MASTER

CORPORATE RESEARCH

EXXON RESEARCH AND ENGINEERING COMPANY • LINDEN, NEW JERSEY

FUNDAMENTAL CHARACTERIZATION OF ALTERNATE FUEL
EFFECTS IN CONTINUOUS COMBUSTION SYSTEMS

SUMMARY TECHNICAL PROGRESS REPORT
FOR THE PERIOD 1 FEBRUARY 1980-31 MARCH 1981

by

R. M. Kowalik
L. A. Ruth
Exxon Research and Engineering Company
P. O. Box 45
Linden, New Jersey 07036

and

R. B. Edelman
E. Wong
R. C. Farmer
Science Applications, Inc.
21133 Victory Boulevard, Suite 216
Canoga Park, California 91303

May 1981

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Prepared for the U. S. Department of Energy
under Contract DE-AC22-77-ET-11313

This report has been released by

H. C. HAYWORTH
CONTRACT RESEARCH DIVISION

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NOTICE

This report was prepared in accordance with DOE Contract No. DE-AC22-77-ET-11313 by Exxon Research and Engineering Company (ER&E). ER&E assumes no responsibility or liability for any third party's use, or the results of such use, of any information, apparatus, or product disclosed in this report. Any mention of trade names or commercial products in this report does not constitute endorsement or recommendation for use.

DISCLAIMER

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, mark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PATENT STATUS

This technical report is being transmitted in advance of DOE patent clearance and no further dissemination or publication shall be made of the report without prior approval of the DOE Patent Counsel.

TECHNICAL STATUS

This technical report is being transmitted in advance of DOE review and no further dissemination or publication shall be made of the report without prior approval of the DOE Project/Program Manager.

FOREWORD

This is the third Summary Technical Progress Report for contract DE-AC22-77-ET-11313 (formerly DE-AC03-77-ET-11313), Fundamental Characterization of Alternate Fuel Effects in Continuous Combustion Systems. The overall objective of this multi-year contract is to assist in the development of fuel-flexible combustion systems which can accommodate future alternate fuels derived from non-petroleum resources, with particular emphasis on liquid hydrocarbon fuels and gas turbine combustors. The specific technical objectives of the program are (a) to develop an improved understanding of the relationships among alternative fuel properties and continuous combustion system effects and (b) to provide analytical modeling/correlation capabilities to be used as design aids for the development of fuel-tolerant combustion systems.

The program is divided into two parallel, highly interactive efforts. Exxon Research and Engineering Company (ER&E) is responsible for all experimental efforts and the overall program direction. Science Applications, Inc. (SAI), under subcontract to ER&E, is responsible for the analytical modeling efforts. Dr. L. A. Ruth and Dr. R. M. Kowalik conduct the ER&E program. They replace Dr. W. S. Blazowski, who transferred to a different ER&E assignment in February, 1980. Dr. R. B. Edelman, Dr. R. C. Farmer, and Mr. E. Wong conduct the SAI program. The present report contains separate experimental and analytical modeling contributions from ER&E and SAI, respectively.

ABSTRACT

Recent efforts under this contract have involved (1) investigations of soot production phenomena in gas phase jet-stirred combustors, (2) preliminary experiments concerning the effects of liquid spray fuel injection on soot production in jet-stirred combustors, (3) development and shakedown of ER&E's new Variable Pressure Jet-Stirred Combustor, and (4) continued development of SAI's quasi-global chemical kinetic model of hydrocarbon combustion/soot production processes. This report discusses progress in each of these subject areas, including experimental results from the first two areas, detailed descriptions of the Variable Pressure Jet-Stirred Combustor and the present quasi-global model, and brief outlooks on future experimental and modeling efforts. Results from the gas phase jet-stirred combustor studies provide information regarding a possible soot formation mechanism change at 1800K, the appropriateness of a separate sooting category for 1-methylnaphthalene and other multi-ring aromatics, the identification of unburned hydrocarbons in the exhaust gases, and the dependencies of soot properties on combustor operating conditions. The liquid fuel spray experiments provide data which relate liquid spray soot yields to fuel type, overall equivalence ratio, atomizing air flow rate, and combustor temperature. Of particular significance is the temperature dependence of the soot yield, which was found to be exactly opposite previous trends obtained in gas phase jet-stirred combustors. The description of the Variable Pressure Jet-Stirred Combustor includes the actual combustor, its versatile air and fuel supply systems, and associated instrumentation and diagnostics. The quasi-global model description contains tentative reaction mechanisms and rate constants and comparisons of model calculations with experimental data.

TABLE OF CONTENTS

	<u>PAGE</u>
A. EXPERIMENTAL PROGRAM PROGRESS	
A.1 Introduction	1
A.2 Jet-Stirred Combustor Experiments	2
A.2.1 Review of Previous Work	2
A.2.2 Experimental Apparatus	3
A.2.3 Low Temperature Toluene Results	4
A.2.4 Toluene/1-Methylnaphthalene Blend Data	4
A.2.5 GC Analysis of Unburned Hydrocarbons	5
A.2.6 Soot Characteristics	12
A.3 Liquid Fuel Jet-Stirred Combustor Experiments	16
A.3.1 Experimental Apparatus	16
A.3.2 Liquid Fuel Results	18
A.3.3 Unmixedness Results	21
A.3.4 Discussion	24
A.4 Variable Pressure Jet-Stirred Combustor	25
A.5 Program Status and Future Work	33
A.5.1 Soot Production	33
A.5.2 Fuel Nitrogen Conversion	33
B. ANALYTICAL PROGRAM PROGRESS	
B.1 Introduction	44
B.2 Development of the Quasi-Global Toluene Kinetics Model	45
B.3 The Quasi-Global Toluene Model	46

PART A

EXPERIMENTAL PROGRAM PROGRESS

R. M. Kowalik
L. A. Ruth

Exxon Research and Engineering Company
Corporate Research-Technology Feasibility Center
P. O. Box 45
Linden, New Jersey 07036

A.1 Introduction

The overall objectives of the ER&E experimental program are to obtain an improved understanding of the relationships among soot production, fuel nitrogen conversion, fuel properties, and combustor operating conditions in highly backmixed systems and to provide a data base for the development of corresponding analytical models/correlations. The approach has been to study soot production and fuel nitrogen conversion processes in several jet-stirred combustors, which provide reasonable simulations of the highly backmixed combustion environments found in gas turbine combustors, yet still retain sufficient experimental simplicity to control and characterize fundamental parameters.

Experiments during the first two major reporting periods of the contract were conducted in ER&E's Jet-Stirred Combustor (JSC). This gas phase combustor, which utilizes prevaporized fuels, premixed with oxidizers, approximates a well-stirred, perfectly mixed combustor. Experiments in the JSC, consequently, investigated the effects of predominantly chemistry related variables (fuel type, equivalence ratio, temperature, residence time) on soot production. Additional experiments have been run in the JSC during the present reporting period; however, the majority of the recent work has been conducted in ER&E's Liquid Fuel Jet-Stirred Combustor (LFJSC). The LFJSC accommodates the introduction of fuel as a liquid spray. Experiments with the LFJSC have considered several chemistry and non-chemistry effects on soot production (fuel atomization, vaporization, and mixing). Initial results have suggested that these non-chemistry effects may significantly alter the sooting trends found in the JSC experiments.

Most of the future experiments in the current program will be conducted in ER&E's new Variable Pressure Jet-Stirred Combustor (VPJSC). The VPJSC has been recently constructed (with ER&E funds) and is almost operational. The unit is designed to operate at pressures from 0.5 to 5 atm with either prevaporized or liquid fuels. Experiments with the VPJSC will investigate the effects of pressure and mixing on soot production for both gaseous and liquid spray fuel injection. An extended plug flow zone downstream of the VPJSC jet-stirred zone will also be used for future fuel pyrolysis and soot oxidation experiments specified in the current contract.

The balance of the experimental report provides more detailed information regarding the completed and planned experiments in each of the three jet-stirred combustors. Section A.2 briefly summarizes the JSC results reported in the previous two Summary Technical Progress Reports and, subsequently, presents the JSC data obtained during the current reporting period. Section A.3 presents and discusses initial results obtained from the LFJSC, and Section A.4 describes the new Variable Pressure Jet-Stirred Combustor. Section A.5 reviews the program status and outlines future work.

A.2 Jet-Stirred Combustor Experiments

A.2.1 Review of Previous Work

W. S. Blazowski [1,2] conducted the soot production experiments in the Jet-Stirred Combustor during the first two major reporting periods of the contract (8/15/77 thru 1/31/80). He studied the sooting characteristics of several pure hydrocarbons and classified them into three general sooting categories. Category 1 consisted of principally aliphatic fuels. With these fuels, the combustor experienced rich blow-out before measurable quantities of soot could be obtained. Significant concentrations of unburned hydrocarbons ($>1\%$ as methane) were also observed before the onset of soot formation. Category 2 contained principally single-ring aromatic fuels. These fuels produced measurable quantities of soot for equivalence ratios greater than or equal to the equivalence ratio at which appreciable concentrations of unburned hydrocarbons ($>0.1\%$ as methane) could be detected in the exhaust gases (hydrocarbon breakthrough). The magnitudes of both soot and unburned total hydrocarbon (THC) concentrations from these fuels were found to be larger for richer equivalence ratios, lower temperatures, and shorter average residence times within the combustor. The common dependence of soot and THC concentrations on these parameters suggested that the THC concentration might be a key factor in the prediction of soot concentrations from Category 2 fuels in gas phase stirred combustors. Edelman, et al. [3] used this idea to develop quasi-global rate expressions for the production of soot from toluene in gas phase stirred reactors.

Blazowski also investigated the sooting characteristics of 1-methylnaphthalene (a double ring aromatic) and several isooctane/toluene blends. 1-methylnaphthalene had sooting characteristics which were similar to the sooting characteristics of Category 2 fuels; however, some soot concentrations from 1-methylnaphthalene were significantly larger at similar combustor conditions. Consequently, a third sooting category (Category 3) was assigned to 1-methylnaphthalene and other multi-ring aromatics. Blends of isooctane (Category 1) and toluene (Category 2) produced soot and THC concentrations which appeared to represent combinations of the Category 1 and Category 2 sooting characteristics. Soot concentrations from the various isooctane/toluene blends were also found to be linearly dependent upon the C/H ratio of the mixture (more soot at larger C/H ratios). These data suggested that soot formation models for each category might be combined to predict the soot produced from various fuel blends.

Although Blazowski identified several general trends regarding soot production in the JSC, important questions regarding more detailed aspects of the data remained. The questions concerned (1) a possible soot formation mechanism change at 1800 K^* , (2) the appropriateness of

* This mechanism change, first proposed by Graham [4], suggests that below 1800 K aromatic molecules form soot rapidly via a ring condensation route and that above 1800 K the rings become unstable, fragment and form soot via a much slower polymerization route.

the Category 3 designation for 1-methylnaphthalene and other multi-ring aromatics, (3) the identification of unburned hydrocarbons, and (4) the dependence of soot properties on JSC operating conditions. These topics were investigated further in the JSC experiments conducted during the present reporting period.

A.2.2 Experimental Apparatus

Detailed descriptions of the Jet-Stirred Combustor (JSC) and its associated instrumentation are available in the two previous Summary Technical Progress Reports [1,2] and are not included in the present report. During the current reporting period, however, several improvements in the calibration/interpretation of JSC diagnostics have been accomplished. In particular, a comprehensive examination of the JSC apparatus, measurement procedures, and available data, conducted after the recent ER&E personnel changes in the present program (See FOREWORD), revealed several peculiarities in the total unburned hydrocarbon (THC) concentration and combustor gas temperature measurements. Further investigations of each diagnostic discovered calibration errors which affect the interpretation of corresponding measurements. Details of the findings are given below.

The THC concentration measurement problem involved the nitrogen dilution scheme, which was implemented during the previous reporting period to extend the linear range of the flame ionization hydrocarbon analyzer. Although this modification corrected the nonlinearities associated with concentrations above 2% (as CH_4), low concentration THC data (<2% as CH_4) from equivalent run conditions before and after the modification indicated that the post modification values were smaller. Subsequent recalibration of the dilution scheme revealed that the previous calibration was in error. In particular, ethylene/nitrogen mixtures initially used to calibrate the system were not metered accurately. The mass flow controller which metered C_2H_4 had been calibrated using N_2 rather than C_2H_4 . Since the flow controller responds to the pressure drop across a laminar flow element, the viscosity of the metered gas affects the calibration. Since the viscosity of N_2 is 1.75 times larger than the viscosity of C_2H_4 , ethylene flow rates were underestimated. Corresponding THC concentration measurements were underestimated by the same factor of 1.75. Corrected versions of the affected tables and figures in the previous Summary Technical Progress Report [2] have been sent to all recipients of the report. All data in the present report are based on the corrected calibration.

The gas temperature measurement problem involved thermocouple radiation/conduction errors. Heat balance calculations from several JSC run conditions suggested that the indicated thermocouple temperatures were of the order 100 K lower than calculated temperatures. A subsequent ER&E funded experimental study (See Appendix 1) indicated that thermocouple errors were of the same order and that the errors were smaller for shorter residence time (larger flow rate) and larger soot concentration conditions. In particular, for sooting, 3 ms residence time conditions, projected gas temperatures were approximately 100 K larger than indicated thermocouple*

* Measured temperatures listed in this and previous reports are indicated temperatures obtained with uncoated Pt/Rh thermocouples; wire diameters were 0.8 mm; bead diameters were 2.0 ± 0.3 mm.

temperatures. For non-sooting, 3 ms residence time or sooting, 6 ms residence time conditions the projected gas temperatures were about 150 K larger. These findings suggest that an average correction factor of 125 K should be added to measured JSC temperatures appearing in this and previous reports. Such correction factors also reduce the differences between measured temperatures and temperatures computed via quasi-global models (See Section B).

A.2.3 Low Temperature Toluene Results

Previous JSC data on toluene soot production suggested that less soot was produced at higher temperatures. Comparisons of data at 1700 K and 1800 K, however, did not support this trend. Since there was also some evidence of a soot production mechanism change near 1800 K [4], an additional set of experiments was conducted to further investigate the effect of temperature on toluene soot production.

For these experiments toluene was burned in the jet-stirred combustor (JSC) at constant indicated temperatures with N_2/O_2 oxidant and equivalence ratios of 1.4, 1.6 and 1.8. Temperatures ranged from 1600 to 1800 K, and residence times (τ) were either 3 ms or 6 ms. Expected dependencies of the net soot emissions and the unburned hydrocarbon concentrations on equivalence ratio (ϕ) were generally found; both increased with increases of ϕ . The temperature dependence of emissions was less certain. At a fixed equivalence ratio of 1.6 ($\tau = 3$ ms), net soot emissions increased as temperature was increased from 1600 to 1800 K. This result is exactly opposite Blazowski's findings (less soot at higher temperatures); however, data from the other low (<1800 K) temperature run conditions did not support either trend. Hydrocarbon (HC) concentrations also exhibited some trends unlike previous high temperature (1800-2000 K) toluene data obtained in the JSC (See Section A.2.1). In particular, relatively large HC concentrations ($>1.5\%$) were detected without measurable quantities of soot. These large HC concentrations were probably caused by the sporadic combustion obtained in the JSC at these conditions. Similar sporadic combustion was thought to be the source of unignited fuel which produced unusually high HC concentration measurements in previous high ϕ , low temperature cases [1].

The sporadic operation of the JSC in the present set of experiments severely limits conclusions regarding the effects of temperature on toluene soot production; nevertheless, combinations of these results with previous high temperature results suggest that soot emissions may peak at temperatures near 1800 K. This trend appears to be consistent with shock tube data reported by Wang, et al. [5] and may suggest the presence of a soot formation mechanism change; however, neither set of data contain sufficient detail to determine whether or not Graham's [4] proposed mechanism change is responsible for the peaks in soot concentrations.

A.2.4 Toluene/1-Methylnaphthalene Blend Data

The JSC soot production data which were used to distinguish Category 2 and Category 3 hydrocarbons left several questions regarding the magnitude of the Category 2/Category 3 sooting differences. In particular, the initial toluene (Category 2) and 1-methylnaphthalene

(Category 3) data, obtained with fuel/air mixtures and uncontrolled temperatures (See Reference [1]), suggested that 1-methylnaphthalene produced substantially more soot than toluene for a given equivalence ratio and residence time. Some later data, obtained with fuel/air/oxygen or fuel/air/nitrogen mixtures and controlled temperatures of 1900 K and 2000 K (See Reference [2]), indicated that the toluene/1-methylnaphthalene sooting differences were almost negligible and that toluene soot production data was similar to the data obtained from the previous set of experiments. Blazowski indicated that the apparent discrepancy may have been due to a change in the soot formation mechanism, which resulted from different temperatures in the two sets of experiments (See Section A.2.1).

To resolve some of the uncertainties regarding these toluene/1-methylnaphthalene sooting differences, a third set of experiments was conducted. For these experiments indicated temperatures were 1900 K, and residence times were 3 ms. Equivalence ratio (ϕ) and fuel composition (toluene/1-methylnaphthalene wt. %) were the independently varied parameters. Net soot emission results from these experiments are displayed in Figure 1. The plots indicate that there were different sooting characteristics among the various fuels and that the sooting characteristics of toluene/1-methylnaphthalene blends appeared to represent combinations of the sooting characteristics of the two pure fuels. The data also suggest that 1-methylnaphthalene does produce more soot than toluene but that the sooting differences between the two fuels are not large when compared to differences among Category 2 fuels (Figure 2).

The different trends obtained from the three sets of experiments may be related to the metering of 1-methylnaphthalene containing fuels. During the most recent experiments, recalibration of the fuel rotameters with the 1-methylnaphthalene containing fuels indicated that the mass flow rates at given rotameter settings had changed since previous calibrations. This finding was not surprising since other experimental difficulties with fuel filters and nozzles were frequently encountered when 1-methylnaphthalene was burned in the JSC. Unfortunately, the extent to which the fuel flow rates in the earlier 1-methylnaphthalene experiments matched past calibrations cannot be verified, and errors in the fuel flow rates may have produced the apparently different 1-methylnaphthalene sooting characteristics through inaccurate equivalence ratios. The strong sensitivities of measured soot concentrations on the mixture equivalence ratios also imply that relatively small errors in fuel flow rate measurements may produce substantial differences in sooting characteristics. Thus, accurate fuel metering is an essential ingredient in quantitative measurements of sooting characteristics, and the recent 1-methylnaphthalene data are thought to be the most reliable. These data suggest that at 1900 K, the Category 3 designation for 1-methylnaphthalene may not be necessary. The possibility that Category 2/Category 3 differences are much larger at lower temperatures is not resolved at this time.

A.2.5 GC Analysis of Unburned Hydrocarbons

During some recent experiments conducted in the JSC, gas chromatographic (GC) analyses of the exhaust gases were performed in order to identify the major hydrocarbon species present. Since a suitable gas chromatograph was not available in the JSC laboratory,

Figure 1. JSC soot emissions for toluene/methylnaphthalene blends;
 $T = 1900 \text{ K}$; $\tau = 3 \text{ ms}$.

Figure 2. JSC soot production for Category 2 fuels at 300°C inlet temperature and 112.5 g/min air flow rate.

samples of the exhaust gases were collected in bombs and sent to ER&E's Analytical Division GC Laboratory for analysis. The associated collection, storage, and syringe transfer (bomb to GC) of the samples caused several experimental difficulties, and three separate procedures were employed to minimize uncertainties in the measurements. Conditions and results of these experiments are summarized in Tables 1 and 2. In Table 2 all hydrocarbon concentrations are expressed as the equivalent mole per cent of methane; "on-line" refers to total unburned hydrocarbon (THC) concentrations measured with a heated flame ionization detection (FID) hydrocarbon analyzer; and $(\text{THC:GC})/(\text{THC:on-line})$ is the ratio of THC concentrations inferred from the GC analyses to the THC concentrations measured with the FID analyzer. Details of the experiments are given below.

In the first set of experiments (Configuration A), exhaust gases were collected in glass bombs which had Teflon stopcocks and rubber septums. During these experiments the bombs were connected to the exhaust lines within the sampling conditioning oven (See References [1,2]). Gas samples were obtained by passing the exhaust gases through the bomb until uniform concentrations were achieved within the bomb and subsequently closing the stopcocks. The bombs were then removed from the oven, allowed to cool to room temperature, and submitted to the GC laboratory. Syringes were then used to extract samples from the bombs and inject them into the GC. Samples were extracted at room temperature and at the sample conditioning oven temperature (100°C). For the 100°C cases the bombs were reheated before syringe samples were withdrawn.

The GC analyses provided measurements of N_2 , O_2 , CO , CO_2 , H_2O and several hydrocarbon concentrations. Unfortunately leaks in the glass bombs, coupled with one to two day delay times between sample collection and analysis and with the heating and cooling of the bombs, produced air contaminated samples. The resulting measurements could not be directly compared with on-line measurements of CO , CO_2 , O_2 and THC; consequently, the extent of air dilution was estimated from the GC measured oxygen concentrations. Oxygen concentration contributions from the sample gases were generally small enough to be neglected in the calculations, and dilution corrected values of CO , CO_2 , THC and H_2O concentrations were found to be in reasonable agreement with on-line measurements obtained with infrared (CO , CO_2) and FID (THC) analyzers and with calculated H_2O concentrations inferred from on-line H_2 and THC measurements and a hydrogen atom balance. Differences between room temperature and reheated bomb samples were sufficiently small to be neglected. The particular GC column used could not separate acetylene from ethylene.

The other two sets of experiments (Configurations B and C) employed stainless steel sample bombs. In configuration B, the bombs were inserted downstream of a cold water (10°C) trap in an unheated section of the sample line which feeds the O_2 , H_2 , CO and CO_2 analyzers. In Configuration C, the bombs were inserted upstream of the trap in a heated section of the same sample line. For the latter Configuration (C), on-line THC concentrations obtained from the FID analyzer showed no significant differences when the sample gases were passed through the normal heated sampling lines or through the lines containing the bombs. The bombs were not heated in either configuration.

Table 1: Experimental Conditions for GC Samples

<u>Run</u>	<u>Sample Configuration*</u>	<u>Fuel</u>	<u>Equivalence Ratio</u>	<u>Temperature (K)</u>	<u>Residence Time (ms)</u>
B-134	A	toluene	1.6	1700	3
B-136	A	toluene	1.6	1900	3
B-137	A	toluene	1.6	1700	3
B-171	B	1-methylnaphthalene	1.4	1900	3
B-172	B	1-methylnaphthalene	1.6	1900	3
B-174	B	1-methylnaphthalene	1.6	2000	3
B-175	C	toluene	1.6	1900	3
B-176	C	toluene	1.7	1700	3
B-177	C	toluene	1.6	1800	3
B-178	C	toluene	1.6	1800	6
B-182	C	isooctane	1.6	1900	3
B-183	C	ethylene	1.6	1900	3

* A = glass bomb, in oven, dilution $\sim$ 35% sample/65% air

B = stainless steel bomb, outside oven, after cold water trap, dilution $\sim$ 80% sample/20% air

C = stainless steel bomb, outside oven, before cold water trap, dilution $\sim$ 80% sample/20% air
(See text for more detailed descriptions of sample configurations)

Table 2: Hydrocarbon Concentrations from GC Samples *

Run	THC: On-line (% as methane)	THC: GC On-line	Percent of THC: GC (as methane)					
			CH_4	C_2H_4	C_2H_2	C_3 to C_5	C_6H_6	C_7H_8
B-134	4.20	0.63	7	(73)		4	6	10
B-136	2.28	0.85	4	(92)		4	--	--
B-137	4.73	1.16	4	(51)		2	11	32
B-171	0.79	1.61	6	2	91	1	--	--
B-172	2.03	0.54	7	1.5	91	0.5	--	--
B-174	0.10	5.54	5.5	1.5	93	--	--	--
B-175	2.64	0.74	8.5	2	86	3.5	--	--
B-176	4.20	0.50	10	2	85	3	--	--
B-177	2.00	0.65	7.5	1	90	1.5	--	--
B-178	1.00	0.44	8.5	1.5	89	1	--	--
B-182	0.80	0.46	9	1.5	88	1.5	--	--
B-183	1.40	0.69	14	4	80	2	--	--

*See text for definitions of THC:GC and THC:On-line.

Sample collection and analysis procedures for the Configuration B and C runs were essentially the same as those described for the Configuration A room temperature samples, except additional GC analyses (same samples) with other columns were performed to obtain separate acetylene and ethylene concentrations. Small leaks were also present in the stainless bombs, and GC oxygen concentration measurements were again used to correct for air dilution effects. Although corrected values of the GC measured CO and CO₂ concentrations were in reasonable agreement with the corresponding on-line values, H₂O and THC concentrations were not.

Absolute GC water concentrations (uncorrected for dilution) were generally between 1% and 2% by volume. These values were significantly smaller than the 6% to 10% values calculated from on-line measurements, and they were also of the same order as room temperature water vapor pressures. Consequently, water vapor probably condensed in the cold water trap (Configuration B) or within the bombs (Configuration C). The hydrocarbon results do not appear to be adequately explained by a simple condensation mechanism. In particular, the discrepancies between GC and on-line THC concentrations seem more pronounced at the lowest (<1%) and the highest (>4%) THC concentrations. At the lower levels, the accuracy of the thermal conductivity detector used in the GC for overall analyses (CO, CO₂, N₂, O₂, H₂O, HC) is questionable since the very low molar concentrations of the hydrocarbons were at or near the detectability limit of the instrument. At the highest THC concentration (Run B-176), only trace amounts of benzene and toluene were found (less than 1% of THC as methane). Configuration A results at similar conditions (B-134, B-137) indicated that significant concentrations of benzene and toluene were present in the samples. Condensation of these heavier hydrocarbons does not appear to fully explain the conflicting results since estimated concentrations of benzene and toluene, based on the discrepancy between GC and on-line THC measurements, were below corresponding room temperature vapor pressures. Additional experiments appear necessary to resolve this anomaly.

The collection of data from the various experiments suggest that following general conclusions regarding hydrocarbon concentrations in JSC exhaust gases:

- (1) At small THC concentration levels (<1%), the principal hydrocarbon species are probably C₂H₂ and CH₄.
- (2) At large THC concentration levels (>4%), heavier hydrocarbons, including parent fuel molecules, probably contribute a significant portion of the THC concentration.
- (3) Within the range of variables investigated, fuel type, temperature, equivalence ratio, and residence time did not appear to significantly affect conclusions (1) and (2).
- (4) The present GC sampling and analysis techniques do not provide totally satisfactory data, and they should be improved for future experiments.

One additional observation regarding the results involves the stability of single-ring aromatic compounds. In the Configuration A experiments, single-ring aromatic compounds were detected in the 1700 K runs, but not in the 1900 K run. This disappearance of the single-ring aromatics as temperature was increased is apparently consistent with Graham's [4] findings that single-ring aromatics are unstable above 1800 K.

A.2.6 Soot Characterizations

During several JSC experiments soot samples were collected and submitted to ER&E's Analytical Division for carbon/hydrogen/nitrogen elemental analyses and for electron microscope photographs. In these experiments toluene-nitrogen-oxygen mixtures were burned with equivalence ratios (ϕ) of 1.6 or 1.8, indicated temperatures of 1700 K or 1900 K and residence times (τ) of 3, 4.5, or 6 ms. All soot samples were collected from the stainless steel probe/Teflon filter system used for soot concentration measurements (See References [1,2]).

Results from the soot elemental analyses are given in Table 3. In two runs (B-134, B-135) samples contained a mixture of soot collected from the Teflon filter and the stainless steel probe tip. In the other runs (B-136, B-137) soot collected from the probe and filter were analyzed separately. The results indicate that the hydrogen weight percentages of the soot samples were of the order of 1%. This finding is consistent with values commonly found for soot; however, the specific hydrogen percentages appeared to depend on the temperature in the combustor and on the location where soot was collected (probe or filter). In particular, relatively larger hydrogen percentages were found in the lower temperature (1700 K) and probe tip samples. Total weight percentages (carbon + hydrogen + nitrogen) also varied between 90% and 100%, and smaller total weight percentages were found in the lower temperature (1700 K) and probe tip samples. We suspect that the total weight percentage variations may have been related to the oxygen contents of the soot samples which were not measured. The hydrogen content trends suggest that higher combustor temperatures and longer sample residence times (probe = short; filter = long) may reduce the number of hydrocarbon fragments attached to the soot.

Scanning electron microscopy (SEM) photographs of soot particles collected on lightly loaded filters were not significantly different. In all cases soot "particle" diameters were found to be of the order of 70 nm. The term "particle" is used to describe what appear to be the smallest observable soot structures in the photographs. Examples of these photographs are given in Figures 3 and 4. Additional transmission electron microscopy (TEM) photographs were taken for some runs. For these photographs soot from heavily loaded filters was removed from the filters and redispersed on microscope slides. Average soot "particle" diameters inferred from these photographs were of the order of 25 nm. An example of the TEM photographs is given in Figure 5.

The apparent discrepancies between the average "particle" diameters inferred from the SEM and TEM photographs may be related to the soot collection and/or redispersal procedures employed. Agglomeration effects may be different for each procedure and these effects may also alter the size of the soot particles after they leave the combustor. Consequently, the relatively small differences observed within each

Table 3: Elemental Analyses of Soot Samples from Toluene-
N₂-O₂ Combustion ($\phi=1.6$, $\tau=3\text{ms}$)

Run Designation	T (K)	C (wt %)	H (wt %)	N (wt %)
B-134)	1700	89.9	2.3	0.4
B-135) Filter + probe	1900	96.2	0.8	0.8
B-136-Filter	1900	99.2	0.7	<0.3
B-136-Probe	1900	88.7	1.4	1.6
B-137-Filter	1700	94.0	2.2	<0.3
B-137-Probe	1700	86.6	3.5	<0.3

Figure 3. SEM photograph of soot samples from Toluene-N₂-O₂ combustion; $\phi=1.6$; $\tau=3\text{ms}$; $T=1700\text{ K}$; scale: $4\text{ mm} = 0.1\text{ }\mu\text{m}$.

Figure 4. SEM photograph of soot samples from Toluene-N₂-O₂ combustion; $\phi=1.6$; $\tau=3\text{ms}$; $T=1900\text{ K}$; scale: $4\text{ mm} = 0.1\text{ }\mu\text{m}$.

015151131

ELECTRON MICROGRAPH

NJ O-6432-74

Material Soot
1 mm = 11 nm Orig. Mag. Final Mag. 93 200 X
Date Aug 80 Al # Sample # B181F

ANALYTICAL AND INFORMATION DIVISION
EXXON RESEARCH AND ENGINEERING CO.

Figure 5. TEM photograph of soot samples from Toluene-N₂-O₂ combustion; $\phi = 1.8$; $\tau = 3$ ms; $T = 1900$ K.

set of photographs (SEM or TEM) may indicate that soot particles produced at the JSC conditions tested were not very different or that the collection/redispersal procedures strongly influenced the size of the photographed soot "particles". More refined experiments appear necessary to resolve this question.

A.3 Liquid Fuel Jet-Stirred Combustor Experiments

Two sets of experiments were conducted in the Liquid Fuel Jet-Stirred Combustor (LFJSC) during the present reporting period. These included liquid fuel soot production experiments and gaseous fuel unmixedness experiments. Following a brief description of the LFJSC, results from both sets of experiments and a discussion of the results are presented.

A.3.1 Experimental Apparatus

The Liquid Fuel Jet-Stirred Combustor (LFJSC) is shown schematically in Figure 6. It contains a spherical jet-stirred zone and a cylindrical plug flow zone. The spherical portion consists of two castable refractory halves housed within a 15.2 cm diameter metal shell. The refractory material is Castable 141A, a product of Combustion Engineering Refractories, which is capable of withstanding temperatures up to 2140 K. Each section is cast separately with a 5.1 cm diameter hemispherical volume--the two sections together create the spherical combustor zone. The cylindrical plug flow section is composed of a 7.6 cm long by 2.2 cm diameter alumina tube.

Combustion air enters the spherical reaction zone through two sets of jets positioned 180° apart. Four 1.1 mm diameter air jets in each side of the combustor (total of eight) are aimed towards the corners of a cube imagined to sit within the spherical combustor (See Figure 6). One set of air jets is rotated 45° with respect to the other to allow the opposing jets to mesh rather than collide. This approach provides for highly turbulent mixing and simulates the recirculating characteristics of gas turbine systems.

Fuel sprays enter the combustor at two positions 90° from each set of air jets. Air atomizing nozzles obtained from Spraying Systems Co. (1/4 J Series) produce the fuel sprays; nozzle assemblies include Model 1650 (0.04 cm inside diameter) fluid caps and Model 67147 (pressure) air caps. The nozzles are positioned approximately 7 cm from the center of the spherical section of the combustor; cylindrical cavities (2.3 cm diameter by 4.4 cm long) cast in the refractory contain the developing fuel sprays.

The LFJSC operates at atmospheric pressure. Estimates of the temperature within the combustor are obtained from a platinum-6% rhodium/platinum-30% rhodium thermocouple positioned at the center of the spherical combustor section; corresponding radiation correction factors are of the order of 50 K (See Appendix 1). Temperature within the combustor is controlled by varying the concentration of oxygen in the main combustion "air" or main combustion and atomizing "air" flows. Metering of all air, oxygen and liquid fuel flows is accomplished using calibrated rotameters.

LIQUID FUEL JET-STIRRED COMBUSTOR

Figure 6. Schematic diagram of the Liquid Fuel Jet-Stirred Combustor.

Combustion products are sampled with a 0.24 cm inside diameter probe which is inserted into the plug flow section of the combustor. This hot water-cooled stainless steel probe is connected to stainless steel transfer lines which are electrically heated to prevent condensation of water or unburned hydrocarbons within the lines. The transfer lines carry the exhaust products to two 420 K ovens in which all sample conditioning (pumping, filtering and valving) is accomplished.

Three types of combustion products analyses are performed. First, soot particulates from metered volumes of exhaust gases are collected on preweighed filters located within one of the ovens. After suitable drying in a dessicator, the filters are again weighed to obtain soot concentration measurements in units of mg/l. Another sample of exhaust gases is filtered, diluted with nitrogen (preheated to oven temperature) and directed through heated transfer lines to a heated flame ionization hydrocarbon analyzer for measurement of total unburned hydrocarbon (THC) concentrations (% as methane). The nitrogen dilution is employed to keep THC concentrations within the linear range of our instrument. A third sample of product gases is filtered, passed through a cold water trap and sent to four different instruments for CO, CO₂, O₂ and H₂ concentration measurements. The instruments include two nondispersive infrared analyzers (CO and CO₂), one amperometric oxygen analyzer and a gas chromatograph (H₂). Material balances are routinely performed to correct the latter four measurements for the effects of water condensation in the cold water trap.

A.3.2 Liquid Fuel Results

Two liquid fuels have been studied in the LFJSC: isooctane (representing Category 1) and toluene (representing Category 2). Several sets of experiments have been run with each fuel to investigate the influence of fuel type, equivalence ratio, atomization air flow rate, and temperature on soot formation in the LFJSC. The average residence time of gases within the combustor (volume/volumetric flow rate at combustor temperature) was approximately 6 ms for all experiments; corresponding total "air" flow rates were approximately 200 g/min.

Figure 7 displays soot concentrations obtained at various equivalence ratios. Atomization air flow rates (no added oxygen) and indicated combustor temperatures were held constant during these runs; temperature was controlled by varying the oxygen concentration in the main "air" jets. The error bars indicate the typical spread among repeated measurements. Toluene data obtained by Blazowski [2] with the JSC are also included in the figure for comparison.

The effects of atomization air flow rates on soot production within the LFJSC are shown in Figure 8. Data for each fuel were obtained at constant equivalence ratio, temperature, and total "air" (air + O₂) flow rates. Temperature was again controlled by varying the oxygen concentration in the main "air" jets; within each set of experiments (isooctane or toluene), overall oxygen concentrations were equal. No data are presently available to characterize the toluene and isooctane sprays at these flow conditions; however, some limited data from similar Jet A/ nitrogen and JP-10/nitrogen sprays in an approximately quiescent, room temperature atmosphere have been obtained with a Malvern Particle and Droplet Sizer (Model ST 1800). These data indicated that Sauter Mean

Figure 7. Dependence of soot concentration on equivalence ratio; atomization air = 15 g/min/nozzle; indicated temperature = 1900K $\pm$ 35K.

Figure 8. Dependence of soot concentration on atomization air flow rate; indicated temperature = $1900\text{K} \pm 35\text{K}$.

Diameters (SMD) for the Jet A and JP-10 sprays were of the order of 30 μm and that smaller diameters corresponded to larger atomization nitrogen flow rates (fixed fuel flow rate).

Figure 9 displays isooctane data obtained for several temperatures at an equivalence ratio of 1.45 and an atomization "air" flow rate of 15 g/min/nozzle. For these experiments, temperatures were controlled by varying the oxygen concentration in the main or main plus atomization "air" flows. The two oxygen distributions at each fixed overall oxygen concentration were included to investigate the effects of gas phase mixing on soot production within the LFJSC. The experimental results indicate that soot concentrations were larger at higher temperatures and that the distribution of oxygen among the inlet "air" flows did not significantly affect the measured soot concentrations. Similar qualitative results were obtained with isooctane at a higher atomization "air" flow rate of 22.5 g/min/nozzle. In these runs, however, collected quantities of soot were too small to be measured, and relative soot concentrations were inferred from the relative darkness of the filters.

Attempts to obtain variable temperature data for toluene sprays were not as successful. Large spreads in the data, similar to those shown in Figure 7, were observed for these runs such that differences in the soot concentrations measured at several temperatures were not large compared to the differences observed among repeated measurements at fixed temperatures. After some toluene runs, coke deposits were also found in the combustor near the cylindrical surface where the spray cavities border the spherical zone of the combustor. Consequently, the effect of temperature on toluene soot production in the LFJSC could not be determined from the available experimental data.

A.3.3 Unmixedness Results

One set of experiments was conducted in the LFJSC with gaseous ethylene fuel and air (no added oxygen). The objective of these experiments was to investigate the effects of gas phase mixing on combustion within the LFJSC. Mixing in the combustor was varied by either premixing ethylene with air entering through the main air jets or separately injecting ethylene through the atomization "air" passages of the fuel nozzles. At average residence times (τ) of approximately 7 ms, differences between measured major species' (CO , CO_2 , O_2 , H_2 , THC) concentrations and indicated temperatures were small. Table 4 presents specific data for an equivalence ratio (ϕ) of 2.4, the largest equivalence ratio tested. At the conditions tested ($\phi < 2.4$, $\tau \approx 7$ ms), filters in the sampling system did not show any evidence of soot deposition for either method of ethylene injection.

A few additional experiments were attempted with larger flow rates ($\tau \approx 4$ ms). Again ethylene/air mixtures were burned, and the same premixed and separately injected configurations were employed. In the premixed case, ($\phi = 2.4$) soot was not deposited on the collection filter, and major species concentrations and indicated combustor temperatures were only slightly different from the larger residence time values (See Table 4). In the corresponding separately injected case, however, substantial leaks developed in the LFJSC, and these leaks prevented the collection of reliable data.

Figure 9. Dependence of soot concentration on temperature for isooctane, $\phi = 1.45$, atomization "air" = 15 g/min/nozzle.

Table 4: Gas Concentrations in Unmixedness
Experiments ($\phi=2.4$)

Configuration	Total Air Flow Rate (g/min)	Temperature* (K)	Concentrations (mole %)				
			CO	CO ₂	O ₂	H ₂	THC (as CH ₄)
Separately injected	200	1473	16.2	3.5	0.1	10.7	8.9
Premixed	200	1478	15.3	4.3	0.3	10.9	11.0
Premixed	360	1583	14.8	4.6	0.2	9.8	9.8

* Uncorrected thermocouple value at center of reactor.

A.3.4 Discussion

The initial data obtained from the LFJSC suggest that the production of soot in jet-stirred combustors is very dependent upon the method of fuel injection, i.e., whether fuel enters prevaporized and premixed or as a liquid spray. Toluene and isooctane both produced significantly more soot when they were injected as liquid sprays, and the amount of soot produced by either fuel was strongly related to the fuel spray characteristics inferred from atomization "air" flow rates. Also, gaseous ethylene, premixed with air or separately injected, did not produce soot in the LFJSC at combustor conditions similar to those at which soot was produced from isooctane sprays. Since ethylene and isooctane (Category 1 fuels) both produced negligible amounts of soot in premixed gas phase jet-stirred combustors, the ethylene/isooctane sooting differences obtained in the LFJSC were probably related to the injection of isooctane as a liquid spray. A Category 1/Category 2 distinction between isooctane and toluene sooting characteristics still appeared to be appropriate for liquid spray combustion in jet-stirred combustors since toluene did produce significantly more soot than isooctane at similar combustor conditions.

The relationships between soot and THC concentrations in the liquid spray experiments, however, were unlike previous trends observed for the two fuel categories in gas phase stirred combustors. In particular, toluene produced larger quantities of soot in the LFJSC before appreciable quantities of THC were measured ($>0.1\%$ as methane). This result is in direct conflict with the previous trends which suggested that measurable quantities of soot appeared only after THC breakthrough and that soot concentrations were strongly related to THC concentrations. The apparently conflicting trends may be partially related to the specific locations of the sample probes in each combustor. A probe was inserted into the jet-stirred zone of the JSC; however, in the LFJSC, the probe was inserted at the downstream end of the plug flow zone. Consequently, some unburned hydrocarbons present in the jet-stirred zone of the LFJSC may have subsequently burned in the plug flow zone. This explanation could possibly account for the large soot/small THC concentrations measured for the toluene sprays. We plan to further investigate this question in future experiments in the VPJSC.

Isooctane produced significant ($>1.0\%$ as methane) THC concentrations for both types of fuel injection, but soot was measured only when isooctane was injected as a liquid spray. For the conditions tested in the LFJSC, soot concentrations appeared to be related to THC concentrations since both soot and THC concentrations increased with increasing equivalence ratio or decreasing atomization air flow rates (fixed temperature). In constant equivalence ratio and atomization "air" flow rate experiments, however, temperature did not appear to significantly affect the THC concentrations over the limited range investigated. This trend for isooctane sprays was unlike previous JSC (prevaporized fuel, premixed with "air") results which suggested that THC concentrations decreased with increasing temperature.

The effects of temperature on soot production in stirred combustors appeared to be exactly opposite for the two types of fuel injection. Blazowski's [2] previous temperature trend for prevaporized toluene/"air" mixtures was in agreement with expectations for premixed flames (less soot at higher temperatures), but the temperature trend reported here for isooctane sprays indicated that a significant portion of the fuel produced soot like a diffusion flame, i.e. more soot at higher temperatures [6,7]. These trends suggested that fuel and oxidizer were not well-mixed in the LFJSC.

This unmixedness was probably related to the presence of liquid fuel sprays in the LFJSC. Data from the various atomization air flow rate conditions suggested that spray characteristics (mean droplet diameters and/or local "air"/fuel mixing) significantly affected both the soot and THC concentration levels, and results from the gas phase mixing experiments conducted in the LFJSC did not suggest that any significant gas phase mixing effects were present at the conditions tested. In particular, variations of the oxygen distribution between main and atomization "air" flows and variations of the method of gaseous fuel injection did not appear to significantly alter the combustion product concentrations or the indicated temperatures. Consequently, gas phase mixing did not appear to significantly affect the soot production mechanisms within the LFJSC, and any dependence of soot production on unmixedness was probably related to the pyrolysis, vaporization, and burning of liquid fuel sprays within the combustor.

A.4 Variable Pressure Jet-Stirred Combustor

Most of the future work under the present contract will be conducted in ER&E's new Variable Pressure Jet-Stirred Combustor (VPJSC). The VPJSC has been constructed with ER&E funds and is currently undergoing shakedown experiments. It should be fully operational by mid 1981. A photograph of the unit is shown in Figure 10; Figure 11 contains a schematic diagram of the apparatus. An overall description of the VPJSC as well as details of major components are given below.

Overall Description. The VPJSC is designed to operate at pressures from 0.5 to 5 atm with either gaseous or liquid fuels. It has a spherical jet-stirred zone followed by a cylindrical plug flow zone. Primary air and fuel are injected into the stirred zone; secondary air may be injected into the plug flow zone. A translatable probe is available for sampling along the plug flow zone center-line; a fixed location probe may also be inserted into the stirred zone. Two sided optical access is available at one location within each zone.

Combustor. The VPJSC is constructed in two modules. The front or stirred zone module contains the spherical stirred zone and the initial section of the cylindrical plug flow zone. The present front module has a 7.6 cm diameter stirred zone. Its corresponding plug flow section is 8.9 cm long and has a diameter of 3.8 cm. A front module with a larger stirred zone diameter (15.2 cm) has also been designed for the VPJSC. Its plug flow section is 5.1 cm long so that the center of its stirred zone coincides with the center of the smaller diameter stirred zone. The stirred zone optical line-of-sight passes through the common center.

Figure 10. Photograph of the Variable Pressure
Jet-Stirred Combustor.

Figure 11. Schematic diagram of the Variable Pressure Jet-Stirred Combustor.

The rear or plug flow module has a diameter of 7.6 cm and a length of 50.8 cm. It interfaces with the front module 12.7 cm downstream of the center of the stirred zone. Secondary air is injected 5.1 cm downstream of this interface, and the plug flow zone optical ports are located 15.2 cm downstream of the secondary air injectors.

Both combustor zones are lined with two layers of castable refractory. The inner layer (Carborundum 66) can withstand temperatures up to 2200 K; the outer layer (Carborundum BI-57) has a lower thermal conductivity to reduce combustor heat losses. Several thermocouples are also imbedded within the refractory lining to measure temperatures for estimates of combustor heat losses and interior wall temperatures.

Primary Air. Primary air is introduced into the center of the stirred zone through two injectors positioned 180° apart. Each injector has a modular nozzle which directs high velocity jets of air throughout the stirred zone. Jet patterns and velocities may be easily varied with different nozzles; total primary air flow rates are limited to 0.065 kg/s by the air supply. The primary air may also be heated up to 900 K with electric preheaters. Primary air flow rates are metered via the pressure drop across a fixed orifice; temperatures are measured with thermocouples.

Fuel. Fuel is introduced into the VPJSC stirred zone perpendicular to the primary air jets. A schematic diagram of the fuel injector is shown in Figure 12. For liquid fuel injection, pressure atomizing nozzles (Wm Steinen Mfg. Co. oil burner nozzles) are used to produce solid or hollow cone sprays. Atomizing gas (air, nitrogen, or steam) may be injected around the spray to enhance atomization and local mixing, and fuels may be preheated up to 800 K with an electric heater. The liquid fuel passages may also be used to inject gaseous (room temperature) or prevaporized fuels. An additional heater is available to vaporize and/or superheat fuels up to 875 K. All fuel flow rates are metered via the pressure drops across fixed orifices. Temperatures are measured with thermocouples.

Secondary Air. Secondary air is injected radially into the plug flow zone through four injectors spaced at 90° angular intervals. Each injector contains either a 1 mm or 3 mm diameter orifice; the total secondary air flow is limited to 0.026 kg/s. Electric heaters are also available to preheat the air up to 750 K. Air flow rates are metered via the pressure drop across a fixed orifice; temperatures are measured with thermocouples.

Combustor Pressure. Pressure within the VPJSC is controlled via a backpressure valve and steam ejector within the exhaust system. Pressures from 1 to 5 atm may be obtained by adjusting the backpressure valve. Subatmospheric pressures (0.5 to 1 atm) may be obtained by ejecting steam into the exhaust gases after they have been cooled via a series of water sprays.

Combustion Diagnostics. The principal combustion diagnostics presently installed in the VPJSC include a translatable sample probe and associated gas analyzers, two thermocouple probes, and a laser

Figure 12. Schematic design of the Variable Pressure Jet-Stirred Combustor fuel injector.

extinction soot concentration diagnostic. The sample probe has a hot-water cooled stainless steel body which is lined with quartz. Its internal and external diameters are 6 mm and 2.5 cm, respectively. Gases collected within the probe are normally transferred through an electrically heated filter and Teflon line to an oven in which additional sample conditioning (pumping, valving, etc.) is accomplished. The gases are then distributed among five analyzers for measurements of O_2 , CO, CO_2 , NO/NO_x , and THC concentrations. The analyzers include one amperometric oxygen analyzer (Beckman Model 7003), two nondispersive infrared analyzers (CO: Beckman Model 865, CO_2 : Beckman Model 864), one chemiluminescent NO/NO_x analyzer (Beckman Model 955), and one flame ionization hydrocarbon analyzer (Beckman Model 402). Alternatively, gases collected in the sample probe may be directed to an auxiliary soot collection filter immediately downstream of the probe. Soot concentrations may then be inferred from the weights of soot collected and metered sample flow rates.

Two platinum/13% rhodium (National Basic Sensor Corp. Model 2RR9912-24-C) thermocouple probes are mounted in the VPJSC for gas temperature measurements. One is inserted into the stirred zone; the other is inserted into the plug flow zone at the same axial location of the optical ports. The magnitude of any radiation/conduction errors in the thermocouple temperatures has not yet been determined.

Figure 13 contains a schematic diagram of the laser extinction soot concentration diagnostic configuration. The basic principle of the diagnostic is that soot particles in the combustor gases absorb and scatter the 632.8 nm laser light which is passed through the combustor at the two locations shown in Figure 13. The degree of extinction of the laser beam by absorption and scattering is determined by the number density and size of soot particles in the gases, the optical and physical properties of the soot particles, and the path length of the laser beam in the soot laden gases. For typical soot particles with diameters of the order of 25 nm, the Rayleigh approximation to the detailed Mie Scattering theory generally applies [8], and the extinction can be reasonably well described by the equation

$$I = I_0 \exp (-\tau)$$

where I_0 equals the laser intensity entering the combustion gases; I equals the laser intensity leaving the combustion gases; and τ equals the optical depth, which can be written for a uniform soot laden gas as

$$\tau = \left[\frac{6\pi L}{\lambda} \right] \cdot \left[\text{Im} \left(\frac{m^2 - 1}{m^2 + 2} \right) \right] \cdot \left[N \left(\frac{\pi d^3}{6} \right) \right]$$

L is the path length of the laser beam in the combustion gases; λ is the laser wavelength; m is the complex index of refraction of the soot particles; N is the soot particle number density; and d is the soot particle diameter. The product $[N(\pi d^3/6)]$ is also the soot volume

Figure 13. Schematic diagram of the laser extinction soot concentration diagnostic for the Variable Pressure Jet-Stirred Combustor.

fraction, f_v . With known values of L , m , and λ , measurements of I and I_0 may be used to calculate line-of-sight averaged values of τ and f_v . The average volume fraction may then be converted into various concentration units using values of the soot, gas, and total carbon atom densities.

Although the technique is relatively straightforward, several problems may be encountered with it. First, reported values for m and the soot density have relatively large (25-50%) uncertainties which produce large uncertainties in the inferred soot concentrations. Second, the laser light may also be absorbed and/or scattered by large molecules, i.e. polycyclic aromatic hydrocarbons, such that soot concentrations calculated via the Mie theory may be overestimated. Finally, for small soot concentrations, differences between I and I_0 may be difficult to measure, and corresponding soot concentration measurements may have large uncertainties.

To minimize the uncertainties associated with these problems, we plan to calibrate the extinction diagnostic with soot concentration measurements obtained from the translatable sampling probe and its filter collection system. The majority of our VPJSC soot data, however, will be obtained with the extinction diagnostic. To increase the extinction diagnostic's sensitivity for small soot concentrations, we have also incorporated a double pass laser beam path.

Some details of the extinction diagnostic components are as follows:

LASER:	Spectra Physics Model 120 He-Ne Laser, 5 mW @ 632.8 nm
CHOPPER:	EG&G Princeton Applied Research Model 125A Light Chopper
DETECTORS:	EG&G Electro Optics Model HUV-4000B photo- diode/amplifier combinations, preceded by Corion #10-6328-2 laser line filters (1 nm bandwidth centered at 632.8 nm) and addi- tional neutral density filters
SIGNAL PROCESSORS:	EG&G Princeton Applied Research Model 128A/70 Lock-in Amplifiers

Computer Control/Data Acquisition. The VPJSC uses ER&E's pilot plant computers for the control of operating conditions and for automated data acquisition. Primary air, secondary air, and fuel flow rates and temperatures and combustor pressure (or vacuum) are all individually monitored and controlled via the computer. Signals from the gas analyzers, thermocouples, and the laser extinction soot concentration diagnostic are also input to the computer, and several data reduction programs are available to transform all the raw data into useful, on-line output.

A.5 Program Status and Future Work

A.5.1 Soot Production

At the end of the present reporting period, planned JSC and LFJSC soot production experiments were complete. The JSC experiments generated a considerable amount of quantitative data and trends regarding the predominantly chemistry aspects (effects of fuel type, equivalence ratio, temperature, and residence time) of soot production in premixed, gas phase stirred combustors. The LFJSC experiments, however, indicated that some of these trends may be significantly altered when fuel is injected separately as a liquid spray. For example, the effect of temperature on soot production was exactly opposite for prevaporized, premixed and liquid spray fuel injection (See Section A.3.4). These important differences will be further investigated in future experiments in the VPJSC. The experiments will also address the effects of pressure and mixing on soot production, the differences among Category 2 and Category 3 fuels, the pyrolysis and partial oxidation of aromatic hydrocarbons and the oxidation of soot.

The pressure and mixing studies address two important aspects of soot production which have received relatively little attention in the combustion literature. Results from these studies should make a significant contribution to the understanding of soot production mechanisms. Experiments with both prevaporized and liquid fuel injection will also provide additional information regarding the different sooting trends obtained with the two types of fuel injection. The Category 2/Category 3 fuels study will attempt to resolve some of the questions regarding the differences among Category 2 and Category 3 hydrocarbons (See Section A.2.4). Since most Category 3 fuels are solids at room temperature, blends of Category 2 and Category 3 fuels will be used in these experiments, the majority of which will be conducted in the VPJSC. The pyrolysis/partial oxidation and the soot oxidation experiments will make use of the VPJSC plug flow zone to obtain time resolved data regarding soot production/oxidation processes. In these experiments major gas species concentration profiles will be obtained from the translatable sampling probe and soot concentrations will be obtained at two locations via the laser extinction diagnostic. These data will also be used by SAI to develop and evaluate a coupled well stirred reactor/plug flow reactor model of the soot production and soot oxidation processes.

A.5.2 Fuel Nitrogen Conversion

Fuel nitrogen conversion experiments conducted (and funded) by ER&E as part of the present contract have been designed to investigate three aspects of fuel nitrogen conversion in jet-stirred combustors. These include the effects of fuel type, residence time, and fuel injection (prevaporized vs liquid spray). Experiments have or will be conducted in all three ER&E stirred combustors; however, all data from the experiments are proprietary to ER&E until October 31, 1981 and are not included in the present report. Table 5 contains planned conditions of the first set of JSC and LFJSC fuel nitrogen conversion experiments. At each experimental

condition, measurements of total fixed nitrogen ($\text{TFN} = \text{NO} + \text{NH}_3 + \text{HCN}$) will be made for pure and pyridine doped (1% N by weight) versions of the listed fuels. Additional efforts will involve more detailed investigations of the most important findings from the initial set of experiments. These experiments will probably be conducted in the VPJSC. At the end of the present reporting period, isooctane experiments in the 5.08 cm JSC were complete.

Table 5: Conditions for Fuel Nitrogen Conversion Experiments

Reactor	JSC d = 3.81 cm	JSC d = 5.08 cm			JSC d = 7.62 cm			LFJSC d = 5.08 cm
Residence Time (ms)	3	3	4.5	6	6	12	18	6
Equivalence Ratios:	1.2	1.0 1.2	1.2	1.2	1.2	1.2	1.2	1.2
	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
Isooctane	1.6	1.6 1.8	1.6	1.6	1.6	1.6	1.6	1.6
Equivalence Ratios:	1.2	1.0 1.2	1.2	1.2	1.2	1.2	1.2	1.2
	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
Toluene	1.6	1.6 1.8	1.6	1.6	1.6	1.6	1.6	1.6

Combustion temperature = 1900 K for all experiments
specific conditions subject to change depending upon results obtained.

Acknowledgments

The authors gratefully acknowledge the excellent technical support of Messrs. R. J. Kuriskin and R. W. Schroeder, who conducted the various jet-stirred combustor experiments, and of Mrs. J. Buczek, who typed this and many other associated contract reports.

References - Part A

- [1] Blazowski, W. S., Edelman, R. B., and Harsha, P. T., "Fundamental Characterization of Alternate Fuel Effects in Continuous Combustion Systems," Summary Technical Progress Report for the period 15 August 1977-14 August 1978 under U.S. Department of Energy Contract EC-77-C-03-1543, September, 1978.
- [2] Blazowski, W. S., Edelman, R. B., and Wong, E., "Fundamental Characterization of Alternate Fuel Effects in Continuous Combustion Systems," Summary Technical Progress Report for the period 15 August 1978-31 January 1980 under U. S. Department of Energy Contract DE-AC03-77-ET-11313, February, 1980.
- [3] Edelman, R. B., Turan, A., Harsha, P. T., Wong, E., and Blazowski, W. S., "Fundamental Characterization of Alternative Fuel Effects in Continuous Combustion Systems," AGARD Conference Proceedings No. 275 - Combustor Modeling, October, 1979.
- [4] Graham, S. C., Homer, J. B., and Rosenfeld, J.L.J., "The Formation and Coagulation of Soot Aerosols Generated by the Pyrolysis of Aromatic Hydrocarbons," Proc. R. Soc. Lond. A 344: 259-285 (1975).
- [5] Wang, T. S., Matula, R. A., and Farmer, R. C., "Combustion Kinetics of Soot Formation from Toluene," 18th Symposium (International) on Combustion, to be published.
- [6] Glassman, I., "Phenomenological Models of Soot Processes in Combustion System," Dept. of Mechanical and Aerospace Engineering Report 1450, Princeton University, Princeton, N. J., July, 1979.
- [7] Glassman, I. and Yaccarino, P., "The Temperature Effect in Sooting Diffusion Flames," 18th Symposium (International) on Combustion, to be published.
- [8] Flower, W. L. and Dyer, T. M., "Time-and Space-Resolved Measurements of Particulate Formation During Premixed Constant Volume Combustion," Paper CSS/CI-80-Q1 presented at the Central States Section/The Combustion Institute Fall Meeting, Baton Rouge, LA, March, 1980.

Appendix 1

Thermocouple Temperature Measurements in Jet-Stirred Combustors

Introduction

Previous data from the JSC and the LFJSC suggested that there may have been significant differences between actual gas temperatures and indicated thermocouple temperatures measured within the combustors. Since analytical approaches to obtain suitable correction factors for the well-mixed, but poorly characterized, flows in the combustors contained large uncertainties, a brief experimental study was conducted to confirm the presence of and to estimate the magnitude of the thermocouple measurement errors. The approach taken was to compare temperature measurements from several different diameter thermocouples at fixed reactor conditions. Extrapolations of these temperatures to values for infinitely small diameters provided estimates of the true gas temperatures.

Results and Discussion - JSC

Table 1.1 contains the dimensions of thermocouples used in the JSC experiments; Table 1.2 contains JSC operating conditions and measured temperatures. Thermocouple 1 was the thermocouple used in previous soot formation experiments, and it was fixed in the reactor. The other thermocouples were sequentially inserted into the combustor through the normal sampling port. Attempts were made to position each inserted thermocouple at a location symmetrically equivalent to thermocouple 1; however, the procedures used in the latter set of experiments (Runs E, F, G, and H) were thought to be more reliable. Consequently, effective heat transfer coefficients were calculated only for these runs, and results are given in Table 1.3. For these calculations, radiative heat transfer from the thermocouple bead to the reactor walls is balanced by convective heat transfer from the gas to the thermocouple bead. True gas temperatures were obtained by extrapolating the measured thermocouple temperatures to a value corresponding to zero diameter; wall (surface) temperatures were extrapolated from temperature measurements within the refractory lining of the JSC.

The results in Table 1.2 and 1.3 confirm the expectation that measured reactor temperatures (T_1) are significantly lower than the actual gas temperature. The reason for the discrepancies, however, does not appear to be solely radiative heat transfer from the thermocouple bead to colder walls. If radiative heat transfer were the dominant mechanism, one would expect the effective heat transfer coefficients to be approximately proportional to $d^{-1/2}$ where d is the thermocouple bead diameter. Also, one would expect effective heat transfer coefficients from larger residence time cases (fixed temperature and equivalence ratio) to be smaller. The results do not support either of these trends; consequently, an alternative heat transfer mechanism was considered, in particular, conductive heat transfer from the thermocouple bead to its ceramic insulating

mount. Approximate calculations suggested that this mechanism could account for a significant portion of the temperature discrepancies if the ceramic mount is assumed to be at the wall temperature. The present data, however, are not sufficient to quantitatively determine the relative importance of radiative and conductive heat transfer contributions to the thermocouple measurement errors.

The JSC results do confirm two general trends regarding the measurement errors. The errors were smaller for shorter residence time (larger flow rate) and larger equivalence ratio (larger soot concentration) cases. Both conditions (larger flow rate and larger soot concentration) should improve heat transfer rates from the gas to the thermocouple, the thermocouple mount and the reactor wall and, thus, reduce the measurement errors.

Some additional calculations were performed to investigate the importance of soot concentration on the measurement errors. Adiabatic, equilibrium flame temperatures were computed for the mixtures from several toluene soot formation experiments which were conducted at a fixed indicated temperature and average residence time with approximately equal heat losses. Results are given in Table 1.4. Since the calculated flame temperatures can be considered a reasonable relative index of the true gas temperature, the results suggest that the differences between thermocouple and true gas temperatures are smaller for richer, more heavily sooting mixtures.

One additional observation from the JSC experiments concerns temperature nonuniformities within the combustor. For several runs temperature differences of the order of 50K in both indicated thermocouple and projected gas temperatures were observed as the location of the inserted thermocouples was varied approximately 0.5 cm in the radial direction. All temperatures reported in this memo correspond to the location at which maximum temperatures were observed.

Results and Discussion - LFJSC

Several thermocouple experiments were also conducted in the LFJSC. For these experiments a probe consisting of three thermocouples and insulators (T_6 , T_7 , and T_8 in Table 1.1) was inserted through a sight port to a position near the center of the spherical reactor. An additional thermocouple was inserted through the normal thermocouple port for a reference temperature. During the experiments the combination probe was sequentially rotated to account for temperature/measurement error differences among the three thermocouple bead locations. Results from these experiments are summarized in Table 1.5. For each condition tested the average residence time was 6 ms, and the atomization air flow rate was 22.5 g/min/nozzle. T_6 values for some toluene runs were not included in Table 5 since the #6 thermocouple receded into its ceramic insulator during these runs.

The limited data do not suggest that significant temperature measurement errors were present in the LFJSC. There were some indications of

measurement errors in the lean, lightly sooting toluene runs (higher temperatures for smaller diameter thermocouples); however, the isooctane data suggested that the measured thermocouple temperatures were approximately equal within experimental uncertainties. Soot concentration measurements were not made during the thermocouple experiments, but results from other experiments indicated that soot concentrations for toluene ($\phi = 1.0$) and isooctane ($\phi = 1.45$) were of the order of 0.1 mg/l. Such soot concentrations significantly reduced thermocouple measurement errors in the JSC. Also the thermocouple probes were inserted 2.5 cm into the LFJSC combustion zone, but only less than 1 cm into the JSC combustion zone. The longer probe length within the LFJSC combustion zone may have raised the temperature of the thermocouple mount relative to the temperature of the combustor walls and, thus, reduced the conductive heat losses from the thermocouple bead to its mount and the associated measurement errors.

Significant nonuniformities in indicated temperatures were also observed in the LFJSC. In particular, the reference thermocouple temperature first increased ($\approx 100\text{K}$) and then decreased ($\approx 200\text{K}$) as it was withdrawn from the center of the combustor. Such nonuniformities may have affected the magnitude of the apparent measurement errors in the thermocouple data. For example, a hot zone along the probe's length may also have reduced the conductive heat losses from the thermocouple bead to its mount and the associated measurement errors. More extensive temperature profiles within the LFJSC would be required to quantitatively assess the influence of temperature nonuniformities on the thermocouple measurement errors.

Conclusions

Results from the thermocouple experiments confirm that there are significant differences between indicated thermocouple and actual gas temperatures in the present version of the JSC. Data obtained from this study may be used to estimate correction factors for thermocouple measurements under similar reactor conditions; however, the complexities of the problem coupled with the limited amount of data preclude the development of a generalized correction factor correlation. Consequently, an average temperature correction of 125 K is recommended for indicated thermocouple data obtained from the JSC. The value may be slightly high ($\approx 25\text{K}$) for heavily sooting condition and slightly low for non-sooting or longer residence time (6 ms) conditions.

For the LFJSC, thermocouple measurement errors appeared to be small ($<50\text{K}$) for moderately soot conditions. For non-sooting conditions in the LFJSC, the errors may be larger, but quantitative assessments of these errors will probably require a more extensive investigation of the temperature nonuniformities within the reactor.

Table 1.1 Thermocouple Dimensions

Thermocouple	Type	Average Bead Diameter (inches)	Wire Diameter (inches)
1	B	.092	.032
2	R	.065	.032
3	B	.053	.032
4	B	.042	.020
5	B	.021	.010
6	B	.020	.010
7	B	.034	.020
8	B	.055	.032

Table 1.2 Thermocouple Temperatures from JSC Experiments with Toluene/O₂/N₂ Mixtures*

Run	Equivalence Ratio	Residence Time (ms)	T ₁ (K)	T ₂ (K)	T ₃ (K)	T ₄ (K)	T ₅ (K)
A	1.6	6	1873	1908	1915	1928	1951
B	1.6	4.5	1873	1900	1903	1910	1933
C	1.6	3	1873	1908	1898	1903	1923
D	0.8	3	1823	1823	1838	1843	1863
E	1.6	6	1878	1905	1943	1931	1988
F	1.6	3	1878	1873	1891	1921	1933
G	1.4	3	1823	1828	1858	1880	1933
H	1.4	3	1933	1890	1948	1978	2058

* Reactor diameter = 5.08 cm

Table 1.3 Calculated Parameters from Selected JSC Experiments

Run	Indicated Reactor Temperature $T_1(K)$	Extrapolated Gas Tempera- ture (K)	Extrapolated Wall Tempera- ture (K)	Effective Heat Transfer Coefficients (W/m^2-s)		
				h_3	h_4	h_5
E	1878	2023	1825	134	915	1474
F	1878	1963	1859	450	455	767
G	1823	1983	1836	51	125	592
H	1933	2103	1926	47	141	1058

Table 1.4 Results from Previous JSC Soot
Formation Experiments (Toluene)

Run	Equivalence Ratio	$\frac{O_2}{O_2+N_2}$ (mass)	$T_{Adiabatic}(K)$	$T_{Measured}(K)$	Soot Concentra- tion (mg/l)
B-152	1.2	0.212	2330	1898	--
B-153	1.4	0.225	2285	1894	<0.01
B-154	1.6	0.250	2260	1898	0.10
B-155	1.8	0.263	2175	1890	0.67

Table 1.5 Thermocouple Temperatures from LFJSC Experiments

Run	Fuel	Equivalence Ratio (ϕ)	Probe Orientation	T ₆ (K)	T ₇ (K)	T ₈ (K)
I	Toluene	0.8	1	--	1900	1889
			2	--	1881	1853
			3	--	1875	1885
J	Toluene	0.9	1	1969	1951	1902
			2	1907	1893	1886
			3	--	1915	1905
K	Toluene	1.0	1	--	2013	1988
			2	--	1950	1965
			3	--	1991	1971
L	Iso- octane	1.45	1	1691	1684	1671
			2	1727	1724	1718
			3	1678	1689	1680
M	Iso- octane	1.45	1	1819	1806	1828
			2	1836	1831	1834
			3	1818	1818	1828

PART B

ANALYTICAL PROGRAM PROGRESS

R. B. Edelman
E. Wong
R. C. Farmer

Science Applications, Inc.
Combustion Dynamics and Propulsion Technology Division
21133 Victory Boulevard, Suite 216
Canoga Park, California 91303

B.1 Introduction

A quasi-global kinetics model for toluene combustion has been developed as a tool for analyzing alternate fuel effects in continuous combustion systems. The model describes not only lean combustion but also rich combustion in which soot is a product. This study also includes the modeling of aliphatic combustion, as typified by octane, and of NO_x emissions, but only the progress on the aromatics model, as typified by toluene, will be presented in this progress report.

Practical kinetics models to describe real fuels must consist of abbreviated kinetics mechanisms and a limited number of chemical species. Elementary reaction mechanisms have only been developed for simple fuel species and are not expected to be developed for real fuels in the foreseeable future. Even if such models were available, they could not be used to analyze the heat transfer and fluid mechanics in a combustion system because of finite computational capabilities. On the other hand, extremely simplified kinetics models, such as those used to describe heat release in a combustor, are not adequate to represent important chemical phenomena nor can they be dependably transferred from one geometrical configuration to another. While the quasi-global kinetics model developed in this investigation is a compromise between computational complexity and the extreme in detail, it represents a comprehensive engineering model of the combustion process. The choices which were made in establishing this balance will be described in the presentation of the toluene model.

The phenomenology of the chemical reactions which accomplish combustion are described in the generic quasi-global model in Table 6. Regardless of the number of species or reactions included in a given kinetics mechanism, if any of the functional steps listed in Table 6 are omitted, certain important physical features of the combustion process cannot be predicted. When a hydrocarbon fuel is subjected to severe thermal conditions, such as in a combustor, the molecules *pyrolyze* into smaller fragments. This endothermic property is important because it allows the fuel to serve as a heat sink, and it is generally the initial step in the combustion process. In the presence of any form of oxygen, an accelerated pyrolysis, *oxidative pyrolysis*, occurs. Many stable and radical hydrocarbon species are made by these pyrolysis reactions. It is this large number of species which makes the description of hydrocarbon combustion difficult. Fortunately, the small stable molecules: acetylene, ethylene, and methane constitute a large fraction of the pyrolyzed hydrocarbon fragments. The fuels and intermediate fragments *partially combust* to CO , H_2 and aldehydes which then react to *completion* to form CO_2 and H_2O . Under rich combustion conditions, soot might both *form* and *gasify*. When soot is present even as small fractions of the hydrocarbon, it dominates energy exchange and combustion efficiency. NO_x *emission* either from *direct fuel nitrogen conversion* or *thermal fixation* might also be of importance. Conceptually, given enough species and reactions any and all combustion phenomena could be described. The abbreviation of the reaction mechanism occurs when specific species and reactions are selected from this general model to represent the combustion of a specific fuel. The concept of the quasi-global model demands that deliberate omissions of species and reactions be made; therefore, the conditions for which the model is valid must be established. Since the model is intended to describe chemical kinetics in an engineering analysis, experiments which typify actual combustion systems will be represented as an essential first step. When this step is accomplished, the range of applicability can be determined and increased systematically when it is desirable to do so. Besides being similar to real

combustion systems, the experiments chosen to verify that the reaction kinetics of combustion process are correctly described must be strongly affected by other factors which complicate the interpretation of the comparison. Turbulent transport, mixing and multi-dimensionality of the reacting flow are such *secondary* factors which must be avoided to obtain valid kinetics data.

With this model development philosophy, jet-stirred combustor (JSC) experiments were chosen as being an excellent means of characterizing primary zones in actual combustors. The Exxon Research and Engineering Co. (ER&E) experiments were designed to measure the reaction kinetics of typical alternate fuels for combustor residence times and thermal histories similar to those encountered in actual stationary gas turbine engines. The quasi-global model development presented herein will be shown to represent the ER&E experimental results and will be compared to other available experimental work prior to completion of the program.

B.2 Development of the Quasi-Global Toluene Kinetics Model

The original quasi-global hydrocarbon oxidation model utilized primarily ignition delay data to establish the global rate parameters [9]. Further applications of the quasi-global model [10] have resulted in recognizing that homologous hydrocarbons might be represented by one global partial oxidation rate. These rates have been evaluated for aliphatic alkanes and aromatics. Different pre-exponential constants were required to represent well-stirred and plug-flow configurations. Although this representation did predict the fuel disappearance and ignition behavior rather well, it over-predicted the appearance of CO₂ in the early stages of combustion and under-predicted the appearance of CO, as shown in Figs. 14 and 15 from earlier progress reports on this study [12]. When this model was applied to JSC data for isooctane combustion good agreement was observed for lean conditions but for rich combustion the extent of the combustion process was overpredicted as shown in Fig. 16. The quasi-global model with revised rate parameters suggested by Westbrook [13] and the 4-step model of the Princeton group [14] are also shown to overpredict the degree of completion of reaction under these conditions. These models were used as they were reported; no attempt was made to reevaluate the rate parameters to obtain a better fit of the JSC data. The quasi-global model was extended to include a global, endothermic pyrolysis step in addition to the partial oxidation step. The pyrolysis step did reduce the over estimation of the temperature, as shown in Fig. 16, but it did not correctly account for the very rapid decrease in temperature at high equivalence ratios that was observed. Although the temperature predictions for these two quasi-global models and the 4-step model are similar, the species distributions predicted by these models vary markedly and do not agree with the trends in the data for rich combustion where soot is likely to form. These concentration comparisons are shown in Figs. 17-21.

The effects of heat losses from the reactor and radiation losses from the thermocouple which was used to measure reactor temperature had to be evaluated before the amount of temperature overprediction by any model could be established. Since all of these thermal measurements were not included in the original test matrix, the experimental program was well underway before the exact amount of temperature overprediction by the model could be established. The toluene data, which will be discussed subsequently, do include the best current measurements of the thermal state within the JSC.

B.3 The Quasi-Global Toluene Model

A tentative quasi-global model to represent toluene combustion has been established and is shown in Table 7. The rates of the pyrolysis of toluene by OH, the oxidation of toluene by O_2 , and the oxidation of acetylene by OH are all comparable with the hydrogen-oxygen reactions in the wet CO mechanism. The result is that under fuel rich conditions these global reactions are so tightly coupled to the elementary rates that the acetylene-OH reaction acts to prevent oxidation by consuming the OH before the CO is converted to CO_2 . Under less rich and lean conditions, the OH concentration is sufficient to consume essentially all of the acetylene. These observations are for test conditions typical of the jet-stirred combustor experiments of about 1 atm pressure and 3 msec residence time.

Detailed comparisons of predictions with this model and the JSC data are shown in Figs. 22-36. Both near adiabatic and isothermal modes of reactor operation were considered in these comparisons. Isothermal operation refers to runs in which the oxygen-to-nitrogen ratio of the mixture was adjusted to maintain approximately constant measured temperatures. Near adiabatic operation refers to runs at a fixed oxygen-to-nitrogen ratio (air); corresponding temperatures varied with equivalence ratio. Heat losses were measured during both modes of operation.

The near adiabatic cases, Figs. 22-26, were used to establish the model. The isothermal data were then compared without further adjustment of the mechanism or rate parameters within the mechanism. These comparisons show the model to be a good representation of the data. The experimental temperature data in Fig. 22 indicate that temperature is not an easy quantity to measure accurately in a JSC experiment, despite its critical importance. The temperature measured and that estimated using measured species must be in agreement before any model can be truly compared with the data. Neither water nor hydrogen were measured in the near adiabatic experiments. The ER&E estimates shown were made with an assumption of chemical equilibrium in the water gas shift reaction. The quasi-global kinetics model does not substantiate this assumption, as shown in Fig. 25 and neither does the isothermal data as shown below. Hydrogen was measured in the isothermal experiments and water was obtained by difference. The isothermal water predictions are good as shown in Fig. 30. Isothermal results for both the 1700 and 1900°K experiments are shown. A 100°K temperature correction was added to the measured temperature to account for radiation losses. Notice in Figs. 27 and 32 that the 1900°K tests indicate much better agreement between the measured temperatures and those calculated from the measured species than do the 1700°K tests. In Figs. 27 and 32, two predicted temperature profiles are shown; the first is the isothermal one estimated from the measure of temperature, the second is a near adiabatic calculation. These should be identical, and in the 1900°K case, the agreement is indeed good. In the 1700°K case; however, differences between the specified temperature and specified heat loss predictions are significantly larger. Thus only one set of predicted species profiles are shown for the 1900°K case and two are shown for the 1700°K case. Predictions are reasonable, but better agreement between the two methods of obtaining temperature must be realized before any conclusions regarding the model are drawn from the 1700°K comparison.

Other products and reactions were considered in the development of this model. The acetylene plus OH reaction was considered to make hydrogen and CO rather than water and CO. To obtain realistic levels of inefficiency

under rich combustion conditions, water had to be the product of this reaction. Physically, the six OH radicals are consumed by hydrocarbon radicals which are in the detailed chain of hydrocarbon chemistry. This one global step avoids having to identify and account for these other hydrocarbon fragments. H and O radicals could also have been treated in this fashion, but the shuffling reactions in the H_2/O_2 system are so fast that the radical pool ($H + O + OH$) behaves just as OH alone does, that is a sink for OH also amounts to a sink for H or O. Parallel O_2 and OH attacks and O_2 only attacks on toluene and acetylene were also investigated. The model shown in Table 7 was the best performing of these other possible models. The global steps involving OH were so strongly coupled to the elementary steps in the wet-CO mechanism that implicit calculations were required for both the global and elementary reactions. H_2CO and H_2O_2 species and elementary reactions to describe their chemistry were also considered, but for the relatively high temperature conditions of the JSC experiments these reactions were found not to be important.

Prior investigations in the program established that soot emissions depend only on the concentrations of unburned hydrocarbons and oxygen and on temperature [15]. This is shown by Fig. 37 from [16]. The rates of soot formation and oxidation given in Table 7 reflect this empirical correlation. In applying the soot oxidation rate expression, a mean soot size is required. The value chosen was 25 nm. Fig. 38 from [17] shows that the net soot emissions from the JSC is not a strong function of this assumed particle size. For the range of conditions investigated herein, the oxidation rate is approximately 25% or less of the formation rate; this accounts for the weak dependency of net soot emissions on particle size.

A quasi-global model similar to the toluene model is being developed for isooctane and will be reported in the next quarterly progress report. Results using the toluene model from Table 7 are shown in Figs. 16-21 for the isooctane cases, to emphasize that the trends of the new model are correct and that the replacement of toluene with isooctane should be relatively simple. The stoichiometry of toluene combustion is such that at the same equivalence ratio about half as much H_2O and about the same amount of CO_2 would be formed in complete combustion. Thus the water comparisons of the toluene model shown in Fig. 21 are not expected to be good.

In conclusion, a quasi-global kinetics model for toluene combustion has been developed. The model has been shown to be accurate for the range of well-mixed combustion conditions investigated by ER&E in their JSC. Further development of the model by testing it over a wider range of applications, such as plug-flow and blow-out behavior, is in progress and will be reported in the next quarterly progress report.

References - Part B

9. Edelman, R. B. and O. F. Fortune. AIAA Paper No. 69-85 (1969).
10. Edelman, R. B. and P. T. Harsha. Progress in Energy and Combustion Science, 4, pp. 1-62 (1978).
11. Glassman, I., Dryer, F. L., and Cohen, R. "Combustion of Hydrocarbons in an Adiabatic Flow Reactor: Some Considerations and Overall-Correlations of Reaction Rate," presented at the Joint Meeting of the Central and Western States Section of the Combustion Institute, April 1975.
12. Blazowski, W. S., R. B. Edelman and P. T. Harsha. "Fundamental Characterization of Alternate Fuel Effects in Continuous Combustion Systems," Summary Technical Progress Report for period August 15, 1977 - August 14, 1978, for DOE contract EC-77-C-03-1543, September 1978.
13. Westbrook, C. K. and F. L. Dryer. "Simplified Reaction Mechanisms for the Oxidation of Hydrocarbon Fuels in Flames," UCRL-84943, Lawrence Livermore Laboratory, Livermore, CA, November 1980.
14. Hautman, D. J., F. L. Dryer, K. P. Schug and I. Glassman. "A Multi-step Overall Kinetic Mechanism for the Oxidation of Hydrocarbons," presented at the Eastern States Section meeting of the Combustion Institute, Princeton, NJ, November 1980.
15. Edelman, R. B., A. Turan, P. T. Harsha, E. Wong and W. S. Blazowski, "Fundamental Characterization of Alternative Fuel Effects in Continuous Combustion Systems, Paper 13, AGARD-CP-275, Combustor Modelling, October 1979.
16. Ruth, L. A. and R. M. Kowalik. Fundamental Characterization of Alternate Fuel Effects in Continuous Combustion Systems, Technical Status Report for period May 1, 1980 - May 31, 1980, DOE Contract DE-AC22-77-ET-11313, June 1980.
17. Ibid. Technical Status Report for period February 1, 1980 - February 29, 1980, DOE Contract DE-AC22-77-ET-11313, April 1980.

Table 6. Generic Quasi-Global Model

I. PURE PYROLYSIS	$\begin{bmatrix} \text{ALIPHATICS} \\ \text{AROMATICS} \end{bmatrix} + \begin{bmatrix} \text{C}_2\text{H}_2 \\ \text{CH}_4 \\ \text{C}_2\text{H}_4 \\ \text{H}_2 \end{bmatrix} \equiv \text{INTERMEDIATES}$
II. OXIDATIVE PYROLYSIS	$\begin{bmatrix} \text{ALIPHATICS} \\ \text{AROMATICS} \end{bmatrix} + \begin{bmatrix} \text{OH} \\ \text{O}_2 \end{bmatrix} + \begin{bmatrix} \text{C}_2\text{H}_2 \\ \text{C}_2\text{H}_4 \end{bmatrix} + \begin{bmatrix} \text{H}_2 \\ \text{C}_x\text{H}_y\text{O}_z \end{bmatrix}$
III. PARTIAL OXIDATION	$\begin{bmatrix} \text{ALIPHATICS} \\ \text{AROMATICS} \\ \text{CH}_4 \\ \text{C}_2\text{H}_2 \\ \text{C}_2\text{H}_4 \end{bmatrix} + \begin{bmatrix} \text{O}_2 \\ \text{OH} \end{bmatrix} + \begin{bmatrix} \text{H}_2 \\ \text{CO} \\ \text{C}_x\text{H}_y\text{O}_z \\ \text{CO}_2 \\ \text{H}_2\text{O} \end{bmatrix}$
IV. ELEMENTARY STEPS TO COMPLETION	$\begin{bmatrix} \text{CO} \\ \text{H}_2 \\ \text{C}_x\text{H}_y\text{O}_z \\ \text{H}_2\text{O}_2 \end{bmatrix} + \begin{bmatrix} \text{O} \\ \text{H} \\ \text{OH} \\ \text{CHO} \\ \text{HO}_2 \end{bmatrix} + \begin{bmatrix} \text{H}_2\text{O} \\ \text{CO}_2 \end{bmatrix}$
V. SOOT FORMATION	$\begin{bmatrix} \text{ALIPHATICS} \\ \text{AROMATICS} \\ \text{INTERMEDIATES} \end{bmatrix} + \text{SOOT}$
VI. SOOT GASIFICATION	$\text{SOOT} + \begin{bmatrix} \text{O}_2 \\ \text{CO} \\ \text{CO}_2 \\ \text{H}_2\text{O} \\ \text{H}_2 \\ \text{OH} \end{bmatrix} + \begin{bmatrix} \text{CO} \\ \text{CO}_2 \\ \text{CH}_4 \end{bmatrix}$
VII. NO _x FORMATION	<div style="display: flex; justify-content: space-between;"> <div> $\begin{bmatrix} \text{FUEL} + \text{N}_2 \\ \text{FBN} \end{bmatrix} + \begin{bmatrix} \text{HCN} \\ \text{NH}_1 \end{bmatrix}$ $\begin{bmatrix} \text{HCN} \\ \text{NH}_1 \end{bmatrix} + \begin{bmatrix} \text{O}_2 \\ \text{OH} \end{bmatrix} + \begin{bmatrix} \text{NO} \\ \text{NO}_2 \end{bmatrix}$ $\begin{bmatrix} \text{N}_2 \\ \text{O}_2 \\ \text{N} \end{bmatrix} + \begin{bmatrix} \text{O} \\ \text{N} \\ \text{OH} \end{bmatrix} + \text{NO} + \begin{bmatrix} \text{N} \\ \text{O} \\ \text{H} \end{bmatrix}$ </div> <div style="text-align: right;"> <p>FUEL NITROGEN CONVERSION</p> <p>THERMAL FIXATION</p> </div> </div>

Table 7. Tentative Quasi-Global Toluene Model

GLOBAL STEPS

Pyrolysis

Form of Rate Expression

$$[C_7H_8^\bullet] = -A [C_7H_8] \exp \{-E/RT\}$$

Oxidative Pyrolysis

$$[C_7H_8^\bullet] = -A [C_7H_8][OH] \exp\{-E/RT\}$$

Partial Oxidation

$$[C_7H_8^\bullet] = -A [C_7H_8]^{0.5} [O_2] T \exp\{-E/RT\}$$

$$[C_2H_2^\bullet] = -A [C_2H_2][OH] \exp\{-E/RT\}$$

Soot Formation

Soot Oxidation

The soot formation rate is given by:

$$[soot^\bullet] = + A T^b [HC]^{1.81} [O_2]^{-0.5} \exp \{-E/RT\}$$

and the rate of oxidation by:

$$[soot^\bullet] = - 12 \left(\frac{k_A P_{O_2}^X}{1+k_Z P_{O_2}} + k_B P_{O_2} (1-X) \right) A_t$$

where

$$X = \left(1 + k_T / (k_B P_{O_2}) \right)^{-1}$$

$$k_i = A_i \exp \{-E_i/RT\}, \text{ for } i = A, B, T, Z$$

$$A_t = A_t \{[soot], \rho_s, D_s\} \text{ (surface area of soot/vol)}$$

$$P_{O_2} = \text{partial pressure of } O_2 \text{ (atm)}$$

Table 7 (Contd.)

ρ_s = soot density

D_s = soot mean diameter

[soot] = concentration of soot (mass/vol)

A, b, E = kinetics constants

Back rates are determined with equilibrium constants where required.

ELEMENTARY STEPS

Wet CO Mechanism

H₂O₂ Mechanism

$$[\text{Reactant}] = A [R_1] [R_2] T^b \exp \{-E/RT\}, \text{ for 2-body reactions}$$

$$[\text{Reactant}] = -A [R_1] [R_2] [M] T^b \exp \{-E/RT\}, \text{ for 3-body reactions}$$

R_i = Reactant 1 and 2

M = Total concentration

Table 7 (Contd.)

<u>Reaction</u>	<u>A</u>	<u>b</u>	<u>E/R</u>
1	1.259E16	0	4.932E4
2	3.5 E13	0	1.510E3
3	6.055E11	1.0	3.271E4
4	1.662E15	0	1.207E4
5	4.66 E14	-1.94	1.611E4
6A	2.0 E1	0	1.509E4
6B	4.46 E-3	0	7.649E3
6T	1.51 E5	0	4.882E4
6Z	2.13 E1	0	-2.063E3
7	4.0 E12	0	4.03 E3
8	3.0 E12	0	2.5 E4
9	6.0 E13	0	0.0
10	1.7 E13	0	2.407E4
11	2.19 E13	0	2.59 E3
12	6.023E12	0	5.50 E2
13	1.8 E10	1.0	4.48 E3
14	1.22 E17	-0.91	8.369E3
15	1.0 E16	0	0.0
16	9.38 E14	0	0.0
17	5.0 E15	0	0.0
18	8.4 E21	-2.0	0.0
19	1.26 E17	0	2.290E4
20	3.98 E13	0	2.144E4
21	1.585E12	0	1.912E3
22	1.0 E13	0	9.06 E2
23	5.01 E13	0	5.03 E2
24	5.01 E13	0	5.03 E2
25	2.50 E14	0	9.563E2
26	2.51 E13	0	3.523E2

Figure 14. Temperature during propane-air reaction.

Figure 15. Chemical composition of spread propane-air reaction.

Figure 16. Isooctane combustion as measured in Exxon JSC and as predicted.

Figure 17. Isooctane combustion as measured in Exxon JSC and as predicted.

Figure 18. Isooctane combustion as measured in Exxon JSC and as predicted.

Figure 19. Isooctane combustion as measured in Exxon JSC and as predicted.

Figure 20. Isooctane combustion as measured in Exxon JSC and as predicted.

Figure 21. Isooctane combustion as measured in Exxon JSC and as predicted.

Figure 22. Model prediction compared to Exxon JSC near adiabatic data; toluene/air combustion.

Figure 23. Model prediction compared to Exxon JSC near adiabatic data; toluene/air combustion.

Figure 24. Model prediction compared to Exxon JSC near adiabatic data; toluene/air combustion.

Figure 25. Model prediction compared to Exxon JSC near adiabatic data; toluene/air combustion.

Figure 26. Model prediction compared to Exxon JSC near adiabatic data; toluene/air combustion.

Figure 27. Model prediction compared to Exxon JSC isothermal data at 1900 K measured temperature; toluene/O₂/N₂ combustion.

Figure 28. Model prediction compared to Exxon JSC isothermal data at 1900 K measured temperature; toluene/O₂/N₂ combustion.

Figure 29. Model prediction compared to Exxon JSC isothermal data at 1900 K measured temperature; toluene O₂/N₂ combustion.

Figure 30. Model prediction compared to Exxon JSC isothermal data at 1900 K measured temperature; toluene/O₂/N₂ combustion.

Figure 31. Model prediction compared to Exxon JSC isothermal data at 1900 K measured temperature; toluene/O₂/N₂ combustion.

Figure 32. Model prediction compared to Exxon JSC isothermal data at 1700 K measured temperature; toluene/O₂/N₂ combustion.

Figure 33. Model prediction compared to Exxon JSC isothermal data at 1700 K measured temperature; toluene/O₂/N₂ combustion.

Figure 34. Model prediction compared to Exxon JSC isothermal data at 1700 K measured temperature; toluene/O₂/N₂ combustion.

Figure 35. Model prediction compared to Exxon JSC isothermal data at 1700 K measured temperature; toluene/O₂/N₂ combustion.

Figure 36. Model prediction compared to Exxon JSC isothermal data at 1700 K measured temperature; toluene/O₂/N₂ combustion.

Figure 37. Comparison of predicted and measured soot concentrations, controlled reactor temperature = 1900 K, toluene.

Figure 38. Effect of soot particle size on net soot prediction.