2120$ K (b) turbulent diffusion flame data for kerosene/air flame at $\varphi = 1.5$ with 1.0 percent N as pyridine. $T \sim 1900$ K [23]

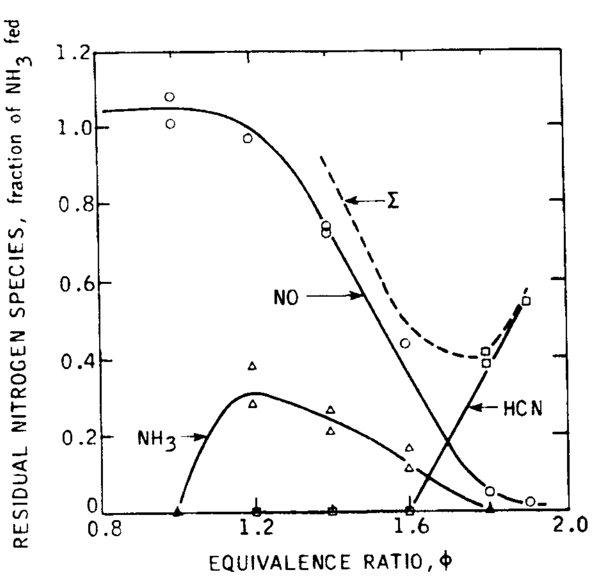


Fig. 6 Residual nitrogen species (dry basis) and temperature profiles as a function of fuel equivalence ratio, at 30 mm above the burner surface. $C_2H_4/O_2/He$ flames doped with NH_3, $He/O_2 = 6.02$ [28]

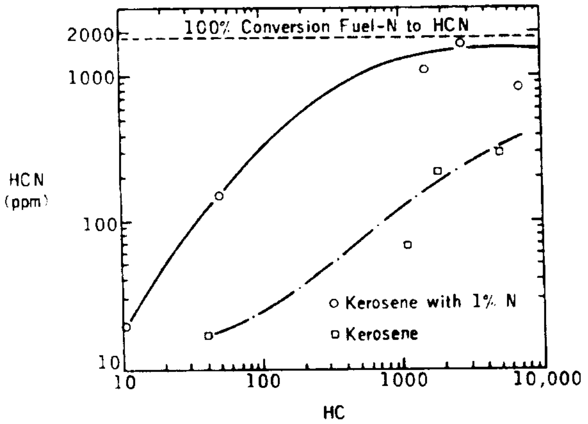


Fig. 7 HCN versus unburned hydrocarbons: $\varphi = 1.5$; $T_{inlet} = 600$ K; ⊙ Kerosene doped with Pyridine to 1 percent N by mass; ■ kerosene; $X/D = 5.0$ [23]

most completely convert to NO_x in the fuel lean second stage. The emission of total fixed or bound nitrogen ($\Sigma X_{NO_x} + \Sigma X_{NH_i} + \Sigma X_{CN}$) 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.

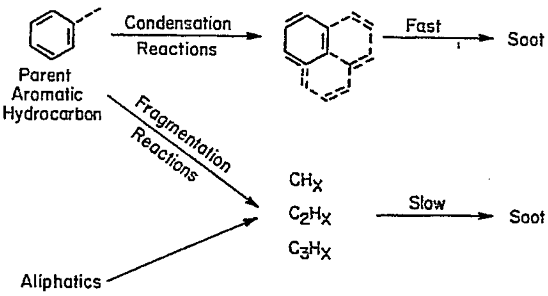
The kinetic constraints can be inferred from time-resolved measurement of HCN, NH_3, and NO obtained in the combustion products of a laminar flat flame of ethylene doped with ammonia (Fig. 5(*a*)) and the spray combustion of kerosene doped with pyridine (Fig. 5(*b*)). Several points need to be made. 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 attributable 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.



(2)

Fig. 8 Equation (2)

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 route. 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

$$CH_3 + NO \rightarrow HCN + H_2O \qquad (3)$$

$$CH + NO \rightarrow HCN + OH$$

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 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 [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 conditions 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

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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.

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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 backmixed 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.

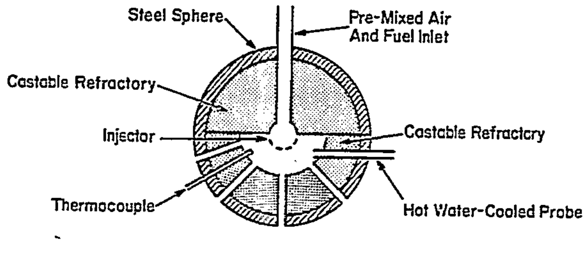
EXPERIMENTAL

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 intepreting 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. 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 N_2.

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 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 μm pore size; the second was a Gellman Type AE with a 0.3 μm 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 ratio[1] 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 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 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.

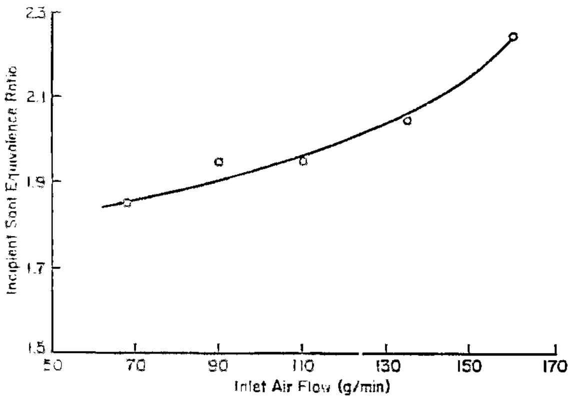


FIGURE 2

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

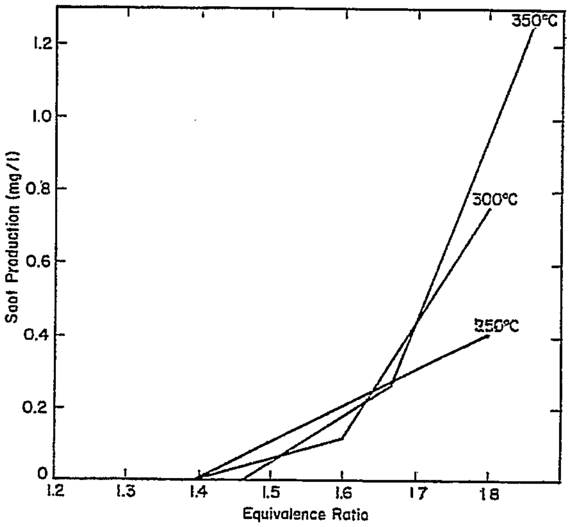
A notable temperature effect observed during this testing was that the darkness of the filter observed at the lowest sooting equivalence ratio increased with mixture inlet temperature. At 25 C the darkness of the soot deposit was very light with increased darkness as temperature was elevated. Another 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 C_2H_4--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

Effect of Inlet Temperature on Soot Production of Toluene



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.

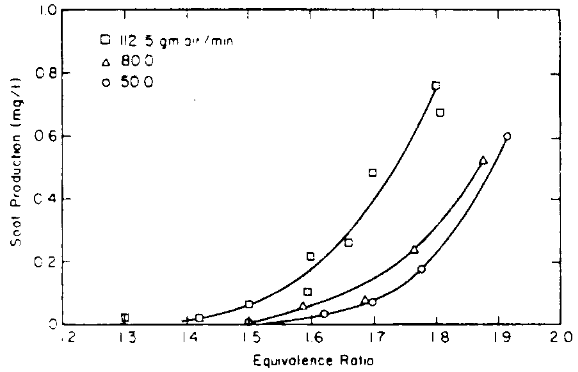
These results for toluene and ethylene indicate a number of potentially important differences between the effects of operating conditions on the soot formation processes of the Group 1 and Group 2 hydrocarbons:

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) 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 (3-8% 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

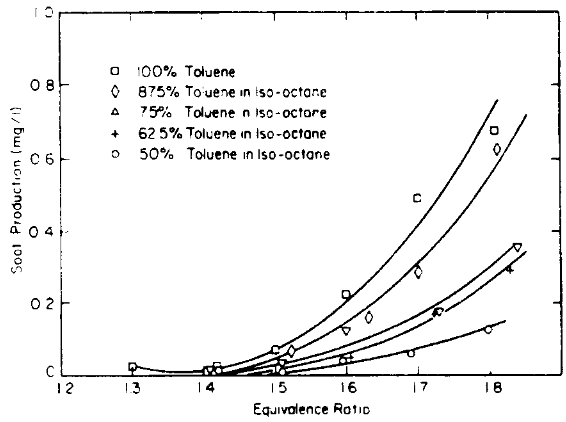
Blends of iso-octane and toluene were tested to determine the behavior of a two-components mixture with like-C_2H_4 and like-$C_6H_5CH_3$ hydrocarbons. These results are shown in Figure 5 and Table 2. Mixtures with 50 or more percent toluene produced soot while a 25% toluene blend did not. Clearly, for 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 (ϕ = 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 prevaporizer. 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-napthalene 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)					

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

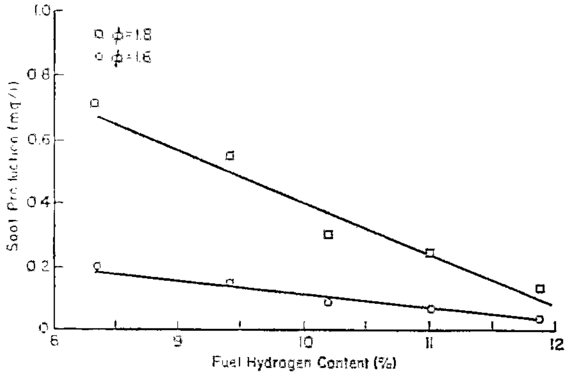
(2) S_T = Total soot combination of soot on filter and in probe.

(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



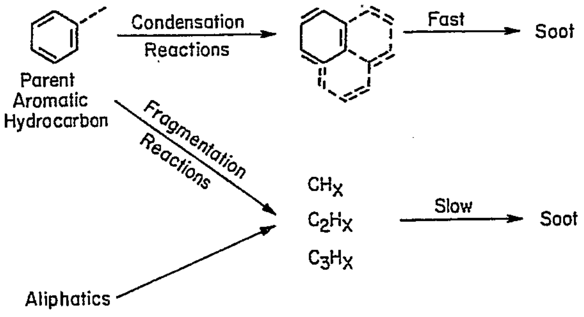
parameter in soot formation has been proposed. In analyzing the data obtained it has been found that useful correlations can be developed. Before presentation of this information, however, it is necessary to more closely examine the data which has been produced very near the rich blowout point. It will 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 loading (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

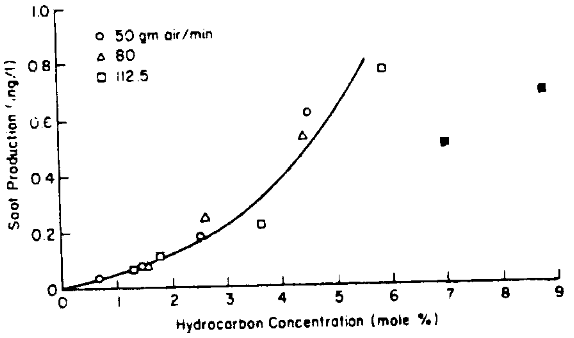
Many mechanistic models for soot formation have been proposed (10-28). Generally, it is recognized that condensed ring aromatic hydrocarbons can produce soot via a different mechanism than do aliphatic hydrocarbons. A simplified mechanism following Graham, et al (18, 19) is as follows:



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 backmixed 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 sysgems. 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

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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

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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.

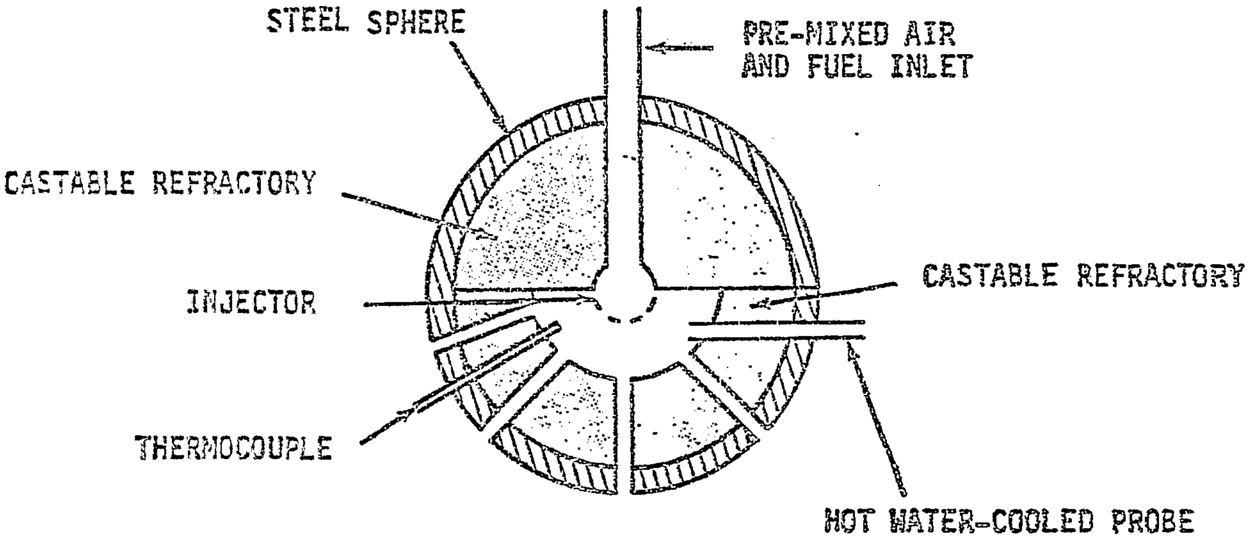
II. EXPERIMENTAL

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 interpretating 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 ± 10°C of the set point. The fuel-air mixture enters the reaction zone through an Inconnel 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 (~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 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 µm pore size; the second was a Gellman Type AE with a 0.3 µm 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.

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*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 Scooting 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°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°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

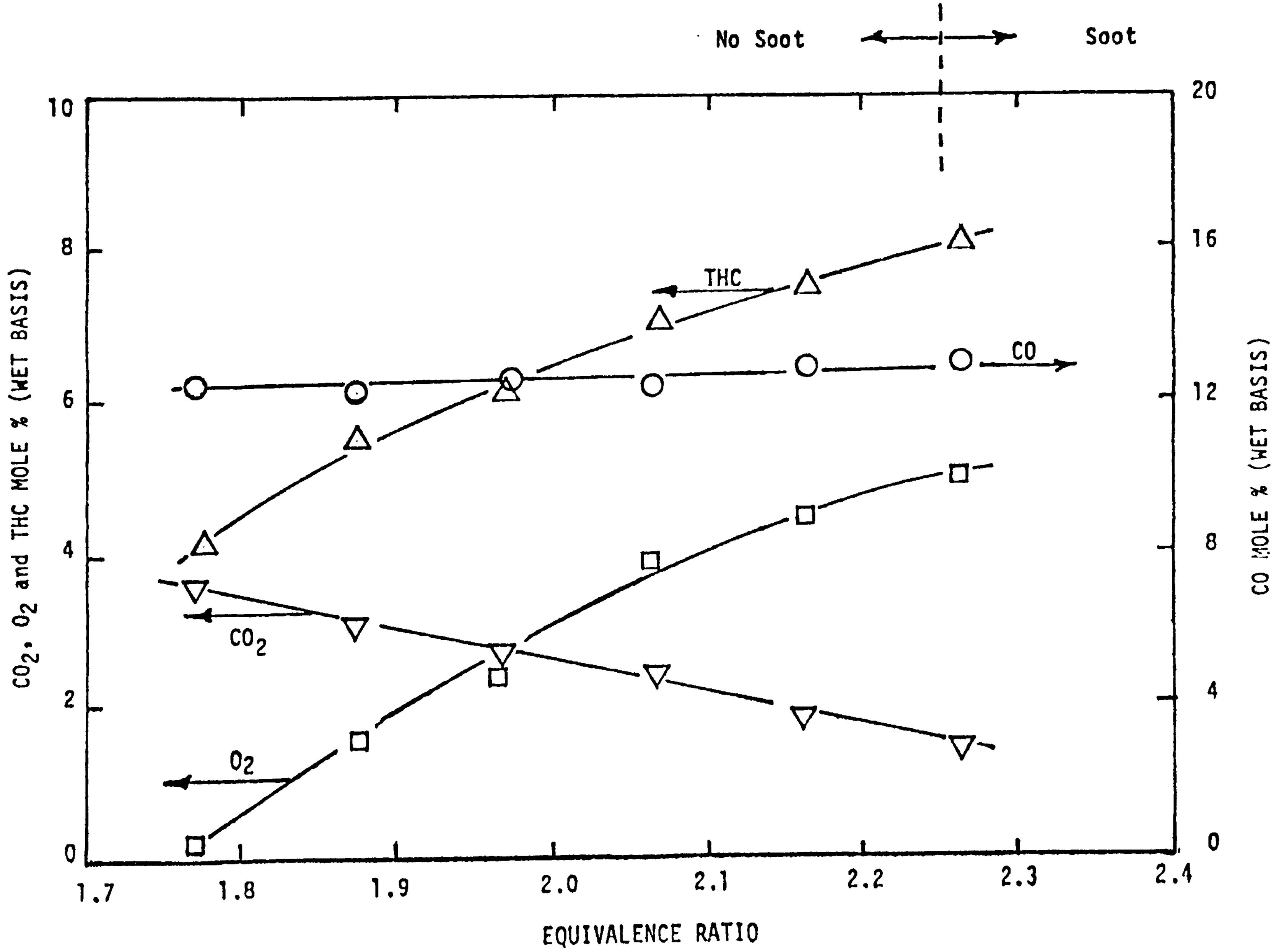

FIGURE 2: Measured Combustion Product Concentrations for Rich Ethylene-Air Combustion (Air Flow = 160 gm/min, Inlet Temperature = 25°C)

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

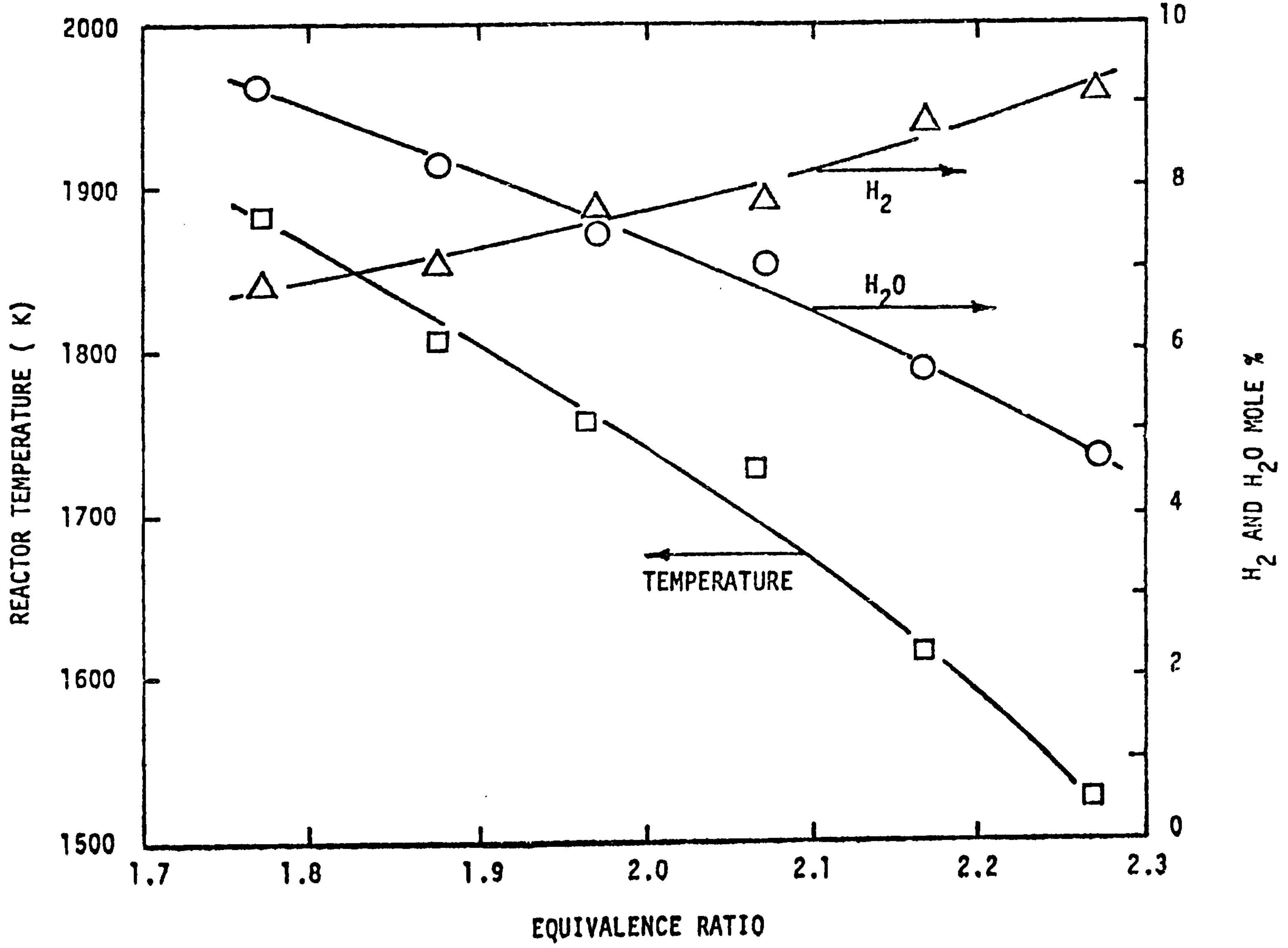

FIGURE 3: Calculated H_2 and H_2O Concentrations and Reactor Temperature for Rich Ethylene Air Combustion (Air Flow = 160 gm/min, Inlet Temperature = 25°C).

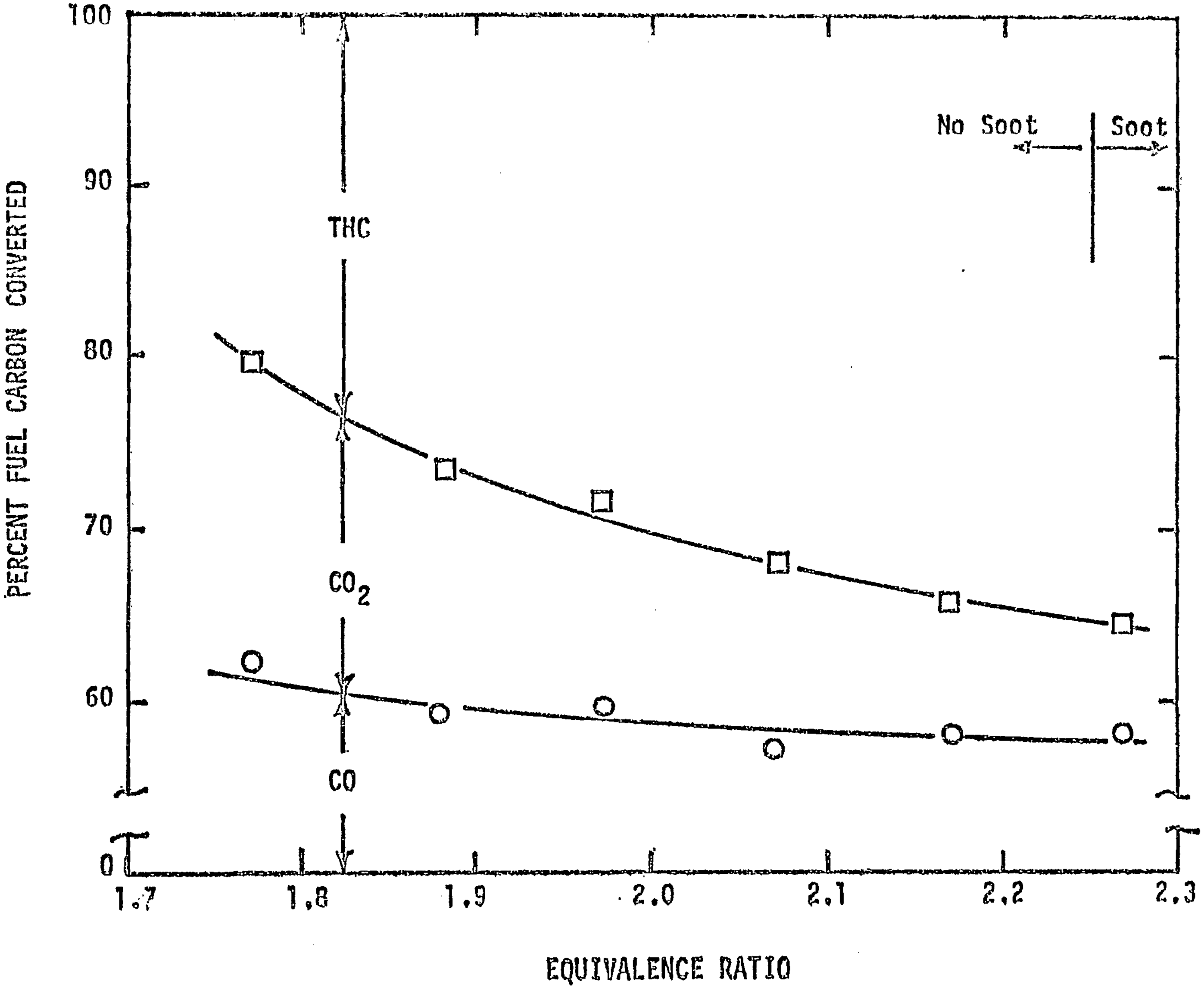

FIGURE 4: Fraction of Fuel Carbon Converted to Each Exhaust Product For Ethylene-Air Combustion (Data from Figure 2).

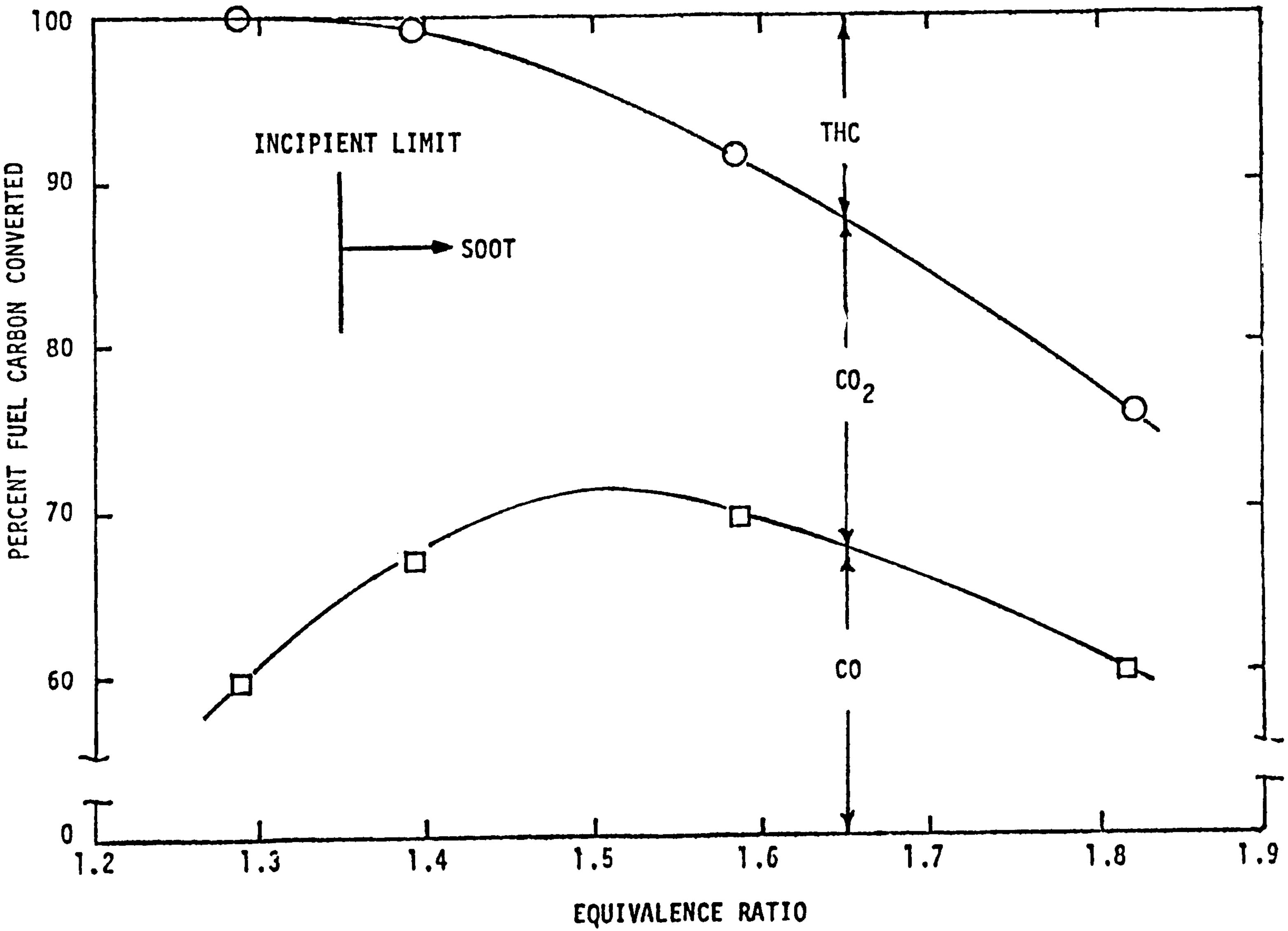

FIGURE 5: Fraction of Fuel Carbon Converted to Each Exhaust Product for Toluene-Air Combustion (Air Mass Flow = 112.5 gm/min, Inlet Temperature = 300°C).

phase behavior by displaying the portions of fuel carbon converted to CO, CO_2, 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 C_2H_4 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 C_2H_4 combustion, significant amounts of hydrocarbons ($\sim$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.

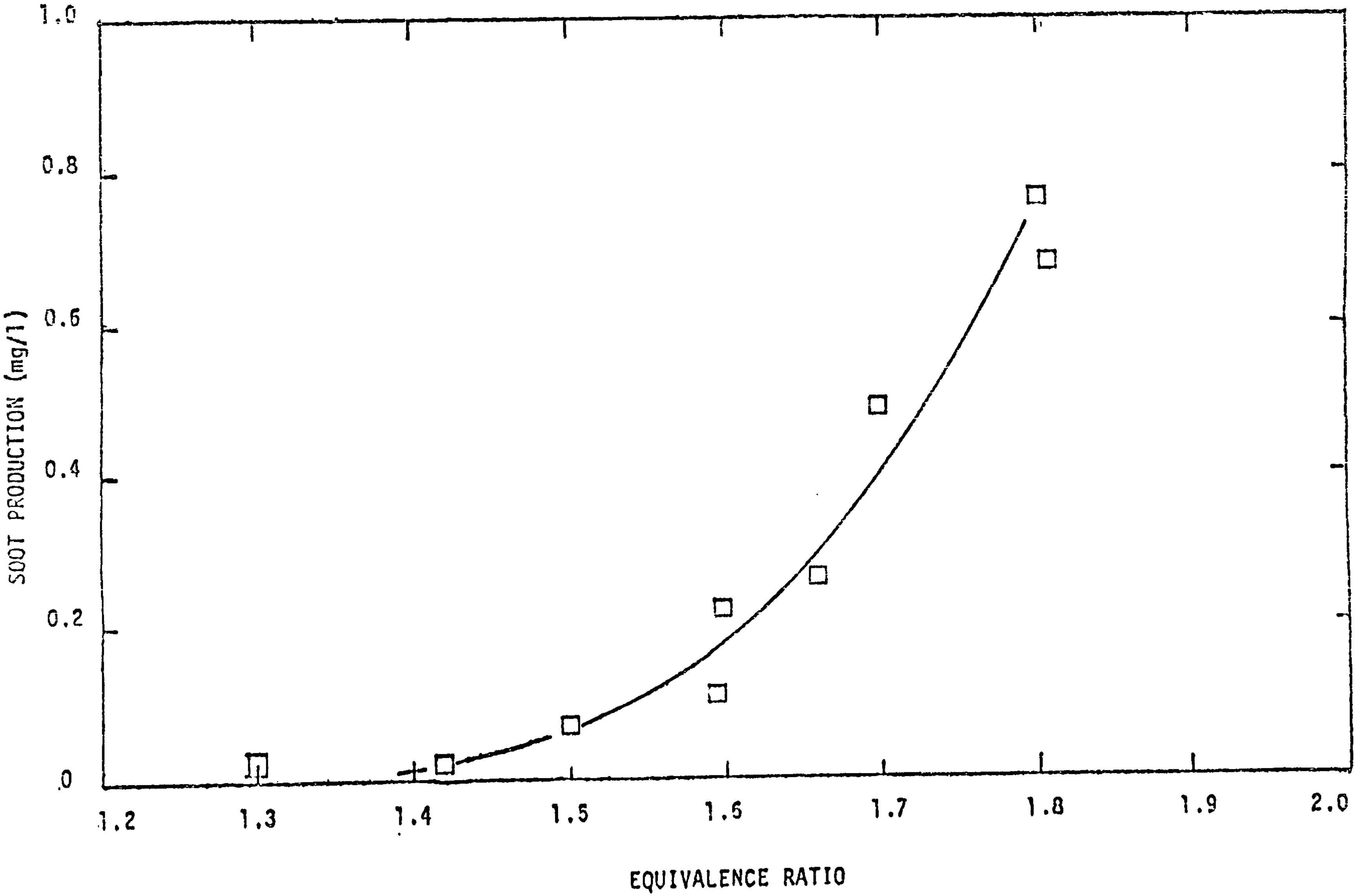

FIGURE 6: Dependence of Toluene Soot Production on Equivalence Ratio (Inlet Temperature = 300°C, Air Flow = 112.5 gm/min)

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

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*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 + 0.2φ		S_T @ ISL + 0.4φ	
	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 occured before condition could be reached.

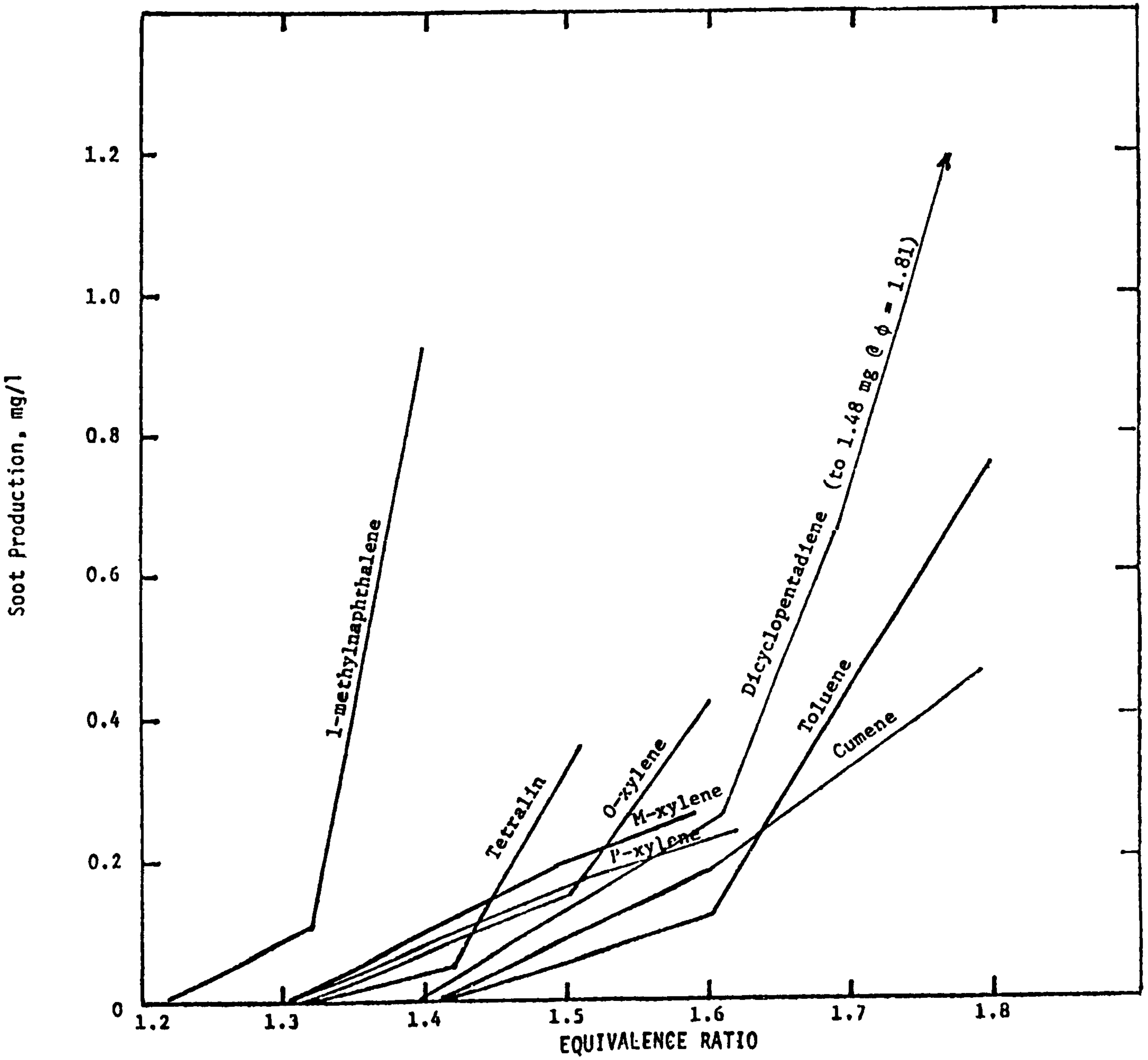
(6) Soot concentration very high; probe plugged before data could be taken.

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-napthalene, 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 (sporatic 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-napthalene 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.

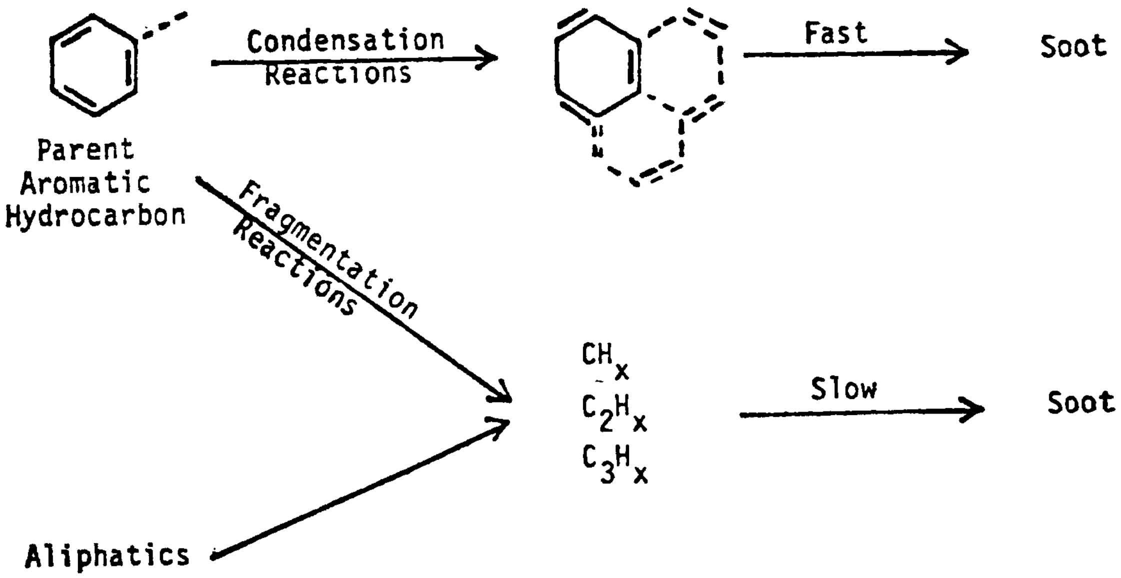
In summary, it was found that all hydrocarbons tested might be grouped into three categories as follows:

Like C_2H_4	Like $C_6H_5CH_3$	Unlike C_2H_4 or $C_6H_5CH_3$
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-methylnapthalene 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 occured) 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

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