FUNDAMENTAL CHARACTERIZATION OF ALTERNATE FUEL EFFECTS IN CONTINUOUS COMBUSTION SYSTEMS. TECHNICAL PROGRESS REPORT NO. 3, 15 FEBRUARY 1978--14 MAY 1978

EXXON RESEARCH AND ENGINEERING CO.,
LINDEN, NJ. GOVERNMENT RESEARCH LABS

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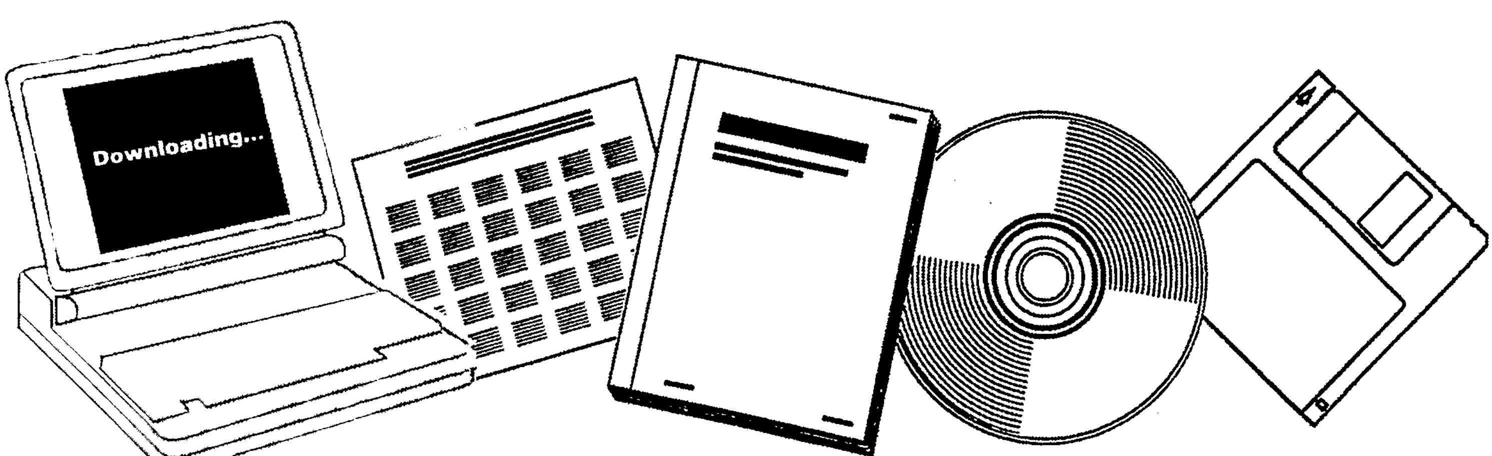

EXXON RESEARCH AND ENGINEERING COMPANY

GOVERNMENT RESEARCH LABORATORIES

FUNDAMENTAL CHARACTERIZATION OF ALTERNATE FUEL EFFECTS IN CONTINUOUS COMBUSTION SYSTEMS

MASTER

Technical Progress Report No. 3
for the Period
15 February 1978 - 14 May 1978

William S. Blazowski

June 15, 1978

Work Performed Under Contract EC-77-C-03-1543

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government research

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FOREWORD

This is the third Technical Progress Report for DOE Contract EC-77-C-03-1543, "Fundamental Characterization of Alternate Fuel Effects in Continuous Combustion Systems." It includes brief descriptions of experimental and analytical information generated during months seven through nine of the program. Experimental information was generated by Exxon Research and Engineering Company (ER&E) and analytical work was performed by Science Applications Inc. (SAI). Dr. Raymond Edelman is responsible for activities at SAI. ER&E is the prime contractor for this program and is responsible for overall program direction and performance.

The data and findings of our work during this quarter must be regarded as preliminary. Much further analysis and confirming data will be provided during the balance of the first program year. Consequently, the description of progress contained herein is of a general nature. The first year Interim Report will provide a full, detailed accounting of the technical data, analysis, interpretation, and conclusions.

William S. Blazowski
Principal Investigator

INTRODUCTION

Alternate fuels derived from coal, oil, shale, and tar sands are expected to play an increasingly important role in meeting the future national energy demand. The properties of these fuels can result in significantly different combustion performance compared with conventional specification fuels. For example, decreased hydrogen content can result in increased flame luminosity and exhaust smoke emission, higher fuel bound nitrogen can result in increased NO_x emissions, and fuel impurities can result in deposition within the combustion device. Although additional refining and fuel treatment can mitigate these problems to some extent, the approach of adapting the combustion system to utilize fuels having "unconventional" properties while operating in an environmentally acceptable manner seems to be most cost effective and energy efficient. This program will provide vital fundamental information necessary for the efficient pursuit of this approach.

The subject program is a multi-year effort to provide an improved fundamental understanding of the relationships between fuel properties and combustion characteristics and to develop analytical modeling/correlation capabilities for the prediction of fuel effects. The work will be limited to investigation of alternate liquid and gaseous fuels used in continuous combustion systems, with gas turbine systems receiving special attention. The program philosophy is to relate fundamental combustion phenomena to fuel characteristics using analytical models developed with and eventually verified by data obtained in carefully designed experiments. Consequently, the program will proceed along two parallel paths, modeling and experimental. ER&E will be responsible for overall program direction and experimentation, while Science Applications, Inc. (SAI) will be responsible for analytical modeling under subcontract to ER&E.

Effort during the first phase of this program (to be undertaken in the first year) will provide a well-developed plan for subsequent years of the program. Key combustion properties and ranges of fuel variation of interest to our subsequent efforts will be surveyed. Experimental work will include the utilization of unique ER&E experimental equipment for evaluation of fuel combustion characteristics. The analytical modeling effort will include new applications of quasi-global modeling techniques as well as predictions of and comparisons with the experimental results generated. Efforts during the second two years of this program will concentrate on solving the problems identified using the approaches defined in Phase 1. These efforts will be characterized by the broad application of experimental combustion facilities available at ER&E. The SAI modeling work will not only attempt to better describe chemical and physical phenomena, but will also provide valuable guidance concerning the design of experiments. This cooperative, iterative procedure will optimize the improvements to fundamental understanding and the generation of an analytical model during this program.

Tasks 1 and 2 of the first year of this effort were completed in January with the Task 1/2 presentation to DOE representatives on the 12th and the submittal of the first Technical Progress Report. The report provides background information which describes the current understanding of alternate fuel effects in gas turbines. A survey of analytical model capability for prediction of fuel effects in continuous combustion systems was provided and sections on computational methods for recirculating reacting flows, turbulent flow modeling, and the phenomena of unmixedness, droplet and spray combustion, and fuel decomposition and combustion were included. Key technical areas requiring additional study and analysis have been identified and prioritized. The presentation summarized this information and described current planning of the second and third program years. An expanded program involving more concentrated effort and larger scale experimentation is envisioned.

The second Technical Progress Report concerned initial experimental and analytical information generated during months four through six. The subject report concerns months seven through nine during which additional experimental information was developed.

Experimental Developments

A very active experimental program employing the Exxon jet-stirred combustor (see Technical Progress Report No. 1) was conducted during the third quarter of this first year of the subject contract. Studies of the soot formation characteristics of ethylene and toluene were conducted and significant differences between these two hydrocarbons were found. Other hydrocarbon types were studied and a screening procedure was adopted to examine a large number of fuels. Finally, qualitative explanation of lean blowout and lean reactor operating characteristics has been realized and the basis for quantitative evaluation of reactor surface effects and quasi-global kinetics under lean operating conditions has been established.

Ethylene Soot Formation

Studies of incipient soot formation limits with ethylene as the fuel were conducted during this quarter. These investigations were intended to satisfy the following objectives:

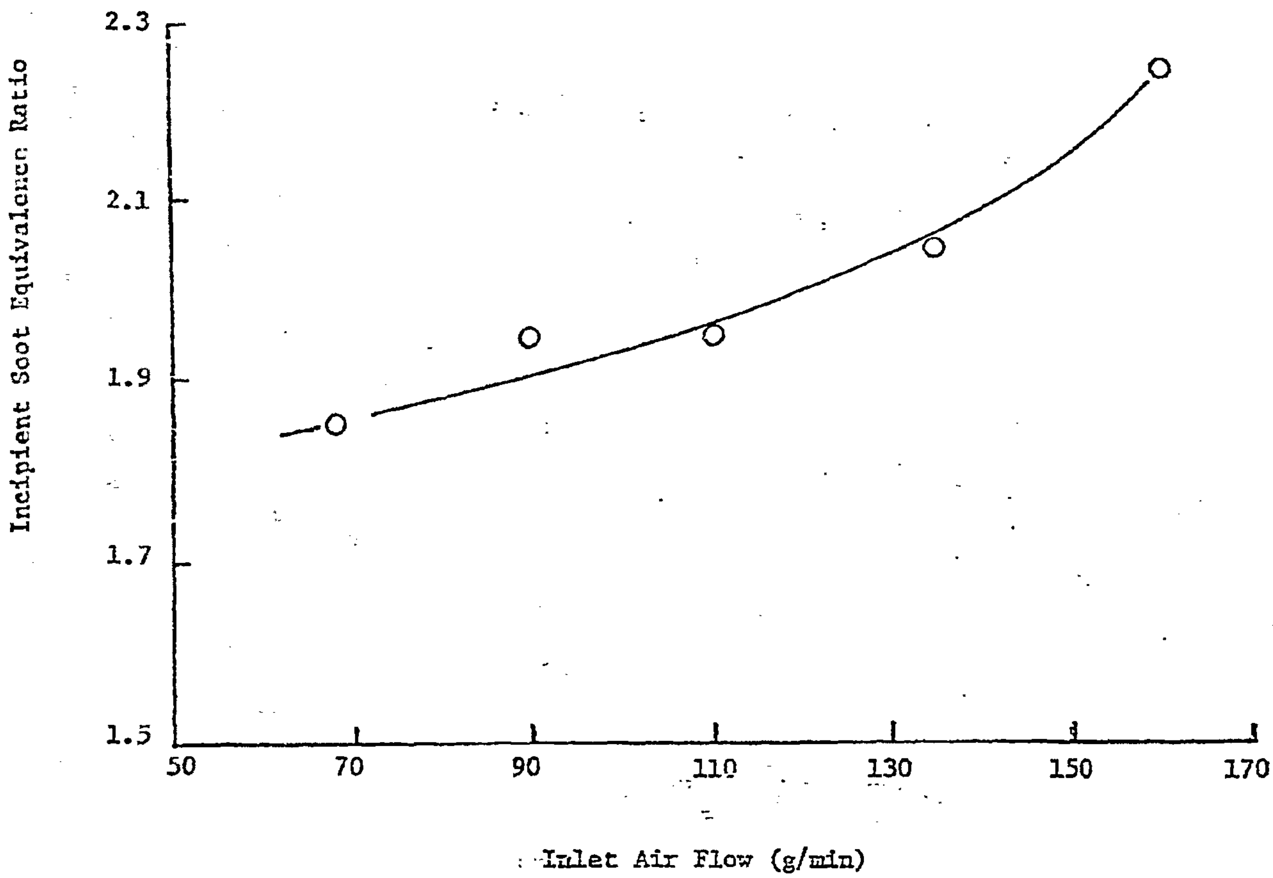
- Determine the dependence of the incipient soot limit on reactor mass flow
- Evaluate the effect of mixture inlet temperature
- Investigate the behavior of gas species at the incipient soot formation limit

Figure 1 illustrates the dependence of the incipient soot formation limit on reactor inlet mixture flow rate. Data was obtained by testing at increasing equivalence ratio increments of 0.1. Results presented represent an equivalence ratio value midway between test points at which we began to observe soot. The flow rate effect appears to be significant with soot limit equivalence ratio increasing from 1.85 to 2.25 over the

FIGURE 1

Incipient Soot Limit Equivalence Ratio Dependence or Mass Flow for Ethylene-Air Combustion

(Inlet Temperature = 25°C)



flow range tested. This is an interesting observation in that at the lower flow rate conditions the equivalence ratio for incipient soot approaches the accepted premixed laminar flame value of 1.8. It can be postulated that residence time effects—the effect of reduced burnedness as reactor loading is increased—are important to ethylene's soot formation process in the well mixed situation.

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 during this reporting period. Wright (Ref. 1) reported a continuous decrease in incipient soot O/C with increasing temperature but considered a broader range of temperatures and identified the critical O/C by observing flame color. It has been our observation that ethylene is a difficult fuel to study in soot formation investigation. Compared with toluene, for example, very small amounts of soot are formed. 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 slight with increasing darkness as temperature was elevated. Another observation was that beyond the soot limit equivalence ratio the soot deposit on the filter became darker and then lighter as the blowout mixture ratio was approached.

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 g/min at 25°C. The portions of fuel carbon converted to CO, CO_2, and total hydrocarbons for these same conditions are illustrated in Figure 3. As indicated, CO is by far the predominant species.

Toluene Sooting Characteristics

The sooting characteristics of toluene were also studied during this past quarter. Results presented below concern the following:

- Effect of reactor mass flow on sooting limit
- Behavior of gas phase species at sooting conditions
- Dependence of soot production on experimental conditions

The incipient soot limit behavior of toluene was determined as a function of inlet mass flow. In contrast with observations made with ethylene as the fuel, no distinct relationship between the incipient soot limit and inlet mass flow was uncovered. Using the technique described in the second Technical Progress Report--leanest operation at which a soiled filter was observed—the limit was consistantly found to be 1.35. Note that this is much leaner than for the case of ethylene combustion where the incipient limit equivalence ratio was found to be 1.95 at these conditions.

TABLE 1

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

($\dot{m}_{air}$ = 110 g/min)

Temp.	ϕ	% O_2	% CO	% CO_2	% HC
25°C	1.95	3.2	25.2	3.45	5.0
100°C	1.85	2.4	26.7	3.70	3.2
200°C	1.95	3.3	28.1	2.95	4.3
300°C	1.95	3.1	29.8	2.80	3.4

FIGURE 2

Gas Phase Species Near the Ethylene Incipient Soot Limit (Air Flow = 160 g/min, Inlet Temperature = 25°C)

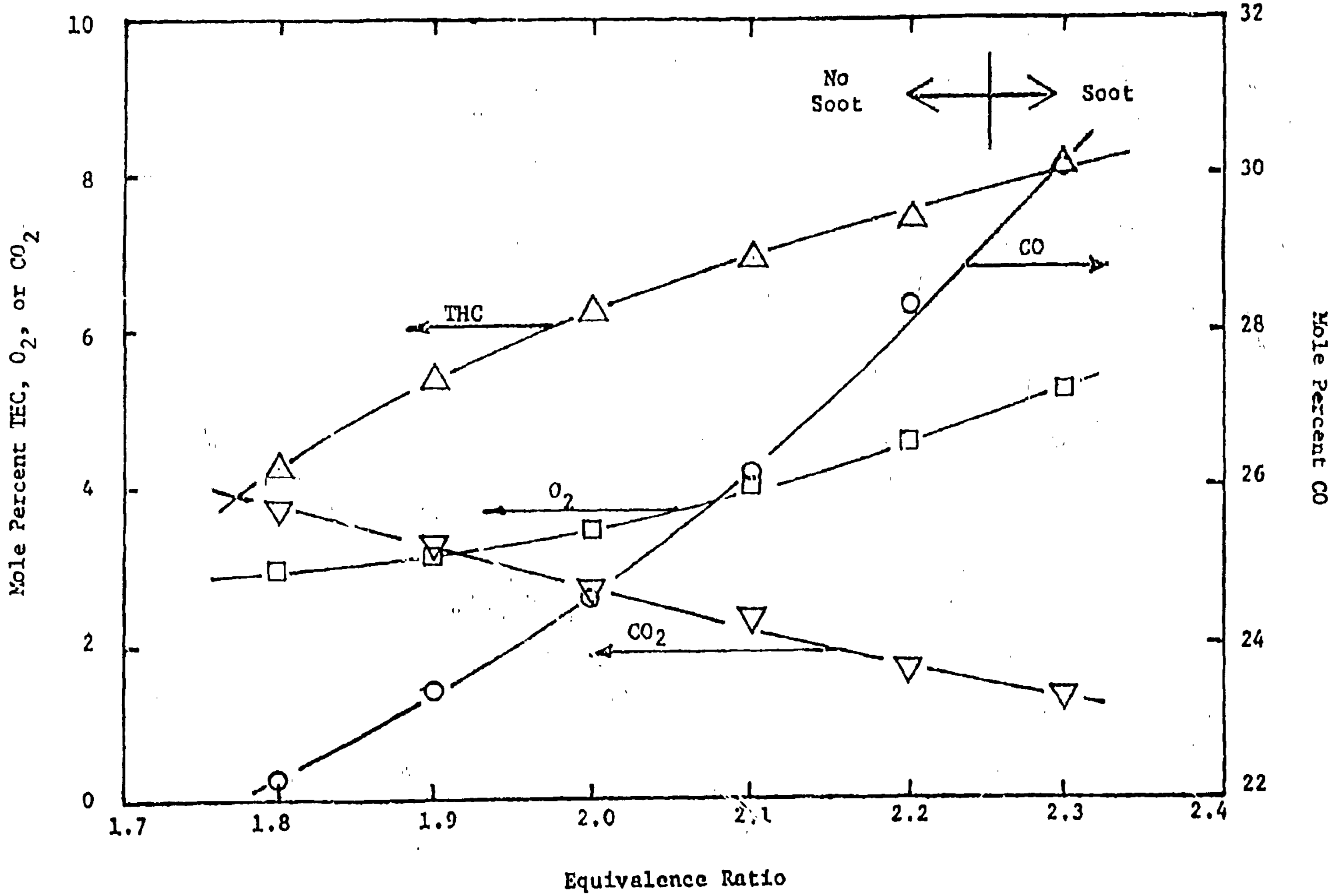
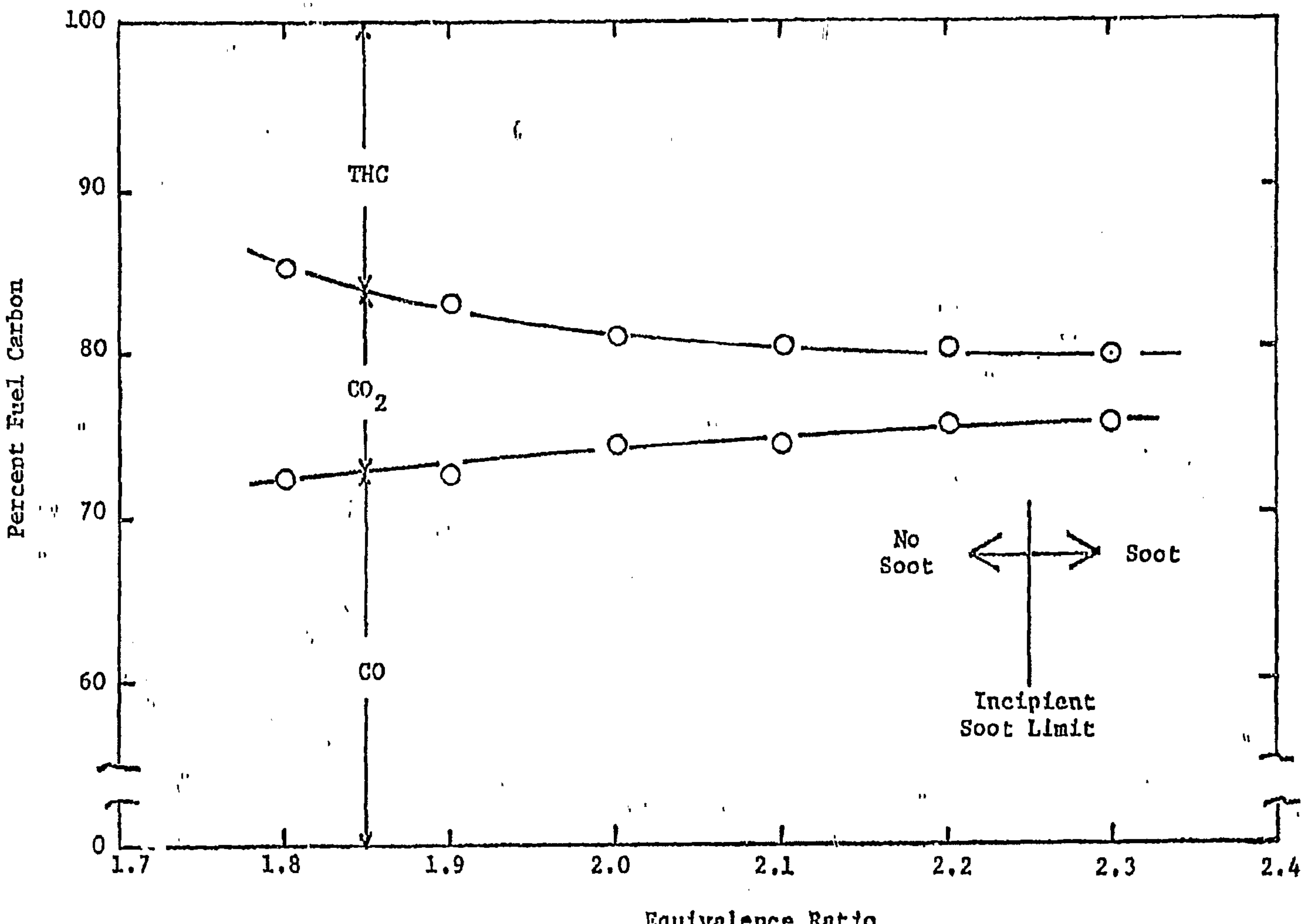


FIGURE 3

Distribution of Fuel Carbon Within Exhaust Products Near Incipient Soot Limit (Air Flow = 160 g/min, Inlet Temperature = 25°C)



Gaseous species concentrations at the soot limit for the 300°C, 112.5 gm/S condition are:

$$\phi = 1.35$$
$$\%\ O_2 = 1.8$$
$$\%\ CO = 15.1$$
$$\%\ CO_2 = 8.0$$
$$\%\ HC = 0.2$$
$$\%\ H_2O = 7.1$$
$$\%\ H_2 = 3.4$$

H_2O and H_2 values are calculated by assuming water-gas equilibrium and performing a hydrogen balance calculation between inlet mixture and combustion products. By appropriate consideration of reactor heat loss characteristics these data can also be utilized to determine reactor gas temperature which was calculated to be 3215°F. Because of this high temperature at the soot limit it was not possible to experimentally determine species behavior for equivalence ratios much lower than 1.30. Leaner operation would have resulted in temperatures which exceed reactor material limitations (3400°F). Measurements have been made at ϕ=1.30 and at the highly sooting conditions for equivalence ratios greater than 1.30.

Figure 4 illustrates the nature of gas phase species present at equivalence ratios at and beyond 1.35. These data were obtained at an inlet temperature of 300°C with an inlet air flow of 112.5 gm/min. The plot illustrates typical gas phase behavior by displaying the portions of fuel carbon converted to CO, CO_2, and total hydrocarbons. As with ethylene, CO is the predominant specie. A substantial difference in comparison with ethylene behavior is the variation of total hydrocarbons at the soot limit. While substantial amounts of hydrocarbons were present with ethylene at equivalence ratios below the limit, toluene sooting commences with the initial presence of hydrocarbons in the reactor.

Soot production was determined at these same conditions. Data are obtained by adding the amount of mass collected on a filter in the measurement system to that which deposited at the entrance to the probe. This latter amount is carefully removed from the probe tip with a fine wire and placed on the soiled filter before final weighing. These measurements correspond to the soot production for a known volume of exhaust gas being passed through the system (usually 10 ℓ). Reduction of this data yields the mg soot produced per standard liter of exhaust product.

Typical results are shown in Figure 5. These data correspond to operation at air mass flows of 50 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, the soot production was substantially less at the lower air mass flow condition.

The results of Figure 5 indicate that soot production increases very significantly as the mixture equivalence ratio increases. However, translation of the data in Figure 5 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.

FIGURE 4

Distribution of Fuel Carbon Within Exhaust Products Beyond Incipient Soot Limit for Toluene-Air Combustion

(Air Flow = 112.5 gm/min, Inlet Temperature = 300°C)

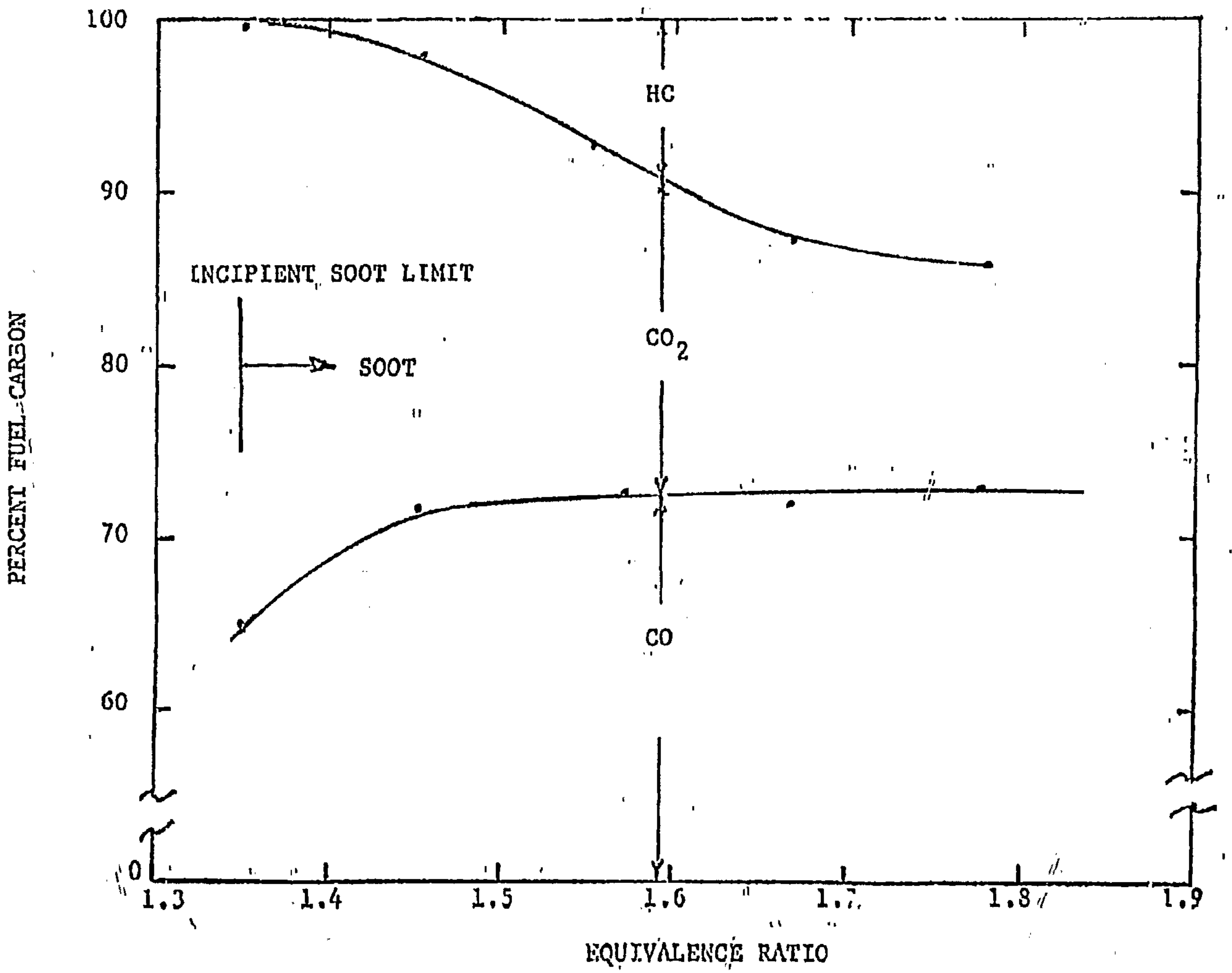
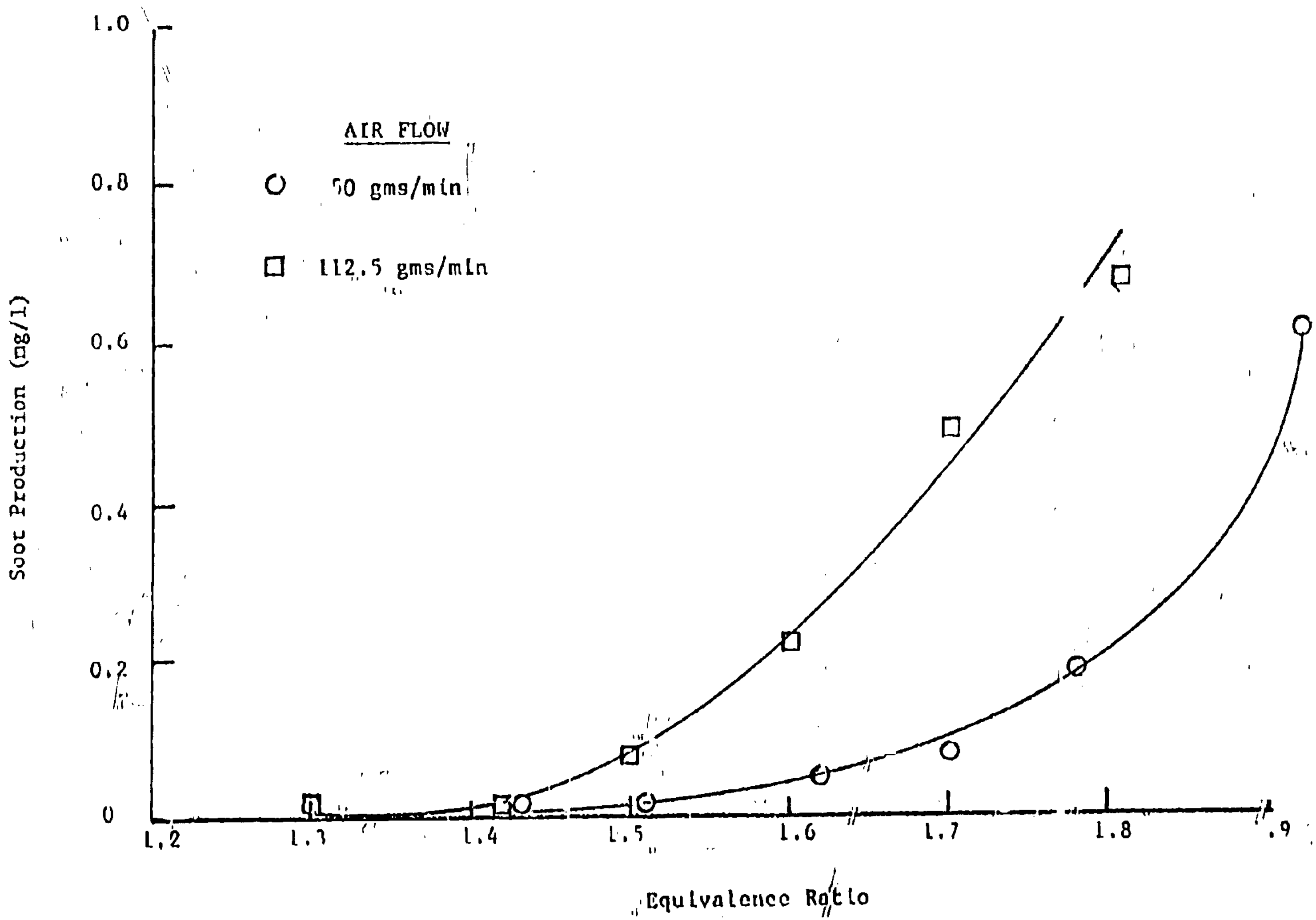


FIGURE 5

Soot Production for Toluene at 300°C Inlet Temperature



The results reported herein indicate a number of potentially 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) The incipient soot limit for ethylene was found to vary with mass flow, but this was not the case for toluene.

c) In the case of C_2H_4 combustion, significant amounts of hydrocarbons (~3-5% 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

These observations 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. The promise of our originally-proposed approach—quasi-global characterization of soot formation characteristics based on hydrocarbon type—is supported by these findings. 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, $C_6H_5CH_3$ or have soot formation characteristics distinctly different than C_2H_4 or $C_6H_5CH_3$.

The first two hydrocarbons studied were hexane and iso-octane. It was not possible to reach sooting conditions with either of these fuels as rich blowout was reached prior to the onset of soot formation. Nevertheless, it was determined that they behaved in a manner similar to that of ethylene—rich combustion resulting in substantial production of hydrocarbons could occur without soot formation. These results were obtained at an air flow of 112.5 gm/min. and a mixture inlet temperature of 300°C.

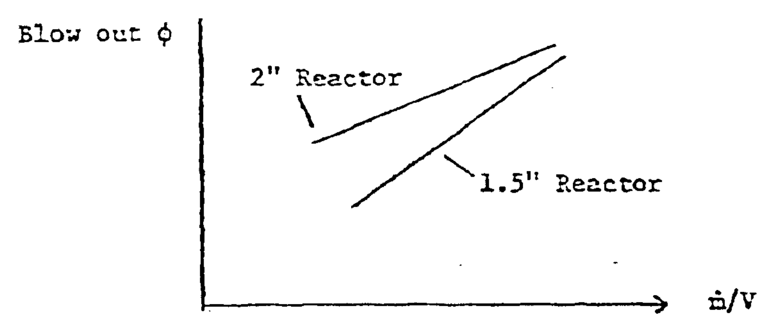
Conditions for additional fuel screening studies were established. Tests using this procedure will involve the balance of the test fuels listed in Technical Progress Report No. 2, a number of pure fuel blends, and actual commercial fuels. The objective of the screening studies is to generally characterize soot formation characteristics of each fuel, especially with respect to similarities between these fuels and either toluene or ethylene. Soot production and gas species will be determined at the following conditions.

Inlet Temperature = 300°C
Air Mass Flow = 112.5 gm/min
Equivalence Ratios: Determine Incipient Limit (I.L.)
I.L. + 0.2
I.L. + 0.4

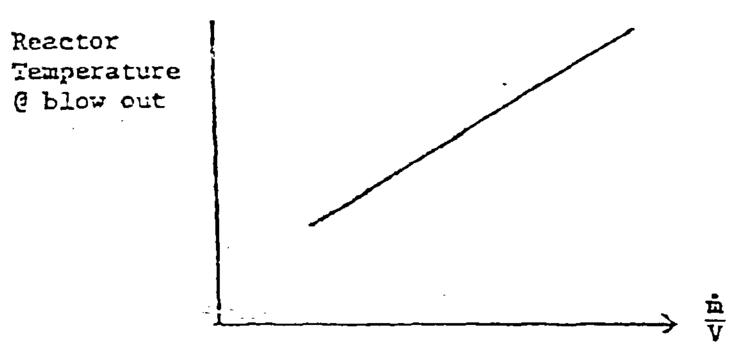
Blowout and Lean Operating Characteristics

Lean blowout limits and CO concentrations in the combustion products at fuel lean operation have been experimentally determined for C_2H_4 and $C_6H_5CH_3$. These results will be of value in developing quasi-global models of hydrocarbon combustion under well-mixed conditions. In addition, data have been acquired for two reactor sizes, 1.5 and 2-inch diameter reaction volume. These results will be analyzed for indication of surface effects which may impact the global chemistry being studied.

Qualitative explanations of blowout and carbon monoxide concentration data for lean operation ethylene-air combustion were developed. Lean blowout results for the 1.5 and 2-inch reactor were evaluated with respect to the heat transfer characteristics of the two devices. Since the 2-inch design has less resistance to heat transfer, it is less adiabatic (loses more heat) and should have a higher blowout equivalence ratio for the same $\dot{m}/V$, mass flow normalized by reactor volume. This agrees with the data. As mass flow is increased through either reactor, the fraction of input fuel energy which is lost through the walls decreases and the difference between the blowout equivalence ratios for the two reactors should diminish as $\dot{m}$ increases (see the following figure). This also agrees with the data and provides an excellent qualitative explanation of our results.



Further quantification in terms of blowout reactor temperature will be performed to verify the chemical similarity between the two reactors of different geometry. The following plot might be developed to examine this question.



Reactor temperature will be calculated from gas analysis data and will be directly measured. Platinum/Platinum-13% Rhodium thermocouples were installed during this reporting period to determine reactor temperature and temperature of the refractory at a radial position close to the reactor internal wall. Chromel-alumel thermocouples are being utilized to determine an internal refractory temperature in the upper hemisphere of the JSC and reactor outside surface temperatures. The internal refractory and outside surface temperatures will provide a direct assessment of reactor heat loss to provide improved accuracy for reactor temperatures calculated by gas analysis.

A qualitative explanation was also developed for the experimentally determined relationship of CO in the combustion products to fuel-air ratio. Results for lean ethylene and toluene combustion show a minima at $\phi = 0.5$ for constant inlet temperature and air flow operation. The lower equivalence ratios show CO increases resulting from lower reactor temperature operation as the blowout limit is reached. At the higher equivalence ratios, two factors cause CO increases. First, the higher temperature causes a density decrease which reduces residence time and hence combustion efficiency. Secondly, equilibrium CO is much higher at the increased temperature which implies that very effective consumption of CO is impeded at the higher temperatures.

Analytical Developments

Development of quasi-global analyses for alternate fuels characterization was conducted at a reduced level of effort in the third quarter of this first contract year. This was done to preserve resources assigned to SAI for a more concerted analytical effort to be conducted with the entire package of ER&E data which will be available in July.

Activity during this period was concentrated in three primary areas:

- Comparison of the existing quasi-global model with available data
- Extension of the quasi-global model
- Obtaining comparisons between calculated results and jet stirred combustor data

In order to continue the effort aimed at establishing the limits of validity of the current quasi-global model, the range of possible fuels allowed for in the current quasi-global code was expanded. Included in the additional fuels was hexane, for which experimental ignition delay results were included in the report by Glassman, et al (Ref. 2). Computations for comparison with these data have been carried out and are being analyzed in conjunction with earlier results.

The multistep quasi-global model was used to compute results for propane fuel for comparison with earlier computations. These computations were carried out by reducing the multistep model to a single-step model (i.e., the additional steps were zeroed out) in order to insure that the basic formulation of the multistep model was compatible with the single-step quasi-global model. The multistep model was shown to properly reduce to the single-step formulation, reproducing the results obtained with the single-step model.

Effort was also concentrated on obtaining comparisons of calculated results made using the existing quasi-global model, for the stirred combustor configuration, with data obtained under this program. Interest is centered on determining conditions under which the carbon monoxide versus fuel-air ratio trends observed in the experiments are reproduced by the computed results.

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