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CARBON SLURRY FUELS FOR VOLUME LIMITED MISSILES

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## GLOSSARY OF TERMINOLOGY

Aggregate - The smallest unit of carbon black composed of fused carbon particles.

Agglomerate - A loosely bound group of carbon black aggregates.

Catalyst - A substance which increases the rate of a chemical reaction without itself being chemically changed.

Carbon Burnout Efficiency - A quantitative measure of fuel carbon utilization.

Cohesive Energy Density (CED) - A measure of intermolecular forces expressed as interaction energy per unit volume.  
( $CED = \delta_D^2 + \delta_P^2 + \delta_H^2$ ).

Cohesive Energy Ratio (CER)  $CER = \frac{CED \text{ (Phase 1)}}{CED \text{ (Phase 2)}}$

Combustion Efficiency - A quantitative measure of fuel energy utilization.

$\delta_D$  - London (dispersion) forces.

$\delta_H$  - Hydrogen bonding forces (also electron transfer).

$\delta_P$  - Keesom (Polar) forces.

Equivalence Ratio - The ratio of the experimental fuel to oxidant conditions to the stoichiometric fuel to oxidant conditions.

Heterogeneous Catalyst - Catalyst which is added directly to the carbon particles.

HLB - Hydrophilic Lipophilic Balance.

Homogeneous Catalyst - Catalyst which is added to the liquid portion of the carbon slurry fuel.

Hydrophilic - water loving.

Lipophilic - oil loving.

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Mach Number - The ratio of the speed of a body to the speed of sound in the surrounding atmosphere.

Residence Time - The reaction time for the fuel and oxidant within the combustor chamber.

Stoichiometric - The amount of air or oxygen required to completely combust the fuel carbon and hydrogen to carbon dioxide and water.

m<sub>μ</sub> - Millimicron, 10<sup>-9</sup> meter (nanometer).

LIST OF SYMBOLS, ABBREVIATIONS ETC.

$\text{\AA}$	Angstrom
Btu	British Thermal Unit
CED	Cohesive Energy Density
$\delta$	Solubility Parameter ( $\delta$ = Greek delta)
$\delta_D$	London (dispersion) forces
$\delta_H$	Hydrogen bonding forces
$\delta_P$	Keesom (Polar) forces
ER&E	Exxon Research & Engineering Company, Linden, NJ
F	Dispersion volume, cc/gm
$H_v$	Heat of Vaporization
K	Kelvin
$m^2/g$	meters square per gram
ms	millisecond ( $10^{-3}$ sec.)
m $\mu$	millimicron ( $10^{-9}$ meter)
$N_c$	Combustion efficiency
NDIR	Non-dispersive infrared
$N_{cb}$	Carbon burnout efficiency
$N_v$	Viscosity
$\phi$	Volume Fraction of the internal phase of a dispersion or emulsion
$\phi$	Equivalence Ratio (combustion related)
PPM	Part per million
PSI	Pounds per square inch
R	Gas Constant
T	Temperature $^{\circ}$ K
t	Time
$\tau$	Residence Time
THC	Total Hydrocarbon

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u        micron ( $10^{-6}$  meter)  
um       micrometer ( $10^{-6}$  meter)  
 $\Delta V$      Molar Volume

## SUMMARY

This report is an accounting of the first year's effort by Exxon Research and Engineering Company (ER&E), under contract to the Air Force Aero Propulsion Laboratory, to develop a high density fuel for future volume limited cruise missile systems. Past efforts sponsored by the Air Force have resulted in development of liquid hydrocarbon fuels with up to 160,000 Btu/gallon. Increases in Btu content are desirable to further improve missile range. As a logical next step in high energy liquid fuels the Air Force and other DOD agencies have sponsored research in carbon/liquid fuel mixtures. Blends of carbon black with high density fuels can provide increases to 180,000 Btu/gallon and above. However, the mixtures prepared to date are slurries which do not meet the performance requirements and have not been adequately tested. This current program is aimed at preparation of a carbon loaded liquid fuel with a minimum of 180,000 Btu/gallon that will perform well in a non-exotic fuel system.

The ER&E program to accomplish the above objective is an iterative approach which recognizes the need to consider the often opposing requirements of fuel system and combustion system performance. An extensive search of the literature was carried out to investigate the properties of carbon black, methods of formulating carbon dispersions in liquid fuels, and combustion characteristics of small carbon particles. While this search revealed a wealth of information on these subjects there was very little guidance provided on specific dispersing agents to provide a stable system with desirable properties. In addition, while the literature on combustion of carbon particles indicates a relationship between carbon particle size and combustion rate, the data showed such a wide range of test conditions and results that considerable uncertainty remains as to what might be expected from combustion of carbon black dispersions in fuel. The major problems to be overcome in formulation appeared to be selection of the carbon black, choice of the proper dispersant or dispersants, and method of mixing these components in a high density fuel, such as JP-10. The most formidable problems of combustion appeared to be identification of conditions for maximum combustion efficiency, comprehension of the combustion process, determination of the carbon burnout rate, selection of the optimum fuel injection system, studies of fuel volatilization in the combustion chamber, and development of data to enable design of a useful combustion system for missile engines.

The approach utilized for formulation was a combination of conventional and novel techniques. The conventional approach was to utilize experience from others who have formulated carbon black dispersions in oil, such as for ink oils and rubber processing. These techniques were used. In addition, several novel approaches were evaluated. The first was to utilize the solubility parameter concept which provides systematic information on physical interactions of materials. This concept is useful in selecting the optimum dispersant for a material such as carbon black in a liquid. The second novel concept was to formulate a three phase carbon dispersion system such that the droplets of carbon black in JP-10 (Phases 1 and 2) would then be emulsified in an external immiscible liquid.

To study the combustion properties of carbon dispersions the ER&E approach was to devise a jet stirred combustor for liquid fuels. Considerable experience had been gained utilizing well-stirred combustors such as the jet stirred combustors for gaseous and vaporized liquid fuels. However, this would not have been appropriate for carbon dispersions. With a liquid fuel jet stirred combustor it is possible to study combustion parameters of carbon dispersions such as overall combustion efficiency, carbon burnout efficiency, effect of various equivalence ratios, rate of combustion, effect of catalysts on combustion, and hardware required to pump and spray these systems.

In addition to studying preparation and properties of carbon dispersions, the anticipated and measured properties were subjected to a Limited Systems Study with the assistance of three subcontractors who provided major inputs on turbine and ramjet engines (GE and CSD, respectively) and other missile system component (Boeing) requirements. This study included consideration of (1) range improvement achievable with carbon dispersions, (2) fuel characterization needs and (3) establishment of fuel evaluation criteria.

Initial results have demonstrated that carbon slurry fuels can be formulated with properties approaching minimum requirements. Two phase dispersions containing up to 69 wt % carbon in JP-10 have been prepared using 2-5% surfactant. Ultimate particle size carbon black varying from 13-300 millimicrons (m $\mu$ ) have been investigated. The viscosity of a 60 wt % 300 m $\mu$  carbon dispersion in JP-10 was 163 cp at -14°C. The fuels showed no signs of phase separation stability problems after 20 weeks of shelf life at room temperature.

Studies with two phase dispersions have shown that viscosity for a given loading increases with decreasing particle size in a complex manner. Viscosity remains nearly constant up to a critical minimum particle size and then increases sharply with smaller particle sizes. For a given particle size viscosity increases exponentially above about 50 wt % carbon loading. The choice of particle size requires a trade-off. Combustion rate is enhanced by reducing particle size but conversely formulation viscosity increases rapidly. Thus, with available carbon blacks, the results indicate that increased attention be given to the use of 300 m $\mu$  size particles.

Choice of surfactants has been shown to be critical and significantly affects the properties of carbon black dispersions. Limited work has also been carried out formulating three phase emulsion fuels which offer the promise of improved performance relative to two phase dispersions. To date, a fuel containing 48 wt % carbon has been prepared consisting of 80% of an internal phase containing a 60% carbon two phase dispersion in JP-10 and 20% of an external phase consisting of formamide and surfactants. Fundamental Cohesive Energy Density measurements have been completed which are expected to help future formulation efforts. The data on two phase systems look very promising and thus further work on three phase systems will be terminated.

Combustion measurements were carried out in a newly designed laboratory well-stirred reactor capable of burning both liquid and multi-phase carbon slurry fuel. Previously, well-stirred combustors were designed only to operate with gaseous fuel. The Liquid Fuel Jet Stirred

Combustor (LFJSC) incorporates both a recirculation region typical of the primary zone and a turbulent non-recirculating zone typical of the secondary and dilution zones of a gas turbine. Development of this new fundamental tool will allow full characterization of the combustion properties of experimental carbon slurry fuels to be obtained with small sample sizes.

Experience gained from the shakedown operation of the LFJSC has shown that fuel injector design for carbon slurry fuels will be a problem and clearly indicates a need for increased attention to this area in the future. Two critical design problems have been identified: (1) prevaporization of the liquid portion of the slurry fuel must be avoided in the fuel lines and nozzles, and (2) the injector must be carefully designed to avoid carbon deposition within the combustion system. Tests in the LFJSC indicated that carbon burnout efficiencies of greater than 90% are achievable with 300  $\mu$  particles in residence times down to 4 ms. Little difference in combustion performance was noted using a range of dispersions containing from 30-50 wt % of carbon. Smaller particle size (75  $\mu$ ) carbon formulations gave higher combustion efficiencies ( $\approx$  3%) than those made with larger carbon particles (300  $\mu$ ). The data indicate that burnout is a function of mixture conditions and that the optimum equivalence ratio is approximately 0.85. Since conventional combustors do not provide substantial time at this mixture condition, combustor redesign to accommodate carbon slurry fuels is probable. Limited tests indicate that smaller carbon particle size may result in improved carbon burnout.

Tests were made to determine if homogeneous catalyst, i.e. the addition of a soluble catalytic material to the liquid portion of the carbon slurry fuel, would accelerate the burnout of the carbon particles. Results to date do not show any improvement with manganese, iron, lead or zirconium based homogeneous catalysts at concentrations up to 1000 ppm. We have concluded that homogeneous catalysts will not significantly accelerate carbon particle burnout, and that it is important that we proceed to investigate the use of heterogeneous catalysts for this purpose. In the heterogeneous approach, small levels of active solid catalyst particles will be added directly to the surface of the carbon particles before the carbon is added to the JP-10 to form the slurry fuel.

The Limited Systems Studies have indicated turbine engines can be expected to benefit more from carbon dispersion fuels (25-35% improvement in range) than ramjets (about 15% improvement in range). Utilizing carbon dispersion fuels with the properties reported herein, the engine manufacturers (GE) do not anticipate any major obstacles to their utilization. Some changes in engine fuel line size, metering systems, nozzles, etc. will be needed to accommodate these fuels. Further studies on actual engines will identify specific requirements.

Although our initial results are encouraging in that they indicate highly loaded fuels with moderate viscosities can be prepared, the results also confirm our general view that the formulation and combustion of carbon slurry fuels is quite complex.

Part II of this report gives classified information generated during the first year of this program. The classified data given is:

1. Identification of surfactants which are assigned codes for use in the unclassified portion (Part I).
2. Details of the CED values which identify specific surfactant requirements of the carbon blacks tested and potential optimum dispersant materials.

## SECTION I

### INTRODUCTION

Improving the range and payload of modern and future cruise missile systems will require the development of fuels with increased volumetric energy content. Air Force and Navy-sponsored research has resulted in impressive advances in fuel Btu content over the past 20-30 years. Liquid fuels such as RJ-5, RJ-6 and exo-tetrahydrodi (cyclopentadiene), now called JP-10, have been developed (1). Further improvements have been made in these bridged-ring saturated hydrocarbons and a series of materials are currently available (2). These fuels allow energy contents up to 160,000 Btu/gal while requiring minimum alteration of the overall missile system.

It now appears that a practical limit is being approached for entirely liquid fuels and further improvements in range through innovation in fuel composition will require the use of slurry fuels.\* Consequently, the Air Force initiated a program with Exxon Research and Engineering Company (ER&E) in late 1978 to develop a solid-carbon-containing fuel which will have a volumetric energy content of 180,000 Btu/gal (3). This report is an accounting of the activities which have taken place during the first year of the program.

The task of formulating a carbon slurry fuel which can meet the energy content requirement and successfully perform in turbine or ramjet-propelled missile systems is extremely complex. As illustrated in Figure 1, if JP-10 were used as the hydrocarbon carrier, the required carbon mass loading would be 60%. Such a fuel can be expected to have many unusual characteristics, but the most significant challenges of the fuel development program are to:

- formulate a fuel which is stable and of sufficiently low viscosity to perform well in a non-exotic fuel system,

- provide acceptable low temperature characteristics,

- assure that the energy content of the fuel carbon is utilized within times which are realistic for cruise missile combustion systems, and

- establish the impact of unusual combustion characteristics on optimum combustor design.

This program addresses each of these issues. The approach being used is iterative in nature and recognizes the key trade-offs between Btu/gallon, fuel system performance, and combustion system performance. Program considerations can be organized into three interactive components: fuel formulation, combustion, and systems implications.

\* Use of the term slurry to describe the type of fuel needed is not accurate. A slurry is usually thought of as an unstable (or only temporarily stable) mixture of solid and liquid phases. In the missile fuel case, long term stability is required, and the fuel would more appropriately be called a carbon dispersion. Nevertheless, since the term slurry is so widely used in the missile development community, we will use the terms slurry and dispersion interchangeably.

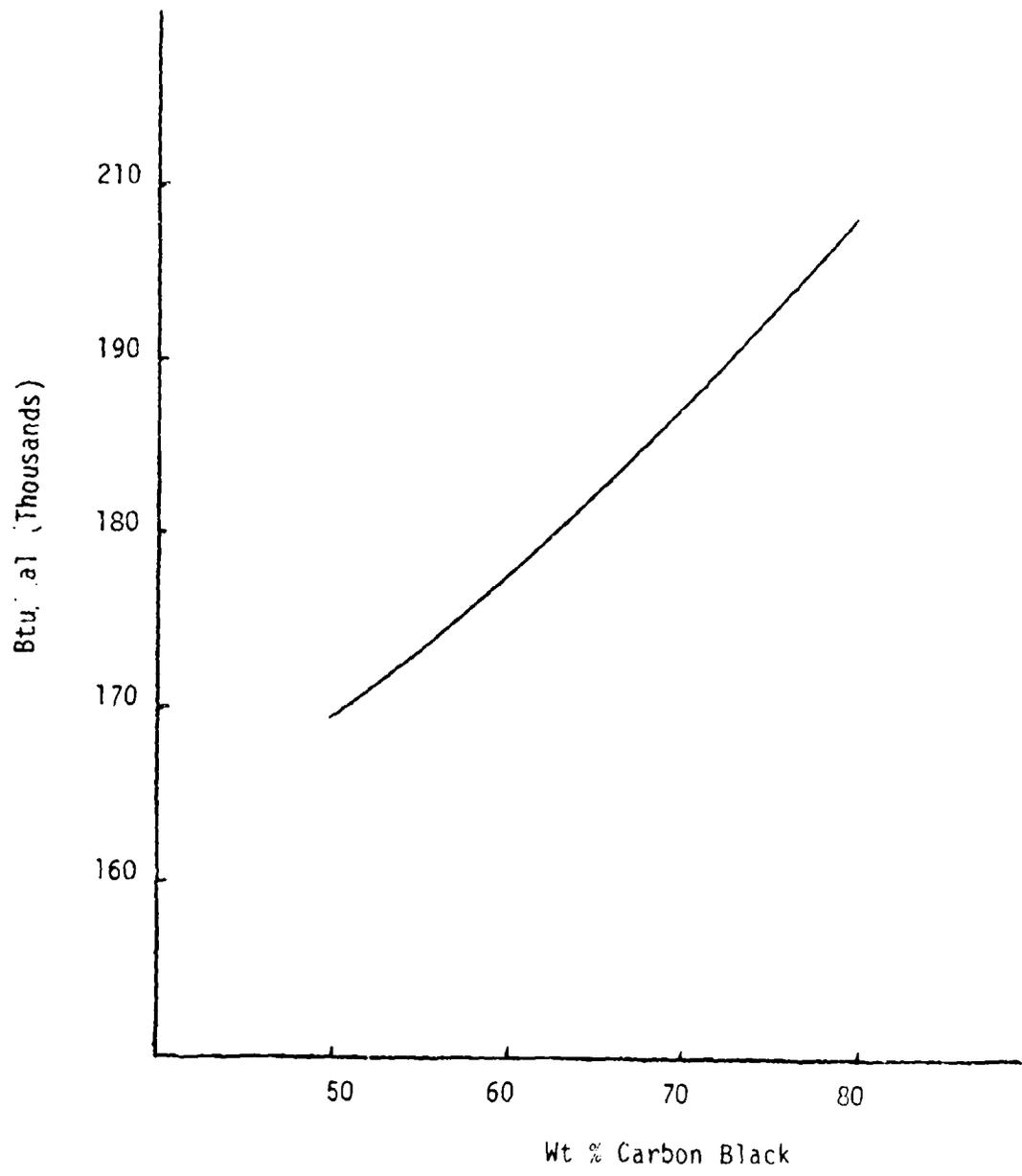


Figure 1. Heat of Combustion of Formulations of Carbon Black in JP-10

Fuel formulation requires detailed consideration of the surface chemistry between dispersed carbon and the liquid hydrocarbon carrier. Interactions of carbon, high density fuels, dispersants, and other ingredients can be related and predicted by measuring a property called the Cohesive Energy Density (CED) of each component (4,5,6). The CED is a measure of the intermolecular forces. The CED may be expressed as a function of the solubility parameters or compatibility of substances with a series of pure liquids. These parameters can readily be measured or calculated and a value assigned to each ingredient. The relationships are based on the first law of thermodynamics and will be described more fully in the text of this report.

While this CED information can be applied to developing two-phase (i.e. carbon in hydrocarbon) dispersions, it can also be applied to the formation of three-phase systems. In this latter case the carbon dispersed in hydrocarbon is the internal phase of an emulsion; the external or encapsulating phase is a liquid (such as formamide) which dominates the emulsion flow properties. Such a system has the potential for lower viscosity, excellent low temperature properties and increased probability of achieving secondary droplet atomization via the use of a higher boiling external phase which could cause the droplets to rupture and "pop". The main disadvantage to this approach is that the third phase is likely to have much less of a contribution to energy content than an equal volume of JP-10 and, hence, dilutes the energy density of the system. In terms of Figure 1, the curve shifts to the right and more carbon loading is required to achieve a given Btu/gallon.

The combustion portion of this program is concurrent with formulation efforts. Burnout of the carbon within the slurry is expected to lag the consumption of the fuel hydrocarbon components. Consequently, it is essential that the influence of carbon type, particle size, and combustion conditions be evaluated early in the program. A problem of particular concern is the trade-off between increased fuel viscosity (negative effect) and reduced carbon burnout time (positive effect) as carbon particle size is reduced. The correct selection of carbon black depends upon the combustion information in conjunction with the results of the formulation study. Further, the need for and ability to catalyze the burnout of carbon must be established early in the program; the inclusion of a catalyst would substantially influence the task of formulation.

A new small-scale laboratory combustor, the Liquid Fuel Jet Stirred Combustor (LFJSC) has been developed for these combustion studies. This device produces results which represent the situation within a turbine or ramjet engine but allows testing with only small (about one liter) quantities of fuel. This allows testing of many more carbon types and formulations than would be possible with a large-scale system.

The final component of the program concerns systems implications. Subcontractors are inputting information and advice at key points in our program in the areas of turbine and ramjet engine technology as well as missile airframe considerations. General Electric is our subcontractor to provide expertise in fuel systems and combustors associated with turbine engines. The Chemical Systems Division of United Technologies provides guidance and key inputs regarding fuel systems and combustors

utilized in ramjets. Finally, Boeing provides knowledge regarding the missile system fuel requirements and net benefits of carbon slurries.

As already mentioned, this is an interim report which concerns only the results of the first program year. During this time the following milestones were met:

Formulation and evaluation of two-phase dispersions with loadings up to 69% carbon.

Development of a small-scale combustion device to study carbon burnout and combustion characteristics.

Initial evaluation of carbon burnout and the effects of particle size, catalyst use, and combustion conditions (fuel-air mixture ratio, temperature and residence time).

Formulation of three-phase systems (emulsions) with 60% carbon in the internal phase (80%) and formamide as the external phase (20%).

CED characterization of all carbon dispersion components.

The balance of the report is organized into four additional sections which more fully describe these accomplishments. The first provides background information which helps define the challenge of developing a carbon slurry fuel. Additional background information in the form of a thorough literature search is included in the report appendix. This is followed by sections describing the approach being used and the results acquired. The results section provides our key results; detailed listing of all information generated has been provided in the appendices.

## SECTION II

### BACKGROUND

This section provides details of our literature review, a discussion of the potential problems anticipated, and the key objectives of our approach to solving these problems.

#### A. Literature Review

An extensive review of the pertinent literature was made concentrating our search mainly on published information dating from 1960 to the present. The reason for selecting this time frame is that there are a number of excellent reviews which already adequately cover the subjects of interest as noted below. We have elected to put the bulk of the results of our literature survey in the appendix and have included below a brief summary of the various major topics.

##### 1 Properties of Carbon Black and Some Liquid Formulations

An annotated bibliography comprising a comprehensive sample of the extensive literature and numerous patents on carbon black has been prepared and is provided in Appendix A. Only samples have been provided which cover pertinent references since it would be repetitive and too lengthy to include all the materials. Included is information on carbon black dispersed in liquids used as pigments, coatings and ink oils. No attempt was made to cover the very extensive literature on the use of carbon black in elastomers and plastics. Over 350 references are included in this review out of thousands searched. A brief abstract is given below and further details are provided in Appendix A.

Some physical and chemical properties are notable. Particles of carbon black are extremely small, ranging from 5 to 500 nanometers, and can be seen only with the electron microscope. Their shape varies from spheroidal to complex; and the particles tend to clump together; indeed, dispersion of the particles is a major problem in the use of carbon black. Surface area is typically in the neighborhood of 100 m<sup>2</sup>/g, with extremes from perhaps 5 to 950 m<sup>2</sup>/g, and 0 to 35% porosity. The surface is usually active with a tendency to react with oxygen and some other substances to form surface groups that influence wettability and pH, which varies from acid to alkaline. There is also some free surface energy that draws the particles together. The rheology of suspensions of carbon black is strongly influenced by these surface characteristics and the suspensions are usually non-Newtonian. Viscosity, for example, is a function of shear history. The technology of carbon blacks in coating and inks entails the adaptation of the peculiarities of carbon black to the preparation of the stable suspensions required in these industries.

##### 2 Carbon Slurry Fuels

Mixtures of carbon in hydrocarbon and other types of oils have been made for centuries and used mainly as inks and pigments. The literature search noted in the previous section covers typical formulations

of this nature. Carbon slurry fuels of interest to the aerospace industry are specifically high energy formulations that would generally contain over 50-60% of carbon black in a high energy density fuel such as JP-9 or JP-10. Such formulations are called slurries because they generally are not stable and the mixture must be kept agitated to assure a uniform dispersion. Some mixtures of high carbon content are used, for example, as components of elastomer masterbatches in which the carbon black is dispersed in a suitable plasticizer (7). While the properties of such materials are of some interest the objectives are different and stability is not a prime concern.

Preparation of high carbon content high energy fuels has been limited mainly to the military. Extensive work has been done since the mid-1940's to develop high powered fuels mainly for rockets and ramjets. Carbon slurries and slurries of metals such as boron and aluminum were generally considered for these purposes, but were usually not preferred since the problems of handling and combustion deposits could not be overcome.

Bryant and Burdette (8) formulated up to 70 wt % carbon black in high density hydrocarbons such as decalin and tetralin and also in conventional kerosene type hydrocarbons. These were evaluated about eight different carbon blacks and graphite in kerosene. Several gelling agents (Shell Development Co's A1MB2, a Dow experimental agent CX3487, and Gellant M4, diacid aluminum soap of isooctanoic acid conforming to MIL-T-50009A) were evaluated and the DOW CX 3487 appeared to show the most promise. In addition, a number of formulations without gelling agents were used for combustion screening tests. Tests on viscosity and storage stability were run. The results indicated the viscosities were probably too high for practical use in missile systems, but the stability looked promising after several months of static and temperature cycling tests.

An excellent review of this subject entitled "High Energy Fuels - Literature Survey" has recently been compiled by the U.S. Army Mobility Equipment Research and Development Command, Fort Belvoir, Virginia (Report 2221, September 1977). This Army work was mainly aimed at searching for fuels to be used in ground based vehicles and concluded slurries were not of interest. They preferred synthetic, low-viscosity, liquid hydrocarbons of high density compared to slurry fuels.

A comprehensive literature search of Carbon Slurries and Gels for the period from 1960 to October 1969 was prepared by the Defense Documentation Center at the request of William Burdette of the Naval Weapons Center, China Lake, California. This report bibliography is classified Secret and is identified by the Search Control No. 02331.

While the previous work contains hundreds of additives found to be useful for dispersion of carbon blacks there are only a few candidates identified for use in the current program, and it would be an immense task to evaluate all the others.

Ashland has recently completed a paper study as a subcontractor to McDonnell Douglas Astronautics Company-East (MDAC-E) to perform ramjet fuels research in support of an Air Force contract to MDAC-E entitled "Supersonic Long Range Missile Integration Study" (SLRMS) (9).

The Ashland work indicated that formulations containing up to 70 wt % of carbon black could be dispersed in RJ-5 and up to 75 wt % in RJ-4. The dispersant used was 2% of TLA 202. (This is a Texaco Petrochemical Company ashless dispersant for automotive and diesel lubricants produced by reaction of P<sub>2</sub>S<sub>5</sub> with polyisobutylene.) The carbon blacks evaluated were standard rubber grade medium thermal blacks from Ashland and Cabot. Formulations were prepared on a laboratory three roll mill commonly used to make ink oils. Properties of these materials are described in the above reference. Viscosities varied from very thick to something similar to a multigrade motor oil. No information was provided on the stability of these materials.

Previous Exxon work (10) covered preparation of both two phase carbon dispersions in JP-4 and TH dimer fuel (Tetrahydrocyclopentadiene dimer), and three phase emulsions of these materials. Carbon blacks used were of 0.25 micron average particle size, generally coated with selected surfactants, dispersed in the fuel, and then emulsified in a hydrophilic liquid. Concentrations containing up to 60 wt % carbon black are reported. These materials were claimed to be quite stable and useful in air breathing rockets. High carbon concentration formulations (2 phase system) were quite viscous and had a reduced tendency to flow under low shearing forces. In addition, the method of manufacture suggested for the high concentration formulations was slow and tedious.

### 3 Combustion

The carbon slurry combustion process involves volatilization of carbon slurry droplets into hydrocarbon vapor and carbon particles, combustion of the hydrocarbon vapor, and combustion of the solid carbon. Each of these processes is reviewed in Section 2 and Appendix B (in detail). Unfortunately, direct combustion experience with actual slurries is lacking and our current understanding is comprised of educated conjecture concerning each of the involved processes.

The primary difficulty with carbon slurry combustion concerns oxidation of the solid carbon to achieve complete energy release. Our evaluation of previous work concerns soot oxidation and carbon particles. Of primary importance are References 11-19. As will be discussed later, this previous work does not lead to a distinct conclusion regarding the required combustion time for the carbon particle and much of the Exxon effort during this first program year concerns the obtaining of this information at conditions relevant to the carbon slurry application.

#### B. Potential Problems

##### 1 Formulation

Inherently carbon black is insoluble in hydrocarbon liquids. Thus, to prepare a formulation of carbon black in a hydrocarbon fuel the resulting mixture must consist of at least two separate phases; the hydrocarbon fuel which is a liquid, and solid carbon black. (For the purposes of the initial phases of this effort JP-10 has been selected

as the high density liquid hydrocarbon fuel. The properties of JP-10 are given in Table 1.) Faced with the reality of such a system the major problems that need to be considered and the trade-off options are summarized below.

### Carbon Black

Selection of the proper carbon black must take into consideration the size and structure of various commercially available materials. The benefits and problems of each option are summarized in Table 2. Carbon black size as given in the literature may be somewhat misleading since it only gives a portion of the picture. The actual particle size given denotes the size of the individual particles which compose a chain or grouping of carbon particles. For example, as shown in Table 2, the size would be a measure of one of the circles shown but these are actually fused to other particles to form an aggregate. This aggregate comprises the smallest size particle, and the dimensions of this aggregate are not generally given but can be determined by microscopic techniques. Carbon structure is a measure of how these chains are formed, and may be shown as linear or compacted aggregates as noted in Table 2. In addition, these aggregates can link together physically to form loosely bound agglomerates. The significance of the different sizes and formations in this program is the effect which size has on combustion rate as well as formulation properties as noted in Table 2. In addition, use of different amounts of shearing force during preparation can cause breakup of the loosely bound agglomerates. No amount of shear, however, will degrade the aggregate which is composed of fused carbon particles. Thus, selection of particle size and structure is critical to providing the optimum formulation and combustion properties.

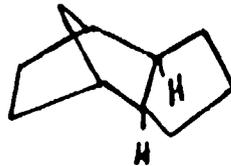
### Dispersing Agent

Selection of a suitable surfactant to disperse the carbon black in JP-10 is a significant problem since there are thousands to choose from with different properties. Table 3 shows briefly some of the benefits and problems of selecting the proper material. A surfactant serves to link together two dissimilar materials. An illustration of the role played by a surfactant in a carbon dispersion is shown schematically in Figure 2. Surfactants may be made to have one end be hydrophilic (water loving) and the other end lipophilic (oil loving). In a carbon dispersion, the hydrophilic end (head) will be attracted to the carbon particles and the lipophilic end (tail) attracted to the JP-10. The strength of these bonding forces will vary with the chemical structure of the various components. To select the proper surfactant the best match must be made among thousands of available surfactants with different functional groups, chemical structure, and molecular weight. Often a mixture of two or more surfactants is required to satisfy these requirements. Choice of the optimum surfactant will provide the most stable system. Making the proper choice is part art and part science. A major problem is the carbon black is not sufficiently characterized to permit selection of the optimum surfactant by known methods of calculation. There are several methods such as the HLB (Hydrophilic/Lipophilic Balance) method (20) and Solubility Parameter approach (4,5,6) which can

TABLE 1  
 PROPERTIES OF JP-10 (MIL-P-87107A, USAF)

Designation    Propellant, High Density Synthetic Hydrocarbon Type  
                   Grade JP-10  
 Composition    100% Exo-tetrahydrodi(cyclopentadiene)

Chemical Structure



Chemical and Physical Requirements and Test Methods

Property	Physical Requirements		ASTM Standards
	Minimum	Maximum	
Color, Saybolt	+25	-	D-156
Chemical Analysis			
Exo tetrahydrodi (cyclopentadiene)	98.5	100	(1)
Other Hydrocarbons	-	1.5	
Iron, ppm	-	10	"
Flash Point, °C (°F)	52 (125)	-	D-93, D-3243
Specific Gravity, (60/60°F)	0.935	0.943	D-1298
Freezing Point, °C (°F)	-	-79 (-110)	D-2386 (2)
Viscosity, cSt at °C (°F)			D-445
-54 (-65)		40	
-18 (0)		10	
Net Heat of Combustion			D-240, D-2382
MJ/kg (Btu/lb)		42.1 (18,100)	
MJ/m <sup>3</sup> (Btu/gallon)		39,400 (141,500)	
Thermal Stability			D-3241 (1)
Change in press. drop, mHg		10	
Heater Tube Deposit visual rating		Code 2	
Existent gum, mg/L		50	D-381
Particulate matter, mg/L		1.0	D-2276
Fuel System Icing Inhibitor, Vol %		0.15	(1)

(1) See above Mil Specification for details.  
 (2) Waived for JP-10.

TABLE 2

FORMULATION PROBLEM DEFINITION: SELECTION OF CARBON BLACKS

VARIABLES	RANGE	TRADE-OFFS	
		BENEFITS	PROBLEMS
● CARBON PARTICLES			
- SIZE	13 m $\mu$	+ GOOD FORMULATION	+ HIGH VISCOSITY
	(FOR BASIC PARTICLES)	STABILITY	+ DIFFICULT TO HANDLE
	TO	+ RAPID COMBUSTION	
	OVER 300 m $\mu$	+ LOW VISCOSITY	+ LESS STABLE FORMU-
		+ EASY TO HANDLE	LATIONS
			+ SLOWER BURNING
- STRUCTURE		+ RAPID COMBUSTION	+ HIGH VISCOSITY
	LOW		+ LESS STABLE
	HIGH	+ GOOD FORMULATION	+ SLOWER BURNING
		+ LOW VISCOSITY	

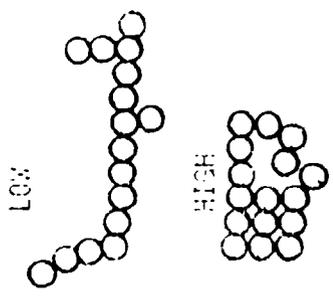


TABLE 3

FORMULATION PROBLEM DEFINITION: SELECTION OF DISPERSING AGENTS

<u>VARIABLES</u>	<u>RANGE</u>	<u>TRADE-OFFS</u>
● <u>SURFACTANTS</u>		<u>BENEFITS</u> <u>PROBLEMS</u>
	CHOICE OF THOUSANDS	+ REQUIRED TO OPTIMIZE      + DIFFICULT TO SELECT
	CARBON DISPERSION	BEST COMBINATIONS AND
	STABILITY AND	CONCENTRATIONS
	PROPERTIES	
+ USE OF CED CONCEPT		+ NEED TO IDENTIFY
WILL QUANTIFY RE-		BOTH SURFACTANT
QUIREMENTS OF VARIOUS		TYPE AND CHEMICAL
COMPONENTS		STRUCTURE
+ IDEAL SURFACTANT		+ LOWER BTU VALUE
GIVES FREE ENERGY		
		= 0

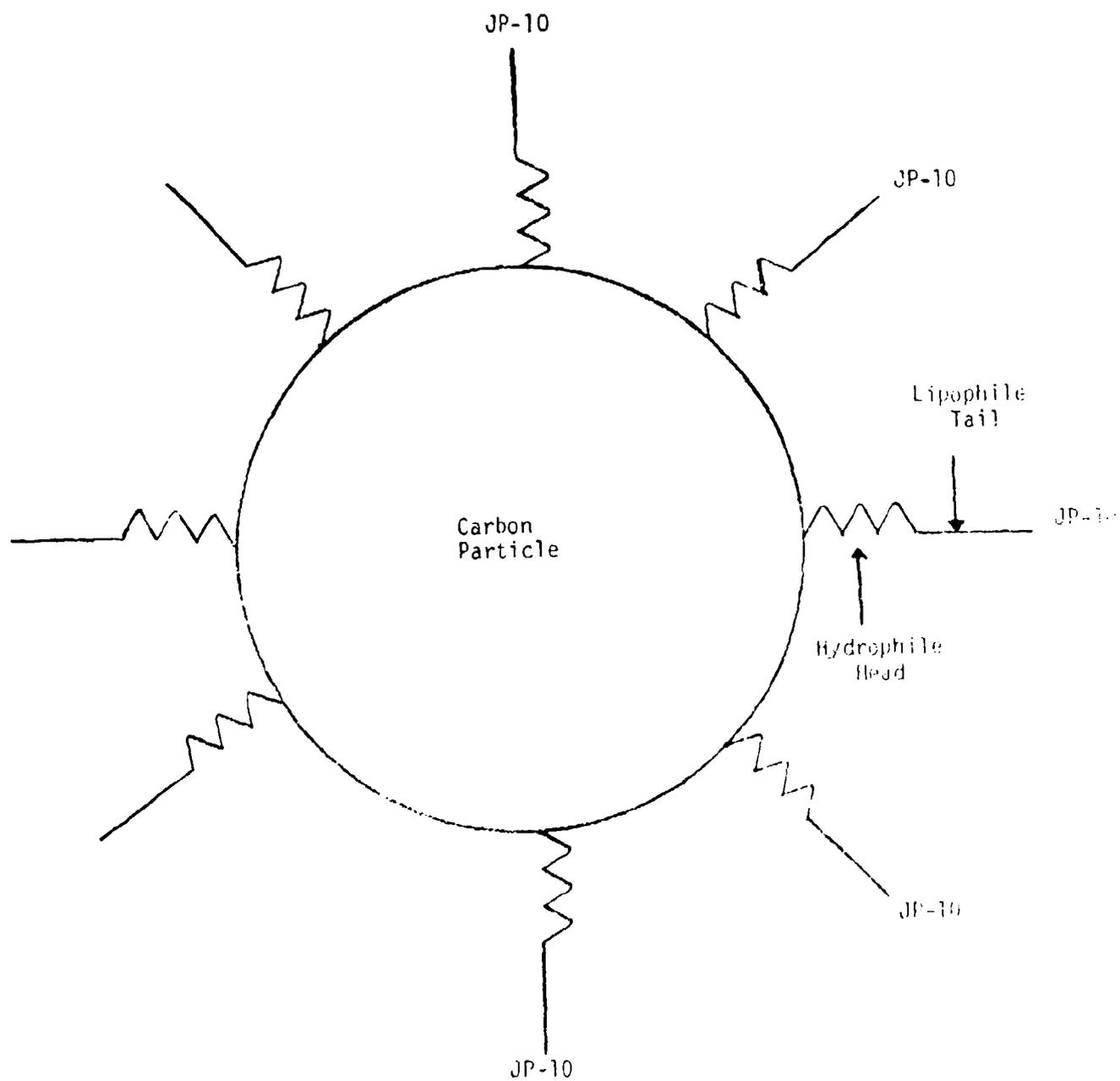


Figure 2. Schematic Of The Role Of A Surfactant In A Carbon Dispersion

be utilized to obtain approximate requirements. These will be discussed later (Section III A 1a).

#### Number of Phases

Two phase systems are the conventional method of preparing a dispersion of a solid in a liquid. The problems with these systems based on past experiences are poor stability and limited flexibility in properties as noted in Table 4. Three phase systems are another approach (see Section III A 1 below) which has certain advantages, but they require an additional emulsion phase which introduces problems in selection of the proper external phase liquid and emulsifying agents. The three phase system contains the two phase dispersion of carbon in JP-10 as the internal phase. The external phase is an immiscible liquid in which the carbon dispersion must be emulsified. The potential benefits for a three phase system, as noted in Table 4, are choice of a three phase which has better low temperature, viscosity and stability characteristics than a two phase system. In addition, the third phase may be selected with a "pop" effect which on combustion might "blow apart" the particles to facilitate combustion and reduce agglomeration. Selection of the proper combination of components is obviously not a simple matter, but such a three phase system could have significant advantages.

#### Method of Preparation

Mixed phase systems are generally prepared with agitation, but the amount of agitation and shear required presents problems which can significantly affect product quality and costs. Several different types of mixers and the benefits and problems of each are given in Table 5. Order of mixing components can also be a critical factor in combining solids, liquids and one or more surfactants.

#### Need for Catalysts

A major challenge in the development of a successful carbon slurry fuel is to achieve complete combustion of the carbon particles in realistic combustion residence times. This problem is discussed from the combustion point of view in Section II B 2. At a fixed temperature and equivalence ratio, smaller carbon particles will combust more rapidly, but tend to increase fuel viscosity in a two phase carbon dispersion. Clearly formulation techniques to accelerate the rate of carbon particle burnout will be highly desirable if not critical.

In the surface kinetically controlled regime, the rate of oxidation of the carbon particles should be capable of being accelerated via the use of catalysts. In principle, such catalysis could be either homogeneous, i.e. the addition of a soluble catalytic material to the liquid portion of the fuel, or heterogeneous, i.e. the addition of active solid catalytic materials directly onto the carbon particles themselves. Homogeneous catalysts would be expected to accelerate the rate of carbon particle oxidation via the generation of enhanced concentrations of active species such as oxygen atoms in the vapor phase which then must migrate via diffusion and/or convection to the surface of the

TABLE 4

FORMULATION PROBLEM DEFINITION: SELECTION OF NUMBER OF PHASES

VARIABLES	RANGE	TRADE-OFFS
NUMBER OF PHASES IN DISPERSION		BENEFITS                      PROBLEMS
●	2	+ EASY TO PREPARE                      + HIGH VISCOSITY + ALL COMPONENTS HAVE HIGH BTU VALUES                      + STABILITY
	3	+ INCREASED FLEXIBILITY                      + MORE DIFFICULT TO FORMULATE IN CHOICE OF EXTERNAL                      DUE TO INCREASED NUMBER OF PHASE i.e. GLYCOLS,                      COMPONENTS AMIDES, BLENDS, ETC. + BETTER VISC., LOW                      + THIRD (EXTERNAL) PHASE HAS TEMPERATURE PROP-                      LOWER BTU VALUE ERTIES, STABILITY + CAN GET HIGH LOADINGS WITH LOW VISC. (EX. HIGH CONC. OIL, WAX AND ASPHALT EMULSIONS HAVE VISC. = WATER) UP TO 95% OIL IN WATER REPORTED IN LITERATURE

TABLE 5

FORMULATION PROBLEM DEFINITION: METHOD OF PREPARATION

VARIABLES	RANGE	TRADE-OFFS	
		BENEFITS	PROBLEMS
● METHOD OF PREPARATION			
- MIXING EQUIPMENT	STIRRERS	+ LOW COSTS + LARGE VOLUME THRUPUT	+ LOW SHEAR
	PUMPS	+ CONTINUOUS OPERATIONS + LOW COST + LARGE VOLUME THRUPUT	+ MODERATE SHEAR
	MILLS (ROLL, BALL)	+ HIGH SHEAR THRUPUT	+ HIGH COSTS + GENERALLY BATCH OPERATION
- ORDER OF MIXING	FUNCTION OF NUMBER OF COMPONENTS	+ CORRECT ORDER CAN PROVIDE OPTIMUM FORMULATION	+ MORE STEPS MAY INCREASE COSTS AND COMPLEXITY OF PREPARATION

particles and attack the carbon. Heterogeneous catalysts would be expected to function via dissociation of molecular oxygen to atomic oxygen on the surface of the catalyst particles which then undergo "spillover" and readily attacks the nearby carbon.

Studies involving direct observations with a transmission electron microscope equipped with a television camera by Dr. R. I. K. Baker of Exxon Research has shown that metal particles added to the surface of carbon will, indeed, catalyze the rate of oxidation. At a sufficiently high temperature the metal particles become mobile and "dig" both channels along the carbon surface and holes into the bulk of the carbon particle. Metal and/or metal oxide catalysts are known to be active for oxidation reactions and the formulation procedures should aim at depositing small (e.g. 50Å), well dispersed particles onto the surface of the carbon so that significant catalysis is achieved at low catalyst loading levels.

## 2 Carbon Dispersion Combustion

The subject of carbon dispersion combustion is exceedingly complex. Superimposed upon the already intricate processes involved in the combustion of gaseous or liquid fuels is the heterogeneous oxidation of carbon particles which may be large compared to the normal soot formed during conventional fuel combustion. The burn time of these carbon particles is expected to lag the consumption of the hydrocarbon component in the fuel but the impact of this occurrence on parameters such as ignition, stability, and combustion efficiency is not known. The background section provides a brief discussion of our current understanding of the carbon dispersion combustion process and problems to be encountered. A more thorough discussion of slurry combustion fundamentals is included in Appendix B.

### The Combustion Process

Figure 3 describes the overall combustion process for a carbon dispersion fuel. Volatilization of the slurry produces a gaseous hydrocarbon vapor and carbon particles. As it would if an entirely liquid fuel were being combusted, the hydrocarbon vapor then undergoes a complex process of pyrolysis and partial oxidation. In simplified terms, the principal products of these reactions can be considered to be hydrogen, carbon monoxide and soot. The  $H_2$  then undergoes chain branching reactions which provide free radicals ( $H$ ,  $O$ , and  $OH$ ) and termination of the process results in the final combustion product  $H_2O$ . These radicals participate in and often dominate, other chemical processes occurring within the combustion process. The pyrolysis process is influenced by these species and  $CO$  disappearance is actually controlled by oxidation by  $OH$ . These gas phase processes are very rapid at the temperatures of interest in aero propulsion application ( $>2000K$ ) and near complete oxidation is possible in less than 2 ms. However, soot oxidation requires heterogeneous oxidation which is slower than that occurring in the gas phase. Figure 3 shows this time requirement as  $t_1$ .

Combustion of the carbon portion of the slurry also requires a heterogeneous reaction. The time required for complete burnout designated  $t_2$  in figure 3, depends upon particle size and combustion

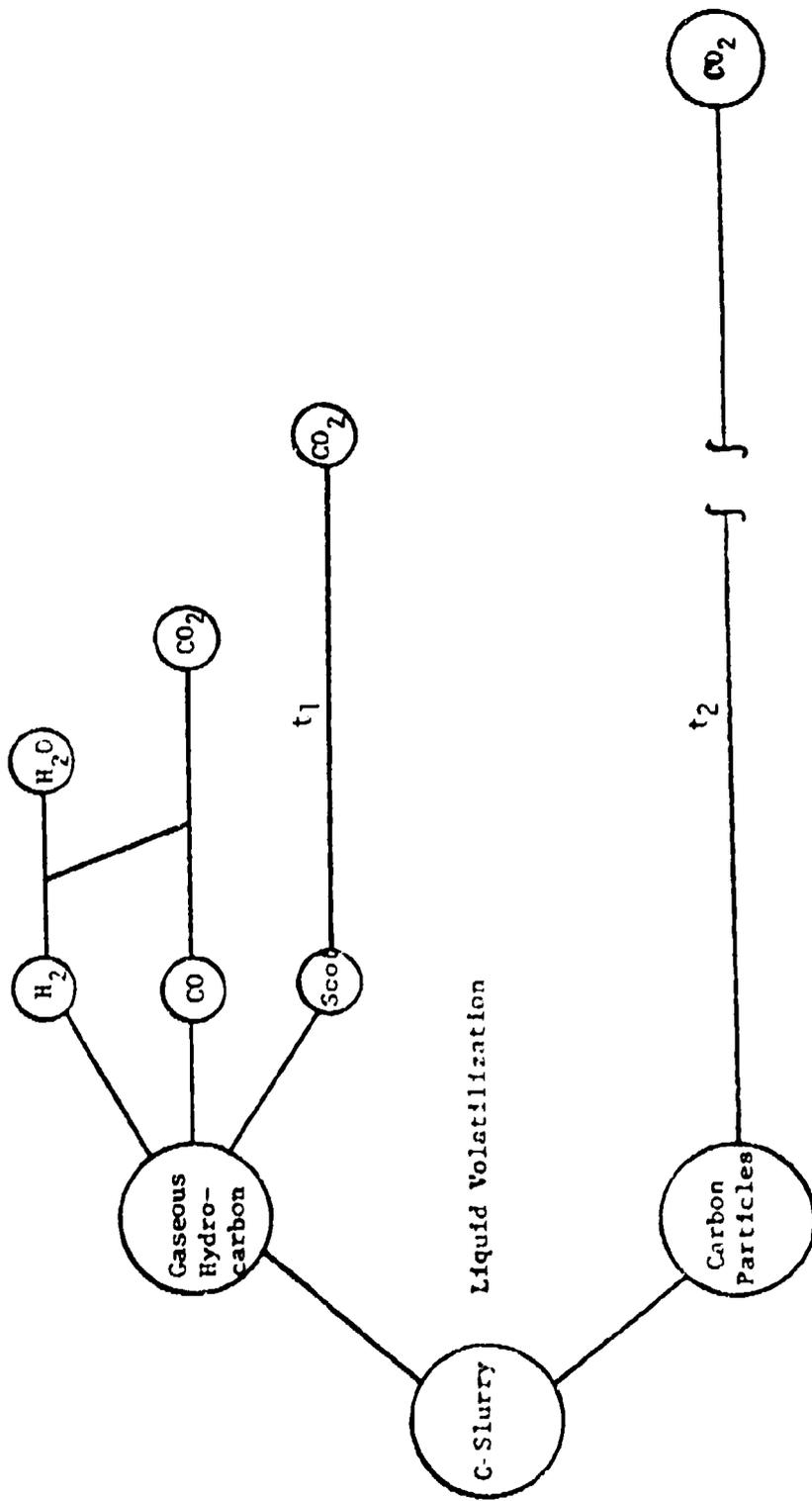


Figure 3. Carbon Slurry Combustion Chemistry Schematic

conditions. Carbon black is usually of a diameter greater than soot. Therefore, the release of the carbon's heating value will require at least as much time as that for the case for a 100% liquid fuel. Consequently, the carbon oxidation process will lag the consumption of the hydrocarbon portion of the fuel.

The soot and carbon oxidation rates will be controlled by the surface oxidation process. Figure 4 illustrates the combustion time required for particles of various diameters burned in the stoichiometrically correct ratio of fuel to air. The band of required times at lower diameters is due to data variation for different types of carbon (further discussion of this later). An abrupt change in the slope of the combustion time/diameter characteristic is apparent at about 10  $\mu\text{m}$ . This corresponds to the transition between diffusional and surface kinetic control of the particle oxidation rate. At the diameters of interest to carbon slurries (<1.0  $\mu\text{m}$ ), the process is definitely kinetically controlled. The substantial difference between the extrapolation of the diffusion controlled behavior and the observed carbon burning times at small diameters indicates that much is to be gained by consideration of methods for acceleration of carbon particle surface kinetics (i.e. selection of the proper carbon type and catalysis).

Consideration of this view of the carbon dispersion combustion process during the first year of this program has allowed identification of three key problems which warrant further explanation in this section: (a) difficulties with fuel injection, (b) droplet vaporization problems, and (c) uncertainties in carbon burnout.

#### Fuel Injection

Two unique types of fuel injection problems are encountered when using carbon dispersion fuels. The first involves the potential prevaporization of the hydrocarbon component of the fuel within hot fuel lines or the fuel nozzle. When 60% of the fuel is solid carbon, loss of even a small amount of liquid carrier will result in immediate plugging. Consequently, special care must be taken to insure against the fuel lines or nozzles reaching temperatures at which prevaporization or slurry instability can take place. Further, the initial flow of slurry into the fuel lines and nozzle must occur with cold hardware. During shutdown, the fuel must not remain in hardware which can become hot (i.e. it must be purged). If the slurry is not purged, deposition of carbon near the hot wall will result and may eventually result in plugging. This phenomenon is analogous to, but much more dramatic than, the afterburner spray bar plugging problem which occurs due to high temperature instability of liquid jet fuels.

The second problem involves deposition of carbon within the combustion system after injection. If the liquid fuel impinges on a hot surface, the liquid portion of the fuel will flash vaporize leaving a deposit of carbon behind. In addition, if the carbon in the combustion zone (after vaporization) is allowed to come close to a colder surface within the combustor, the carbon will be attracted to and deposit on the surface. This phenomenon is known as thermal phoresis. In either case a substantial carbon deposit can build up distorting the aerodynamics

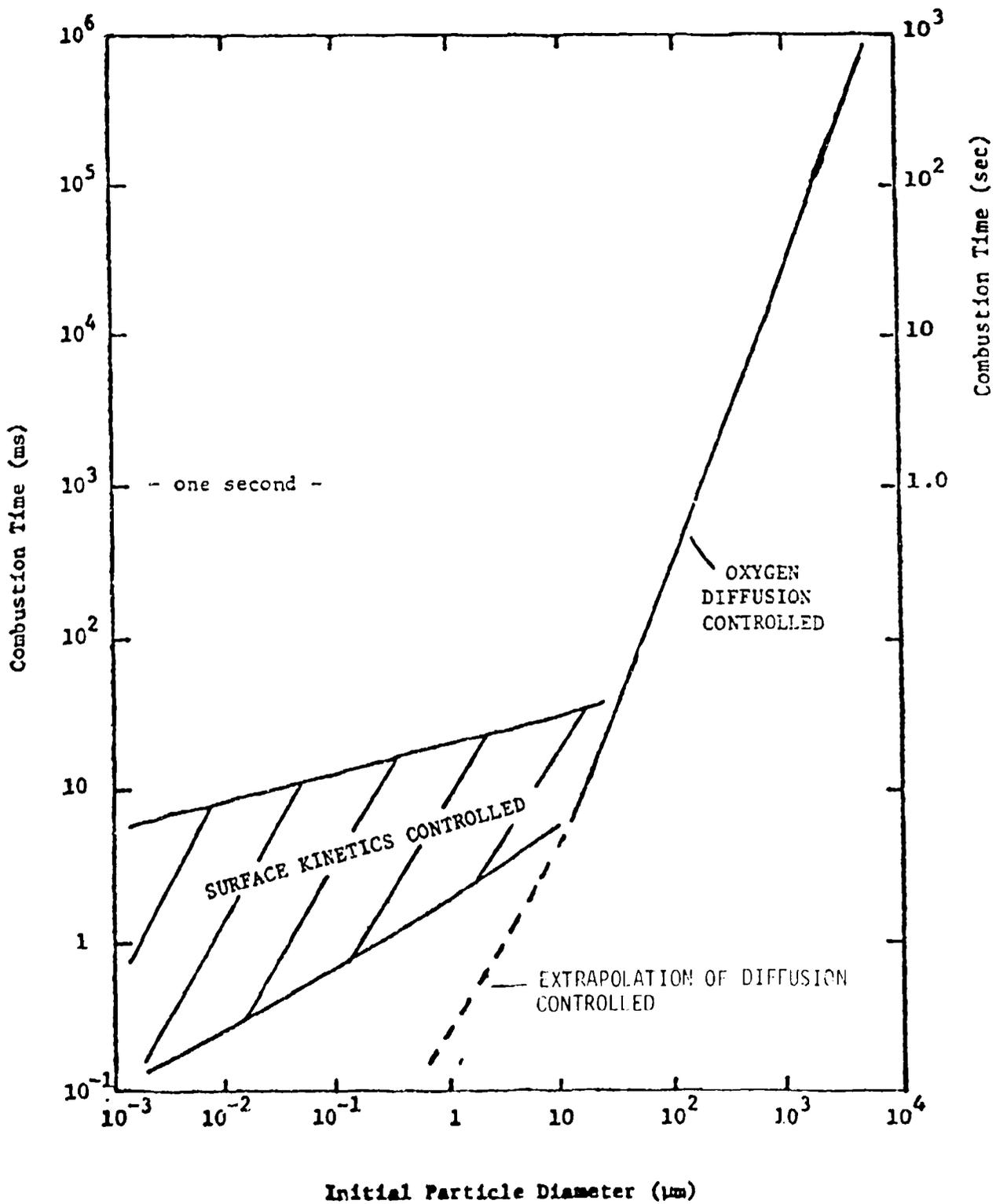


Figure 4. Dependence of Carbon Particle Combustion Time on Particle Diameter

of the combustion process and/or the hardware cooling scheme. Further problems can result if the carbon breaks away from the deposit site in masses large enough to erode downstream engine components. Deposits of soot in combustion systems have been shown to destroy turbine hardware in this manner (11). These problems will require special attention in systems which utilize low pressure air atomization fuel injection methods. Prevention of carbon deposition on air swirling devices will be especially difficult.

### Volatilization

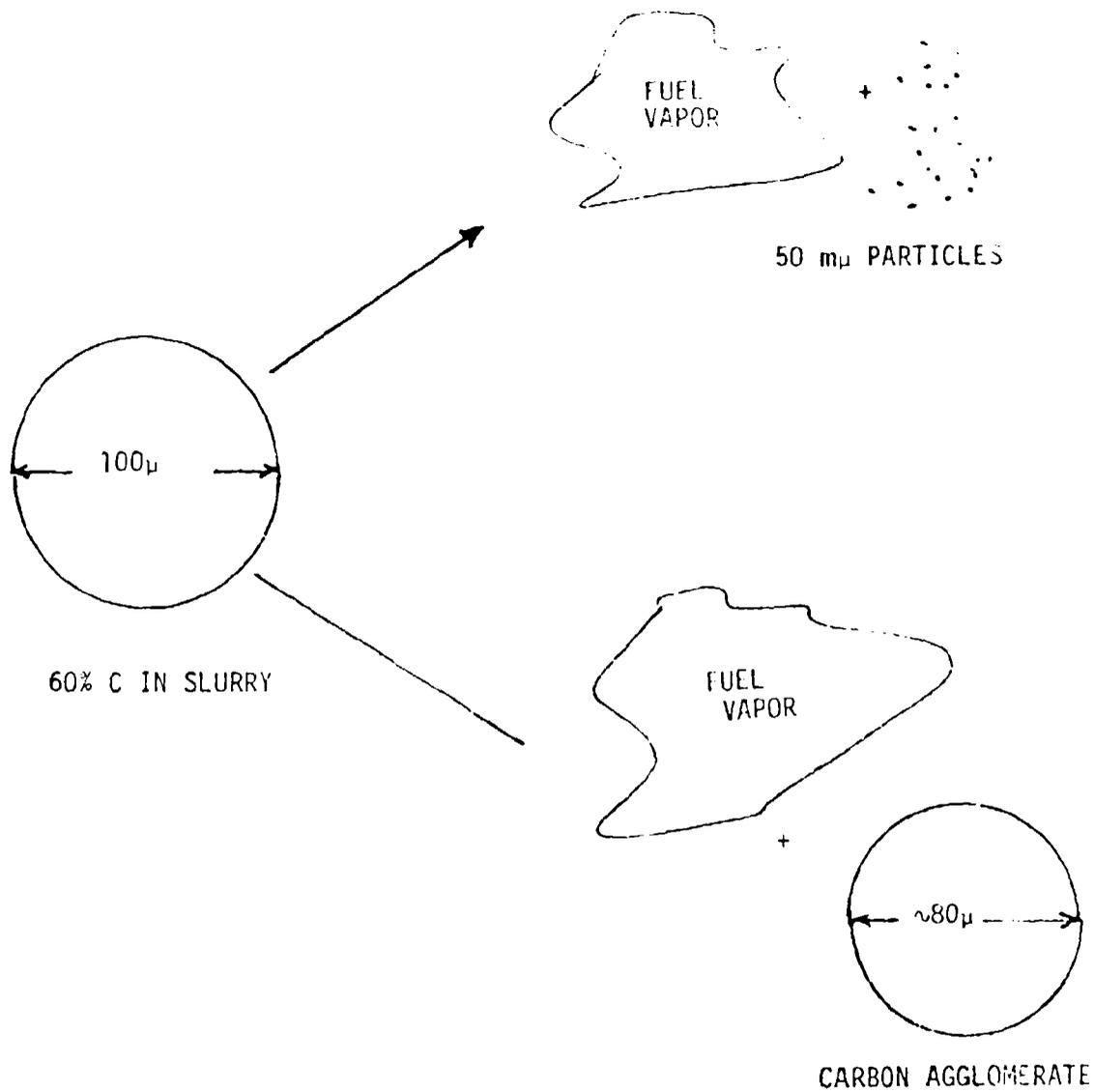
Since carbon oxidation is likely to be the limiting step in the complete combustion of carbon slurry fuels, our current emphasis in slurry formulation has been on the use of sub-micron carbon particles (0.01-0.3 $\mu$ ) which would be expected to have short burnout times. The slurry enters the combustion system as liquid droplets containing approximately 60% by weight of this very small particle size carbon. Depending on the injection technique utilized, the average droplet diameter may range from about 50 to 150 $\mu$ ; and, therefore, each drop contains millions of small carbon particles.

The vaporization of the slurry droplet must be such that the carbon particles enter the gas phase individually or in small groups. If agglomeration occurs --all the liquid is removed without causing the carbon particles to disperse-- a large, 40-120 $\mu$  mass of carbon will remain, as shown in Figure 5. The burning rate of such a large diameter particle would be diffusion rate controlled. In this case the combustion benefits of providing the small particle size will be lost. In fact, if the agglomeration problem cannot be avoided, the practicality of combusting the slurry carbon content in the short time available (1-5 ms) will be in serious doubt.

One approach for solving this problem is to maximize the volatility difference between the internal (high density hydrocarbon) and external (hydrophile) phases of a three phase carbon slurry formulation. This would result in a droplet fragmentation process which forces individual or groups of carbon particles to separate from the parent droplet. Other approaches might involve some treatment of the carbon particles to result in repulsive forces upon heating or even a modified fuel injection technique. In any case, it is important to be able to observe the droplet vaporization process so that an understanding of these approaches may be gained and correlations for formulating slurries which minimize agglomeration may be developed.

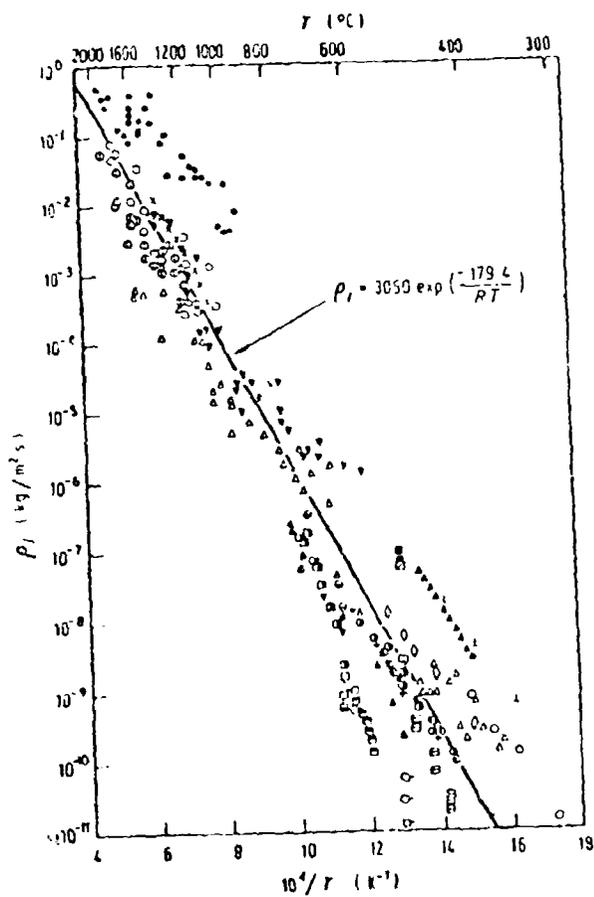
### Carbon Burnout Rate

Many of the postulated problems concerning the combustion of carbon slurries could be at least scoped if we had a dependable means of predicting carbon particle oxidation rates. However, the overall picture now extant of carbon particle and soot oxidation leaves much to be desired. A comparison study of the literature, which includes measurements of soot oxidation as well as various forms of carbon particles, reveals that the range of burning time is quite large, encompassing several orders of magnitude (Figure 6). Even for a specific type of carbon, such as graphite, there is a range of almost two orders of magnitude. Clearly oxidation rates



CARBON AGGLOMERATE BURN TIME WOULD BE  $> 1s$

Figure 5. Vaporization Process For A Carbon Slurry Fuel Droplet



### Key to Symbols in figure

Ref. no.	Symbol	Material
5	•	Petroleum coke
(6)	▲	
6	■	
2	△	Brown-coal char
7	○	Lignite char
5	○	Anthracite
8	▲	
1	○	
5.9	▽	Semi-anthracite
6	u	Bituminous-coal char
15	x	Metallurgical coke
6	□	Soot
11	○	Pitch coke
12	○	Pitch resin
13	△	
14	○	
15	+	
15	+	Nuclear graphite
15	+	
16 (a)	■	Cracked carbon (unoxidized)
16 (b)	■	
17	○	Cracked carbon (oxidized)
18	○	AGKSP graphite
19	○	AGKSP graphite
20	○	Alb
19	○	SFI
21	○	
22	○	Spectroscopic graphite
22	○	
(1)	○	Graphite
23	○	
14	○	Purified carbons
20	○	
23	○	Storing 11
23	○	Acetylene 11
23	○	Asbestos 11

(a) Tyler (personal communication, 1974)

(b) Wouterlood (personal communication, 1975)

Figure 6. Variability In Available Data On Carbon Oxidation Rates  
(Reference 13)

are in serious disagreement; there are virtually no conditions under which we can assume accurate knowledge of the time for carbon burnout.

Table 6 provides carbon burnout time information for the conditions of interest to cruise missile combustion systems. Information was extracted from data or correlations were applied for conditions of 2000K and an oxygen partial pressure of one atmosphere. Some of this background information recognizes the influence of fuel-air ratio on burnout, but much assumes the carbon burning in a non-depletable atmosphere of oxygen --i.e. very fuel-lean. Such information underpredicts the actual required time for burnout. It is evident that the disagreement for carbon burnout time among these previous workers exceeds an order of magnitude. And the range of uncertainty, from less than one millisecond to ten, spans time requirements at which efficient slurry combustion would certainly appear to be feasible to times at which application of the concept is in serious doubt.

It should be noted that the possibility that burnout times may be on the order of one millisecond is extremely encouraging. If burnout time were on this order, the "lag" expected for carbon burnout may be negligible and the combustion process of a slurry may become very much like that of a liquid. Consequently, even if a burnout time for carbon of 2-3 ms were determined, motivation to increase the rate of burnout would remain with the overall objective of making the dispersion behave as much like a liquid as possible. It is evident that the objective of developing an optimum carbon dispersion fuel will be substantially enhanced by additional study of carbon oxidation chemistry. Oxidation kinetics of the actual carbon being utilized in dispersion formulations should be established and the impact of various fuel formulation variables (especially catalyst behavior) evaluated.

### C. Key Objectives

#### 1 Formulation

To overcome the formulation problems noted above (Section B) the following objectives have been established.

Obtain a thorough understanding of the interactions among carbon, fuels, dispersants, and other ingredients to permit preparation of carbon dispersions with optimum properties.

Preparation of carbon dispersions that are stable in both static and dynamic tests, and which will remain stable and usable over a temperature range of -60 to +140°F.

Formulation of a fuel with a minimum of 180,000 Btu/gallon which is compatible with anticipated missile systems.

#### 2 Combustion

To overcome the combustion problems noted above the following objectives have been established.

TABLE 6  
CALCULATED CARBON BURNOUT TIMES

Researcher(s)	Type of Information	Burn Time for 300m $\mu$ Particle* (ms)
Essenhigh (14)	Analytical Model of Carbon Oxidation	<1
Mulcahy and Smith (15)	Correlation of Data for Coal, Char Graphite, and Carbon Black	~2
Lee, Thring, and Beer (16)	Equation Based on Data for Oxidation of Soot	2.3
Bryant and Burdette (8)	Graphite Particles (~5 $\mu$ ) Burning in a Flat Flame	0.9
Radcliff and Appleton (17)	Calculated from Soot Burnout Information at Gas Turbine Conditions	~8
Park and Appleton (18)	Shock Tube Measurements of Carbon Black (~18m $\mu$ ) Oxidation	~10
Bradford and Bernard (19)	Carbon Black (100-200m $\mu$ ) Oxidation in Laboratory Burner	~5
Cassel (21)	Graphite (3-6 $\mu$ ) Oxidation in Laboratory Burner	~1

\* Where possible, information was extracted or correlations were applied for conditions of 2000K, P<sub>O2</sub> = 1 atm.

Evaluate the combustibility of different carbon blacks which may be utilized in a carbon slurry with special emphasis on carbon particle size.

Determine dependence of carbon slurry combustibility on mixture ratio, temperature, and time.

Examine the utility of catalysis to accelerate carbon oxidation to allow a slurry which combusts in times similar to hydrocarbon fuels.

Ascertain difficulties associated with slurry fuel injection.

## SECTION III

### APPROACH

The overall approach utilized in this program is an iterative examination of the key combustion effects which must be considered during formulation of candidate fuels. In this way, the key variables --including type of carbon, size, loading, type and amount of surfactants, method of preparation, the need for catalysts, etc. will be logically and thoroughly considered. Our approach to both formulation and combustion studies are discussed below.

#### A. Formulation

##### 1 Discussion

To evaluate the variables noted above both conventional and novel techniques were used. Conventional approaches were used for selection of carbons, equipment and procedures for mixing. In selecting the required surfactants and final composition of the carbon dispersion both conventional and novel techniques were employed. Another feature of our approach was to incorporate catalysts in these formulations. These novel techniques were:

- (1) Use of solubility parameters to select the optimum surfactants.
- (2) Formulation of a three phase system in which a two phase dispersion of carbon black in JP-10 is emulsified in a hydrophilic liquid; the latter serves as the external phase.

These are discussed in more detail below.

##### Solubility Parameters

To prepare stable emulsions and dispersions formulators may use various techniques to aid in selection of the proper surfactant. The HLB method of Griffin (20) is useful for liquids and the Solubility Parameter technique of Hansen and Beerbower (4,5,6) is useful for liquids to form emulsions and also for dispersing insoluble solids in a liquid (dispersions). The latter technique is of special interest since the required values may be calculated if the chemical structure of all the components are known. While the chemical structure of carbon black is not sufficiently known to permit calculation, it can be determined by experimental methods. This approach was used in our program. The value of this approach may be seen by an explanation of the basis for the Solubility Parameter, Cohesive Energy Density (CED), and Cohesive Energy Ratio (CER) concepts.

The interactive forces present when a solid is contacted by a liquid are due to physio-chemical interactions of the specific molecules involved. These interactions may be expressed as three separate partial parameters as was done by Hansen and Beerbower.

- (1)  $\delta_D$  represents the London ("dispersion") forces which are present in all liquids. In paraffinic and naphthenic hydrocarbons, these are the only forces present, and  $\delta = \delta_D$ , where  $\delta_D$  is the London force contribution. These forces are omnidirectional and arise from the cyclic field produced by the orbital electrons.
- (2)  $\delta_P$  represents the Keesom (polar) forces generated by permanent dipoles in certain molecules. The Keesom forces are dominant in nitriles and nitro compounds, and quite strong in esters and ketones.
- (3)  $\delta_H$  is designated "hydrogen bond" parameter, but actually includes forces due to several kinds of electron-transfer interactions.

The relation of all these to one another is essentially based on the first law of thermodynamics which states that energy is neither lost nor gained. In this case, it is the "Cohesive Energy," (CE),

$$CE = V\delta^2 = \Delta H_V - RT = V\delta_D^2 + V\delta_P^2 + V\delta_H^2 \quad [1]$$

where  $V$  = molar volume and  $\Delta H_V$  = heat of vaporization and  $RT$  are the conventional gas constant and temperature, respectively. (In the case of fused metals or salts, two more terms for metallic and ionic energies would be needed.)

From this, dividing by  $V$  we obtain the "Cohesive Energy Density,"

$$CED = \delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad [2]$$

Methods for determining the partial  $\delta$  values for liquids are well understood, and many have been tabulated (4,5,6,22). For liquids whose  $\Delta H_V$  is not known, excellent approximations can be built up from group contributions (4,22). This expression (CED) can be determined for the various components of a system. The Cohesive Energy Ratio (CER) of the two phases may be adjusted by use of surfactants to get a minimum value (4).

$$CER = \frac{CED \text{ Phase 1}}{CED \text{ Phase 2}} \quad [3]$$

A minimum value of CER means that the heat of mixing will be essentially zero and the dispersion should have optimum stability. There is also some evidence to indicate that the same criteria lead to minimum viscosity (22).

### Three Phase Systems

In addition to investigating conventional two phase systems, three phase systems were investigated. This concept of making the carbon dispersion in JP-10 as the internal phase of an emulsion, a three phase system should have major advantages (10,23) compared to a two phase system as noted below:

- A suspension of a viscous material (carbon dispersion) in a thinner liquid (external phase) tends to have a viscosity which depends only on the viscosity ( $\eta_0$ ) of the external phase and the volume fraction ( $\phi$ ) of the internal one. For very dilute emulsions the Einstein equation

$$\eta = \eta_0 (1 + 2.5 \phi) \quad [4]$$

holds fairly well, but as  $\phi$  increases, more complicated functions are necessary (24). However, the viscosity of the internal phase never enters the equations.

- The presence of an external phase can be useful in imparting properties to the system which are significantly different from the carbon dispersed in JP-10 alone. For example, using ethylene glycol, dimethyl formamide and other hydrophilic liquids (10) it is possible to alter the wetting characteristics, flow properties, temperature effects, and other parameters.

- The third phase can be selected to have a significantly different volatility than the JP-10 so that the sprayed particle "pops" and provides secondary atomization. This effect is anticipated to reduce the tendency for the carbon dispersion in JP-10 to agglomerate when the fuel is vaporized in the combustor.

This three phase approach requires preparation of a system with multiple interfaces as shown in Figure 7. Using the CER concept, all of the interfacial parameters can be determined and it is possible to select the optimum combination of surfactants with a minimum of trial and error.

## 2 Experimental Methods

### a. Preparation of Formulations

#### Carbon Black Selection

Carbon blacks of varying particle size (13, 25, 75 and 300 m $\mu$ ) and low (linear) structure were selected to determine the effect of particle size on combustion and formulation properties. Formulations containing from 20 wt % to over 65 wt % were prepared.

#### Mixing Equipment and Techniques

Standard laboratory mixers, a colloid mill, and roll mill were the major types of equipment employed. The mixing procedure generally used was to mix the surfactant with the JP-10 until dissolved (10-20 minutes at room temperature); add this to the colloid mill, and then add the carbon black slowly (over 10-20 minutes) while circulating. After all ingredients were mixed recirculation was continued for another five minutes.

- |              |  |
|--------------|--|
| Interface #1 | Carbon to hydrophile of the dispersing agent |
| "            | Hydrophile attached to dispersing agent      |
| "            | Lipophile attached to dispersing agent       |
| "            | JP-10  |
| "            | Lipophile attached to JP-10                  |
| "            | Hydrophile attached to external phase        |
| "            | External phase (Hydrophile)                  |

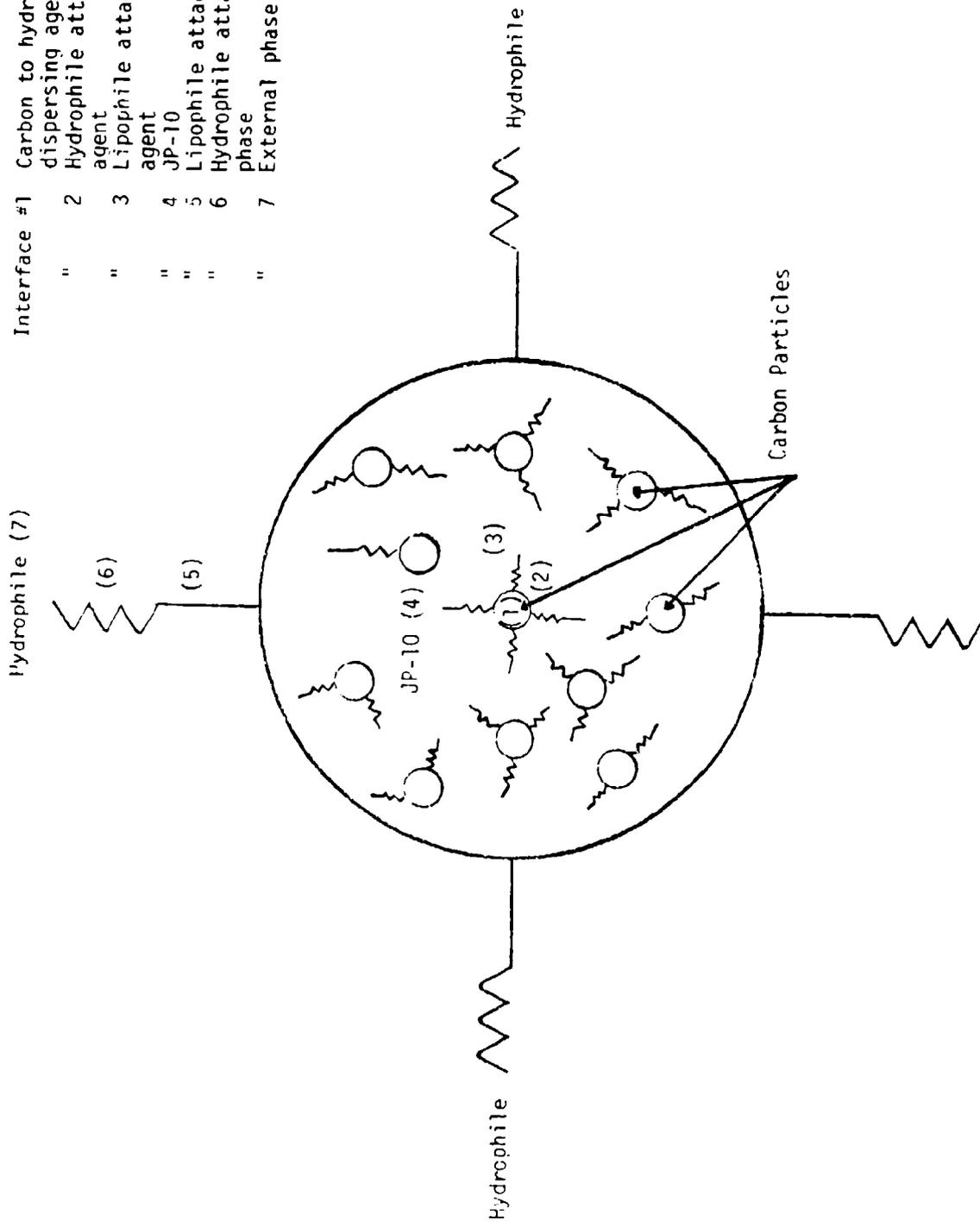


Figure 7. Schematic Of Three Phase Carbon Dispersion/Emulsion System Showing Multiple Interfaces

In some cases the materials from the colloid mill were then processed on the roll mill by passing through the rolls from two to ten times.

#### Dispersant Selection

Choice of surfactants for initial screening was made on the basis of our own internal knowledge, the existing literature and information from our consultants on this program (Prof. A. C. Zettlemoyer of Lehigh University and Mr. A. Beerbower, an ER&E annuitant). These formulations were used extensively for evaluating carbon dispersion properties and combustion evaluations.

Parallel efforts were also carried out to determine the surfactant requirements of carbon black by CED (Cohesive Energy Density) techniques. This procedure involves measurement or calculation of solubility parameters as described below:

To measure the partial solubility parameters of particulates, it is necessary to test the particulates' interactions with a range of solvents. The preferred method for determining the partial solubility parameters of the particulate surface is the sedimentation technique of Hansen (5). In this method about 0.5 gm of dried carbon black is shaken in a 10 ml graduated cylinder with 5.0 ml of a reference liquid having known values of  $\delta_D^2$ ,  $\delta_P^2$ , and  $\delta_H^2$ . The mixture is allowed to stand until no further settling occurs and the volume of carbon black in suspension is measured at the carbon/liquid interface taken as the equilibrium dispersion value. (it generally required 2-30 days to reach equilibrium.) Samples were run in duplicate using clean (washed with cleaning solution), dry glassware. A series of seventy-nine reference liquids (listed in Table 7) were used. The dispersion volumes obtained from the laboratory results are converted as follows to cc of dispersion/gm (F factor).

$$F = \frac{\text{Volume of Dispersed Carbon, cc.}}{\text{Weight of Carbon Black, gm}} \quad [5]$$

The F values are then plotted in an order of ranking by the methods employed by Hansen (5,6) and Panzer (21). A summary of this procedure is given in Appendix C and is shown in the results (Section IV A 2). The data obtained from this procedure identifies the type of surfactant required to disperse or emulsify one material in another.

For materials of known chemical structure, the solubility parameters may be calculated from group contributions of partial solubility parameters shown in Table 8. The procedure used may be illustrated by the following.

For example, to calculate the solubility parameters of the compound shown below (using Table 8) the compound is broken down into functional groups and the values determined as noted.

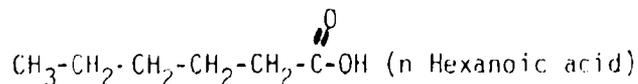


TABLE 7

## REFERENCE LIQUIDS USED FOR SOLUBILITY PARAMETER DETERMINATION

Reference Liquid	Cohesive Energy Density Parameter, (cal/mole) <sup>1/2</sup>		
	$\delta_D$	$\delta_P$	$\delta_H$
1 Hexane	7.3	0	0
2 Octane	7.6	0	0
3 Dodecane	7.8	0	0
4 Hexadecane	8.0	0	0
5 CCl <sub>4</sub>	8.7	0	0.3
6 Carbon disulfide	10.0	0	0.3
7 Diethylamine	7.3	1.1	3.0
8 Isobutylacetate	7.4	1.8	3.1
9 Cyclohexylamine	8.5	1.5	3.2
10 Anisole	6.7	2.0	1.3
11 Bromoform	10.5	1.5	0.4
12 Diisopropylamine	7.5	0.7	2.9
13 o-xylene	8.7	0.5	1.5
14 Chlorobenzene	9.3	2.1	1.2
15 n-Bromonaphthalene	10.5	1.2	1.0
16 Diethylene glycol	7.9	2.2	10.1
17 2-Aminoethanol	8.4	2.0	10.4
18 Formamide	8.4	17.0	9.3
19 Water	7.0	7.0	20.7
20 Acrylonitrile	6.9	2.2	2.1
21 Nitroethane	7.6	2.0	2.7
22 Nitromethane	7.9	2.2	2.5
23 Acetonitrile	7.5	8.0	3.0
24 Propylene carbonate	9.8	5.8	2.0
25 Butyronitrile	7.5	6.1	2.5
26 Nitropropane	7.0	5.9	2.6
27 Methanol	7.3	6.0	10.5
28 Ethylene glycol	7.3	5.4	11.7
29 Glycerol	8.5	5.9	14.3
30 2-Ethylbutanol	7.7	2.1	6.1
31 Cyclohexanol	8.5	2.0	6.0
32 o-Cresol	8.0	2.5	6.3
33 2-Butoxyethanol	7.0	2.5	6.0
34 Methyl salicylate	9.5	2.5	6.0
35 Aniline	9.5	2.5	6.1
36 Butanol	7.8	2.0	7.1
37 Furfuryl alcohol	8.5	3.2	7.4
38 Triethyl phosphate	8.7	3.0	5.0
39 Diethyl sulfide	9.0	6.0	5.0
40 Pyridine	9.3	4.3	2.9
41 Nitrobenzene	9.5	4.2	2.0
42 Methylene iodide	11.8	1.7	0.5
43 Acetone	7.0	5.1	3.4
44 n-Propanol	7.0	3.3	3.5
45 Iso-butanol	7.7	4.3	9.5
46 Propionitrile	7.5	7.0	2.7
47 2-Furaldehyde	9.1	3.3	2.5
48 Diethyl phthalate	9.0	1.4	1.4
49 Ethyl succinate	9.4	1.4	3.0
50 Ethyl n-propyl alcohol	8.0	3.0	7.2
51 Benzyl alcohol	9.6	3.1	6.2
52 Butyraldehyde	7.1	3.9	4.7
53 Ethyl acetate	7.7	2.1	3.7
54 Tetrahydrofuran	8.2	2.0	3.9
55 Spinoline	10.2	2.7	2.0
56 Methyl iso-butyl ketone	7.5	3.0	2.8
57 Tri-n-butyl phosphate	7.9	1.7	3.0
58 Bromobenzene	9.6	1.1	1.4
59 Diethyl phthalate	8.6	4.7	2.0
60 Diethyl 2-pyrrolidone	8.8	6.0	6.5
61 Cyclohexanone	8.7	4.1	2.5
62 Diethylene triamine	8.7	5.5	6.0
63 Benzyl ether	8.0	1.1	1.0
64 Propylene	8.1	4.0	3.6
65 1,1,1-trichloroethane	8.3	2.7	1.0
66 Diethyl acetamide	8.2	5.6	5.0
67 Methyl acetate	7.0	2.8	5.1
68 Methyl sulfate	7.7	5.9	3.5
69 n-Propanol	7.7	3.0	3.0
70 2-Ethoxyethanol	7.9	4.0	3.0
71 Methyl alcohol	7.9	5.0	3.0
72 Ethylpropylate	7.8	3.0	1.4
73 Ethyl formate	7.8	4.1	4.1
74 Diethyl alcohol	7.7	4.0	3.0
75 Isobutyl isobutyrate	7.4	1.4	2.0
76 Butyl sebacate	6.3	0.9	3.3
77 Isobutanol	7.4	2.0	2.1
78 Methylene chloride	8.9	3.1	2.0
79 n-Butane	7.0	0	0

(a)  $\delta_D$  Dispersive Parameter $\delta_P$  Polar Parameter $\delta_H$  Hydrogen Bonding Parameter



Functional Group	Molar Volume $\Delta V$ cal/mol	Partial Solubility Parameters, cal/mol			Solubility Parameters <sup>(1)</sup>		
		London $\Delta V\delta_D^2$	Polar $\Delta V\delta_P^2$	Electron Transfer $\Delta V\delta_H^2$	London $\delta_D$	Polar $\delta_P$	Electron $\delta_H$
1 CH <sub>3</sub> group	33.5	1125	0	0			
4 CH <sub>2</sub> groups	64.4	4720	0	0			
1  C-OH group	28.5	3350	500	2750			
TOTAL	126.5	9195	500	2760	8.5	1.99	4.66

(1) The Solubility Parameters are calculated by dividing the individual Partial Solubility Parameters by the Molar Volume ( $\Delta V$ ) and then taking the square root. The unit for Solubility Parameter is called a hildebrand  $(\text{cal/mol})^{1/2}$ .

### Catalyst Preparation

For the preparation of homogeneous catalyst formulations, the material was blended during processing in the colloid mill.

### Two Phase Systems

The methods described above were used to prepare two phase systems. In all cases the mixtures of carbon black, surfactant and JP-10, with or without a catalyst, resulted in a two phase dispersion.

### Three Phase Systems

Formulation of a three phase system always started with a two phase dispersion such as described above. This two phase system was then added to the hydrophile containing one or more surfactants. For example, a dispersion containing 50 wt % carbon black in JP-10 was added to Formamide containing surfactants with stirring. Simple mixing was all that was required to form an emulsion.

## b. Evaluation of Formulations

### Rheological Properties

The most significant means of evaluating initial properties of carbon dispersion formulations is to measure rheological properties. Visual observations during preparation provide a qualitative measure of whether the material flows readily or forms a mayonnaise type fluid. For quantitative measurements several instruments and methods were employed. These are listed below.

#### Fann Viscometer

This instrument was used for most rheological determinations. It is a direct reading concentric cylinder type viscometer. A stationary bob and the rotating cylinder are immersed in the liquid contained in a cup. Measurements were generally made at room temperature, but it was also possible to use this instrument for readings at lower or higher temperatures by cooling or heating the sample and measuring cylinders. This instrument is capable of operating over a range of shear rates by simply adjusting a knob to change the speed of the rotating cylinder.

#### Haake Rotovisco

The Rotovisco is a rotating viscometer in which the substance to be measured is introduced into a gap between a rotating and fixed surface. The instrument used had a Couette (cup and bob) system, the gap is a circular one between two coaxial cylinders --one of which is stationary while the other rotates. The viscosity is determined from the resistance (to rotation) caused by the sample material. The factor actually measured is torque. With the Rotovisco, the measuring bob or cone can be rotated at different fixed speeds which permits investigations over a wide shear range. Measurements can also be made at different temperatures by heating or cooling the sample and detecting parts of the instrument.

#### ASTM Methods

For testing of promising formulations ASTM D-1092 was used for measuring viscosity and ASTM D-2884 for yield stress and shear stress.

#### Stability

Static stability was measured by placing a sample in a graduated cylinder or tall bottle and measuring the amount of material which separated out on standing. This was a semiquantitative measure since the amount settled was estimated by probing with a metal spatula and estimating the percentage of solid material which settled as a function of time compared to the total amount present. However, as a preliminary screening procedure this was very useful since the goal was no separation. More severe tests such as shaking, pumping, and centrifugal tests will be utilized in the future for the more promising samples.

### Heat of Combustion

ASTM-D-2040 or 2382 were used for Net Heat of Combustion in Btu/gal. Calculations were also used for predicting Btu values of blends.

### Pour Point

ASTM-D-97 was used for pour point. The significance of this test for measuring the flow properties of systems such as described herein is subject to considerable question. Experience in the petroleum industry indicates that many products will flow below the pour point determined by this method, and conversely some will not flow above the pour point given by this determination. Thus, the results may be used as a general guide, but not as an absolute measure of the flow characteristics of a system. Actual pump tests are the best criteria, and measurement of the yield stress and shear stress by ASTM-D-2884 may prove to be more informative than pour point. Not enough data has been obtained to date on carbon dispersions to resolve this question.

### Nozzle Tests

Spraying through a nozzle is often a critical parameter to measure in systems such as described herein since the shear encountered may cause a serious breakdown of the dispersion and/or emulsion. Tests on nozzles are described in Section III B1 on Combustion Experimental Methods.

### B. Carbon Dispersion Combustion

Development of a viable high density carbon dispersion fuel involves fully understanding its combustion characteristics. Therefore the combustion performance capabilities of the candidate slurry fuels are being considered in detail during the fuel formulation process. Parametric studies of slurry combustion characteristics are underway. Areas being investigated include: 1) combustion and carbon burnout efficiencies as a function of temperature, residence time, and equivalence ratio; 2) the effect of carbon type, particle size and loading on carbon burnout; and 3) the potential for catalytic acceleration of carbon burnout.

During the early stages of the program, where the influence of carbon type, size distribution, and catalytic effects must be evaluated, a small-scale (less than one liter per hour fuel consumption) combustion system is being utilized which provides fundamental carbon oxidation data. This approach has definite advantages at this point in the program: 1) more potential slurry candidates can be inexpensively screened due to the small scale nature of the experiments and 2) small scale equipment can be more easily modified to meet program needs.

The combustor produces results that are meaningful to actual operation in gas turbine or ramjet engines. Experience has shown that the recirculation regions of gas turbine primary zones or the steps of ramjet dump combustors are well mixed in nature and can be simulated by stirred reactors (Appendix B). Regions like the secondary and dilution zones of gas turbine or the centerline flow of a ramjet are highly turbulent, non-recirculating flow, and often analyzed as plug flow zones. The unit designed for this program, the Liquid Fuel Jet Stirred Combustor (LFJSC), incorporates both these features. The LFJSC was designed and constructed during the past year and is now operational. A description of the facility is presented below.

## 1 LFJSC Design

The LFJSC is composed of two sections, a spherical reactor and a cylindrical one (Figures 8,9). The spherical portion of the LFJSC consists of two castable refractory halves housed within a 15.2 cm diameter metal shell. The refractory material is Castable 141A, a product of Combustion Engineering Refractories, capable of withstanding temperatures of up to 1870°C. Each section is cast separately with a 5.1 cm diameter hemisphere -- the two sections together create the spherical reactor zone. The cylindrical plug-flow section is composed of a 7.6 cm long by 2.2 cm diameter alumina tube. Residence times of 2.4 to 6.0 and 1.6 to 4.0 msec, respectively, can be achieved in each section with this design. Scale-down or scale-up could allow expansion of these residence time ranges. Each of the following aspects of the facility will be discussed:

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

### Air Injection

Combustion air enters the spherical reaction zone through two air injectors positioned 180° apart. Each injector consists of four jets. These jets are aimed towards the corners of a cube imagined to sit within the spherical reactor. 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 excellent mixing and simulates the recirculation characteristics of gas turbine systems.

### Fuel Injection

Fuel enters the reactor at two positions 90° from each air injector. The rear fuel nozzle assembly (usually only used for liquid fuel) consists of a 1/4J body, a 0.030 cm fuel cap (Model 1250) and a pressurizing air atomizing cap (Model 67147) all acquired from Spray Systems Co. This pressurizing cap provides for premixing of the fuel with the atomizing gas (air or nitrogen) prior to exiting the nozzle tip. Carbon slurry is introduced into the reactor through the front nozzle.

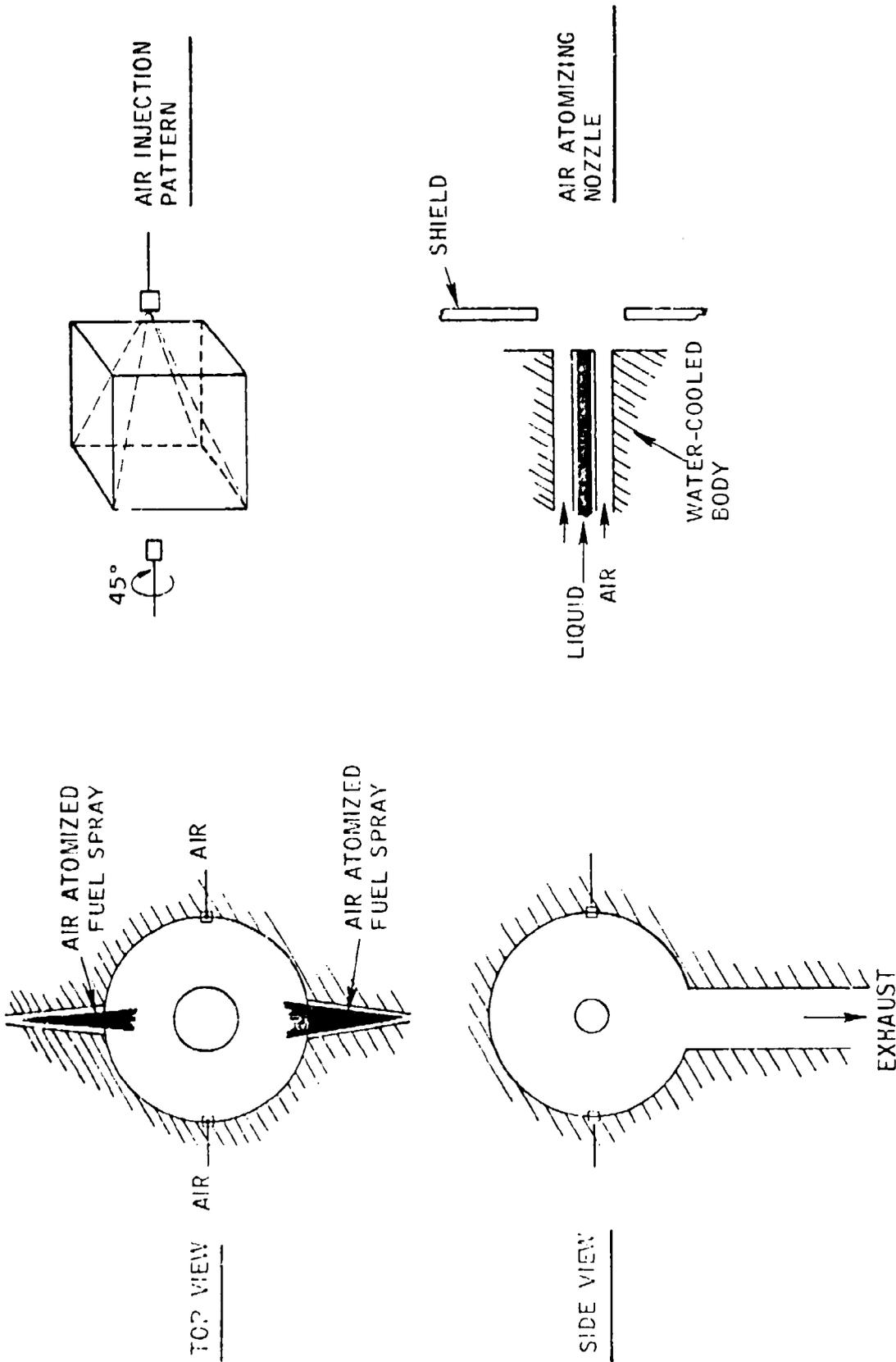


Figure 8. Liquid Fuel Jet Stirred Combustor

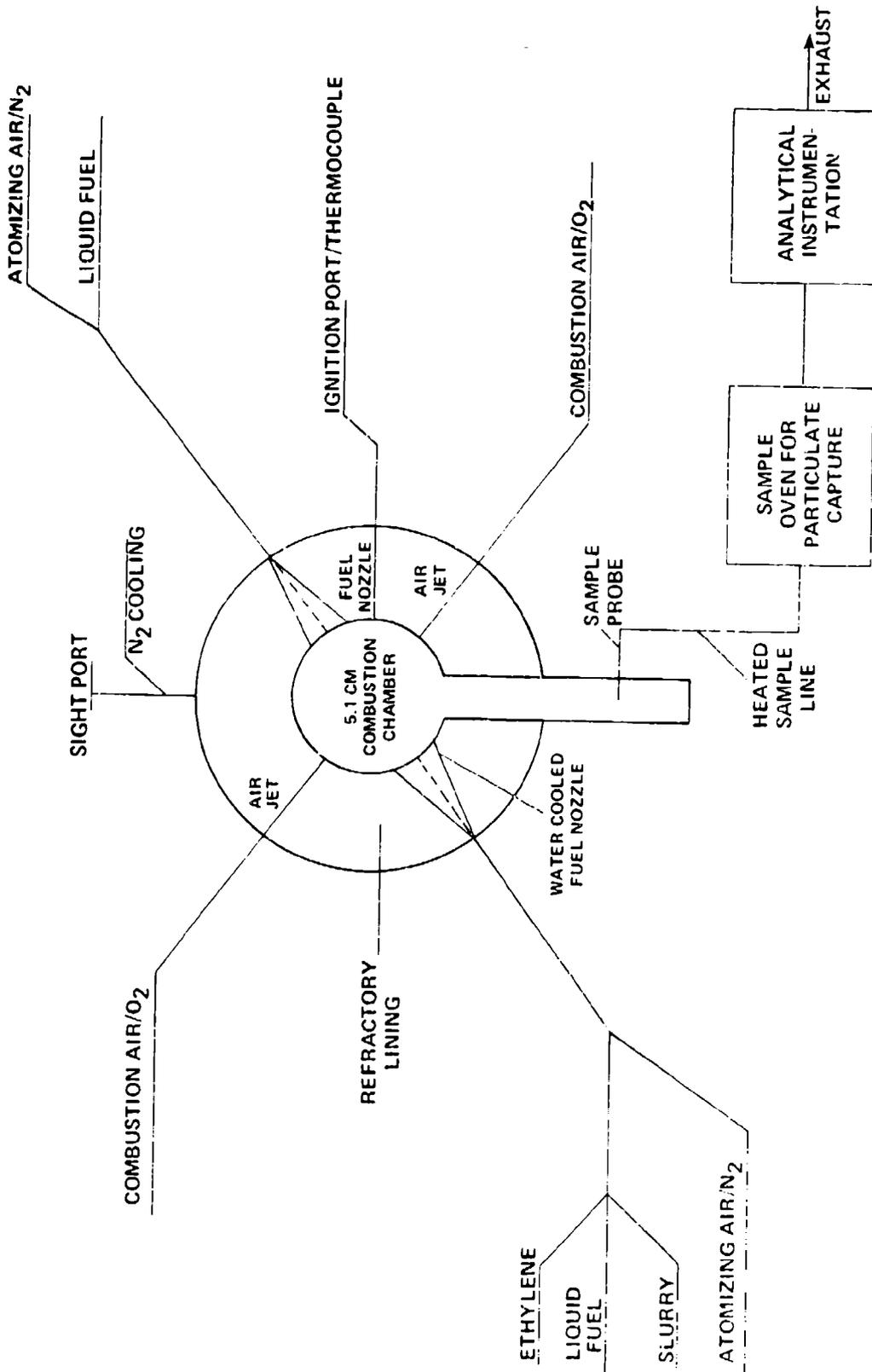


Figure 9. Schematic of Combustion Equipment

The major problem with injecting carbon slurry fuels into a combustor is prevaporization of the hydrocarbon carrier, leaving the carbon behind to plug the nozzle. Several types of commercially available fuel nozzles (Figure 10A-B) were examined with no success. The first attempt at solving the prevaporization problem was to cool the atomizing gas by passing it through a dry ice bath and also to incorporate a radiation shield in front of the nozzle (Fig. 10C). Both of these modifications proved insufficient. Consequently, a specially designed water-cooled nozzle that incorporates specific features needed for successful operation with carbon slurries was developed (Fig. 10D). This nozzle utilizes the basic concept and some similar components of the Spray Systems Co. device, (0.040 cm Model 1650 fuel cap and Model 64 siphon air cap) but provides for cold water cooling of the fuel and atomizing gas up to the point of injection. Initial testing of the slurry using a pressure air cap resulted in internal plugging and it was for this reason that the siphon air cap (no premixing) was utilized in the design. This design also incorporates a cleanout needle which is used to clear any carbon that has deposited on the nozzle tip during the experiment. A later modification was to weld a 0.318 cm stainless steel heat shield to the end of the nozzle (Fig. 8). The purpose of the shield is to protect the nozzle tip from the intense radiation from the combustor (helping to prevent prevaporization) and also to keep any unburnt carbon from depositing directly on the tip. The injector point of the nozzle can be positioned at any distance between the outside of the combustor and the spherical reaction zone. This enables any fuel impingement on the reactor walls to be corrected.

#### Metering of Fuels and Air

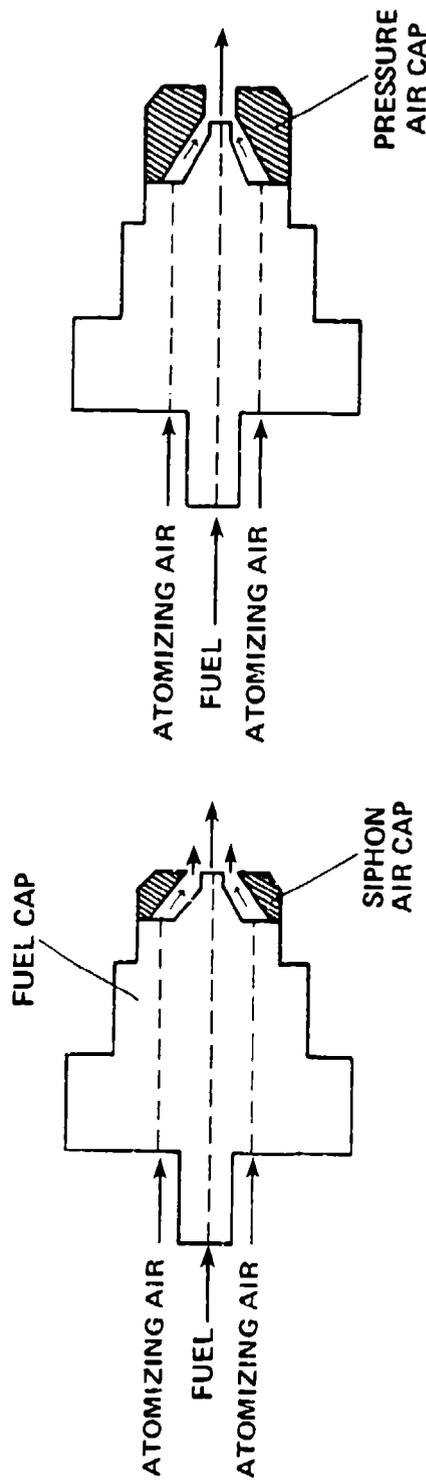
Metering of the combustion air, atomizing gases and liquid fuels is accomplished using calibrated rotameters. A reciprocating piston pump with a pulse dampener (Fluid Metering Inc. Model Nos. RP-G150 and PD-60-LF) is used for metering the carbon slurry since visual observation of the rotameter float is impossible with this fuel.

#### Oxygen Injection

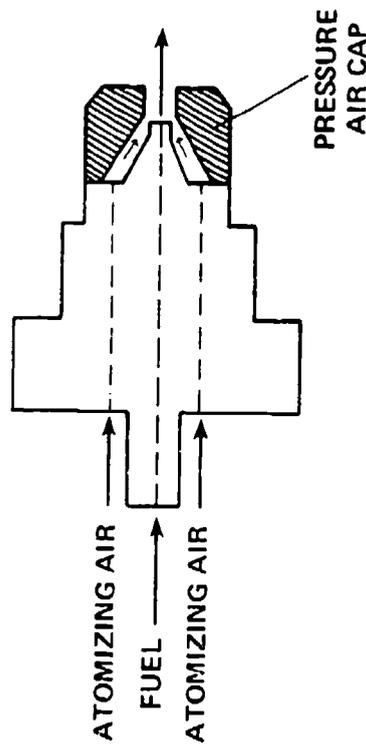
Oxygen can be utilized to increase the combustion temperature at a given equivalence ratio. Its addition to the combustion air reduces the nitrogen content, which is a flame temperature diluent. The oxygen is measured through a calibrated rotameter and then introduced to the air stream prior to its metering. This provides for a uniform air/O<sub>2</sub> mixture.

#### Exhaust System

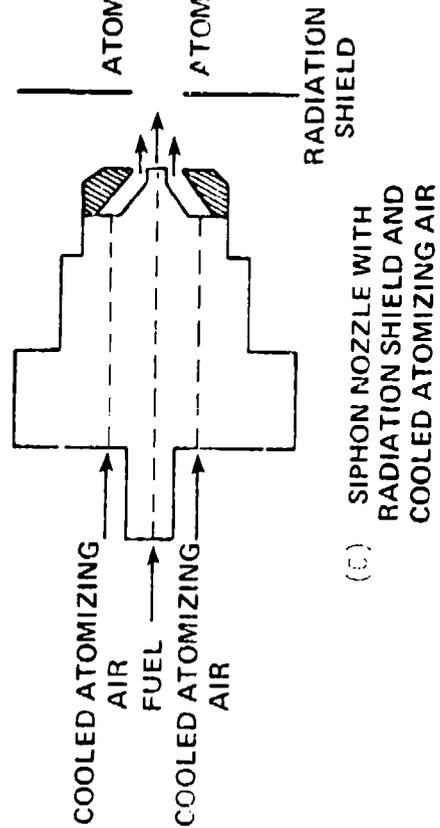
The combustion products exit the well-stirred zone and enter the plug flow region. A small portion of the gas sample is obtained by inserting a probe through the sample port at the base of this section. The remainder of the exhaust stream passes through a water cooled heat exchanger. Additional cooling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



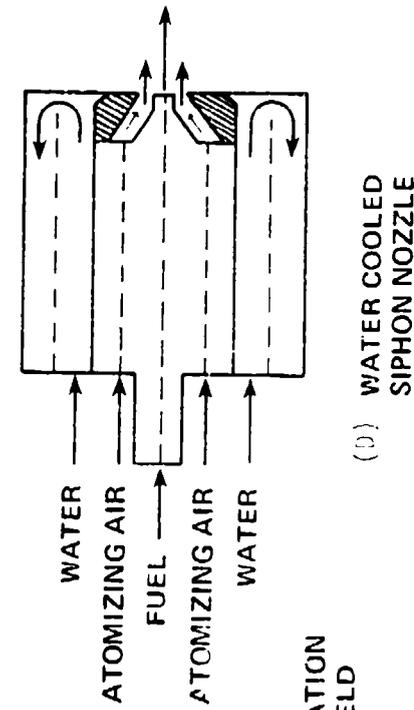
(A) SIPHON NOZZLE



(B) PRESSURE NOZZLE



(C) SIPHON NOZZLE WITH RADIATION SHIELD AND COOLED ATOMIZING AIR



(D) WATER COOLED SIPHON NOZZLE

Figure 10. Fuel Nozzles

## Temperature Measurement/Sight Port

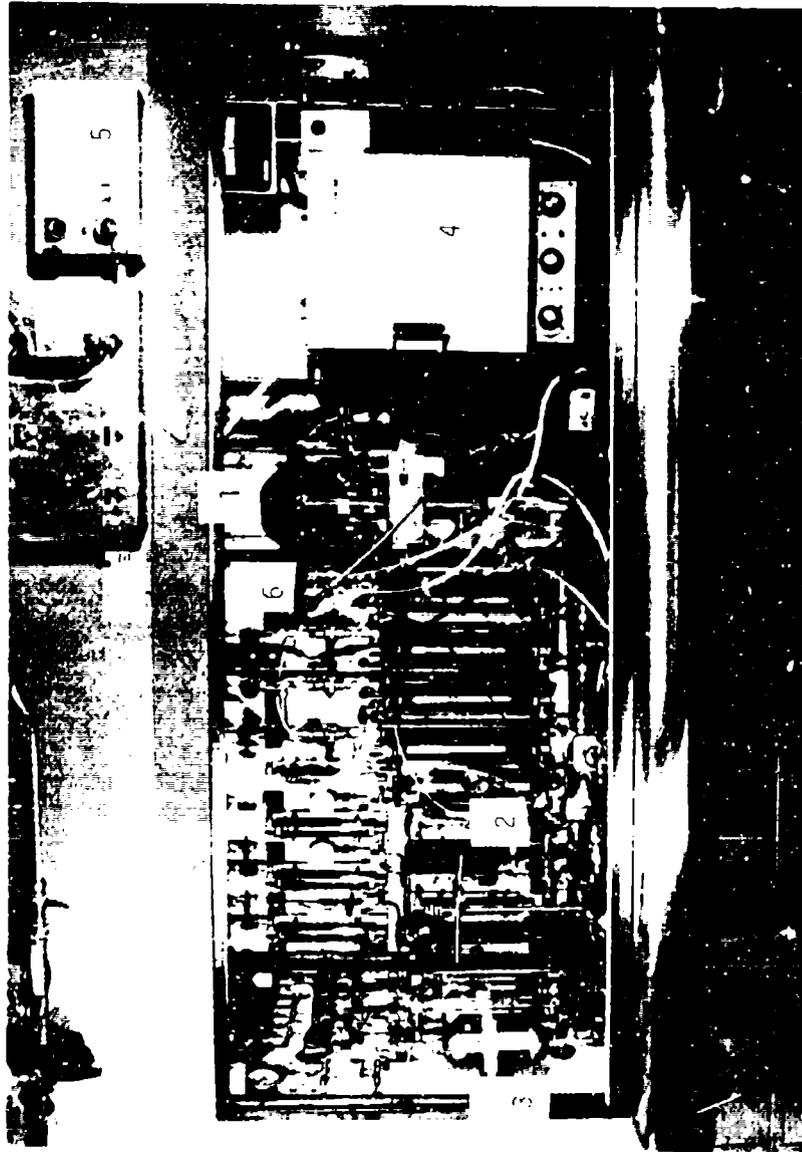
Temperature within the reactor is measured by utilizing a Type B (platinum-6% rhodium/platinum-30% rhodium) thermocouple which enters the combustor through the ignition port. Addition of thermocouples in several key locations (inside the refractory and on the outer shell) is planned for the future. These will enable the refractory temperature gradient and heat losses to be calculated. A nitrogen-cooled sight port, positioned in the front of the reactor, provides optical access inside the reactor. An overall view of the LFJSC is shown in Figure 11.

## 2 Combustion Product Sampling

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

Gas analysis is accomplished with conventional process instrumentation. Particulates are first removed from the gases by passing the exhaust stream through a 90 mm Gellman Type AE glass fiber filter located within the oven. One sample gas stream leaving the sample conditioning system is chilled to eliminate condensable water (to a dew point of about 10°C) and hydrocarbons prior to introduction into Non-dispersive Infrared (NDIR) analyzers for CO and CO<sub>2</sub>, a electrolytic analyzer for O<sub>2</sub>, and a gas chromatograph for H<sub>2</sub> measurements. The NDIR analyzers are both Beckman Model 864 instruments with the maximum CO range being 10 mole percent and the maximum CO<sub>2</sub> range being 20 mole percent. The oxygen analyzer is a Beckman Model 77C and has a maximum range of 25 mole percent. The gas chromatograph is a Carle Model 8706-A which utilizes a three column separation technique (silica gel and molecular sieves). A second unchilled stream leaving the oven is transferred through electrically heated lines (maintained at approximately 150°C) to a Beckman Model 402 Flame Ionization analyzer for total hydrocarbon (THC) measurement. The reported THC results are measured "as methane."

The particulate sampling system uses different filters located within the sample-conditioning oven. Two 47 mm filters sealed in a stainless steel holder were used in "series." The first was a Millipore Mitex (Teflon) filter with a 5 μm pore size; the second was a Gellman Type AE with a 0.3 μm pore size. The Teflon filter was necessary to prevent the glass fiber material from sticking to the Viton O-ring sealing the filter holder. Nearly all the soot collected in the experiments was found on the first (Teflon) filter. Any soot that was deposited at the probe top was blown out onto a Gellman filter by introducing a N<sub>2</sub> back flow through the probe. This additional weight was then added to the soot measurement already obtained from the sample oven filter to determine an overall value.



LEGEND

1. Combustor
2. Slurry Fuel System
3. Liquid Fuel System
4. Sample Oven
5. Safety Alarm System
6. Water Cooled Nozzle

Figure 11. Overall View of Liquid Fuel Jet Stirred Combustor Facility

### 3 Operating Procedure

The LFJSC has the capability of operating on gaseous, liquid, or carbon slurry fuels. A gaseous fuel, such as ethylene, is utilized for daily start-up of the reactor and is fed through the front nozzle. It is ignited by a flame from a small propane torch which enters the combustor through the ignition port. Once the ethylene has ignited and the flame is self-sustaining, the propane torch is shut off. Next, the ethylene and combustion air flow rates are gradually increased until the combustor temperature reaches 1300°C. This phase of heat-up takes approximately one hour. Next atomizing gas (air or nitrogen) is introduced into the combustor through the rear fuel nozzle. At the same time, the ethylene and combustion air rates are adjusted to maintain a constant temperature of 1300°C. When the desired atomizing gas rate is achieved, liquid fuel flow to the rear nozzle is started.

Once the combustor is operating smoothly on both fuels, the ethylene flow is decreased, while the liquid rate is increased in order to maintain a constant temperature. This continues until the ethylene flow is completely off. At this point the atomizing gas (air or N<sub>2</sub>) is started to the front nozzle. When the proper rate is established, liquid fuel to this nozzle is introduced. Experimental conditions (i.e. temperature, equivalence ratio, and residence time) are first established operating the LFJSC on liquid fuel. After steady-state conditions are reached, the carbon slurry test fuel is injected through the front nozzle. In most cases the rear nozzle continues to operate on liquid fuel, providing continuous combustion if difficulties occur with the slurry. The combustor can also be operated with carbon slurry alone.

### 4 Data Reduction

A data reduction computer program was developed to calculate carbon burnout and overall combustion efficiencies, equivalence ratio, residence time and percent material balances of carbon and oxygen. These parameters are defined as follows:

Carbon burnout efficiency:

$$NCB = \left( 1 - \frac{\text{Mass of unburnt carbon (soot) in exhaust stream}}{\text{Mass of carbon in slurry}^*} \right) \times 100 \quad [6]$$

\*Includes only carbon added to liquid hydrocarbon fuel

Combustion efficiency:

$$NC = \left( 1 - \frac{\text{Unreleased energy in flue gas resulting from incomplete combustion of fuel to CO, HC, H}_2 \text{ and carbon}}{\text{Total Energy Input}} \right) \times 100 \quad [7]$$

Equivalence Ratio:

$$\phi = \frac{\text{Fuel to Oxidant Ratio at Experimental Conditions}}{\text{Fuel to Oxidant Ratio at Stoichiometric Conditions}} \quad [8]$$

$\phi > 1$  for fuel-rich conditions;  $\phi < 1$  for fuel-lean conditions

Residence Time:

$$\tau = \frac{\text{Reactor Volume}}{\text{Total Volumetric Flow Rate Corrected to Absolute Combustion Temperature}} \quad [9]$$

Percent Material Balance (PMB) of Species (I) [10]

$$\text{PMB} = \left( 1 - \frac{\text{Mole species (I) from flow rates} - \text{moles species I from flue gas analysis}}{\text{Mole species (I) from flow rates}} \right) \times 100$$

PMB < 100.0 -- Flow rate moles greater than flue gas moles for species (I)

PMB = 100.0 -- Flow rate moles equal to flue gas moles for species (I)

PMB > 100.0 -- Flow rate moles less than flue gas moles for species (I)

Figure 12 is an example of the output from the computer program. Experimental run conditions, such as combustion temperature, mass flow rates of JP-10, carbon slurry, atomizing gas (air or nitrogen), combustion air, oxygen, and nitrogen are inputted into the computer program and summarized on the data output sheet. Additional inputs include: JP-10 and slurry elemental weight composition, slurry carbon loading, fuel heating values, gas phase emissions analysis and unburnt carbon (soot) measurement.

The computer program calculates carbon and oxygen percent material balances to check the consistency of the measured fuel and total oxygen rates using equation 10. Total oxygen is defined as the sum of the oxygen mass rate plus the oxygen present in the air mass rate. The stoichiometric fuel to oxidant ratio is calculated for both JP-10 and the carbon slurry based on their respective elemental weight composition. The equation is as follows:

$$\left( \frac{\text{Grams fuel}}{\text{Grams oxygen}} \right)_{\text{Stoichiometric}} = \frac{3}{8 \text{ WC} + 24 \text{ WH} + 3 \text{ WS} - 3 \text{ WO}} \quad [11]$$

Where WC, WH, WS, WO are fuel weight fraction of carbon, hydrogen, sulfur, and oxygen

The respective fuel to oxygen ratios are calculated by dividing the fuel rate by the total oxidant flow rate. Equivalence ratios based on mass feed rates are determined by using equation 9. In addition, the fuel to oxygen ratio and equivalence ratio based on flue gas species concentrations are calculated using the following equation:

$$\text{Value Based on Flue Gas} = \text{Value Based on Mass Flow Rates} \times \left( \frac{\text{Carbon \% Material Balance}}{\text{Oxygen \% Material Balance}} \right) \quad [12]$$

DATE : OCT 2, 1979  
 RUN NUMBER: 100-A

FRONT FUEL: STATER MT 308  
 REAR FUEL: JP-10

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 312.0  
 REAR FUEL 534.0

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 10044.0  
 REAR FUEL 9436.9

CARBON MATERIAL BALANCE  
 96.9

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 4098.0  
 REAR COMBUSTION AIR 4098.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 3137.1

OXYGEN MATERIAL BALANCE  
 101.4

NITROGEN FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC  
 FUEL TO OXIDANT RATIO  
 F FUEL 0.322  
 R FUEL 0.304

BASED ON MASS FEED RATES  
 FUEL TO OXIDANT RATIO  
 F FUEL 0.099  
 R FUEL 0.170  
 OVERALL 0.270

BASED ON FLUE GAS ANALYSIS  
 FUEL TO OXIDANT RATIO  
 F FUEL 0.31  
 R FUEL 0.56  
 OVERALL 0.87

TOTAL GM-MOLFS/HR  
 422.4

LEFT FLUE GAS ANALYSIS (MOLE PERCENT)  
 CO 0.37  
 CO2 14.03  
 HC 0.0007  
 NO 0.0  
 NOX 0.0  
 O2 4.04  
 O3 0.0

SOOT MEASUREMENT (GRAMS/HR)  
 H2 0.0146  
 H2O 10.48  
 3.8

COMBUSTION TEMPERATURE (K)  
 1953.1 ± 5.0

RESIDENCE TIME (MILLISEC)  
 6.3

EFFICIENCIES  
 CARBON BURNOUT 96.0  
 COMBUSTION 98.1

Figure 12. Liquid Fuel Jet Stirred Combustor Data Output

These two values give an indication of the actual operating mixture conditions. During extremely fuel-rich operations (equivalence ratio greater than 1.4) the CO concentration may exceed the maximum range of the analytical instrument (10%). If this occurs, the computer program utilizes the carbon balance to calculate the CO concentration. In this case, a consistency check between flow rates and gas analysis is not valid. Therefore the message "Not Applicable" is printed for the material balance value.

Calibration equations for the non-linear NDIR CO and CO<sub>2</sub> analyzers were incorporated into the program. This enables the gas concentrations (CO and CO<sub>2</sub>) to be directly calculated from the instrument range and scale reading inputs. In addition, the program employs an iterative approach to calculate simultaneously the water content in the exhaust stream and the total moles of flue gas produced during the combustion process. The iteration begins by assuming values for these two parameters. First, by using the assumed value for the moles of flue gas and a hydrogen material balance (i.e. moles hydrogen from fuel rates = moles hydrogen in the flue gas), the computer program iterates until the calculated water mole fraction equals the assumed value. Once this calculation has converged, the nitrogen mole fraction is calculated (i.e. 1 - sum of all other mole fractions in exhaust stream). Next the flue gas moles are calculated using a nitrogen balance and the nitrogen mole fraction. If the calculated value equals the assumed value, the entire iteration has converged. However, if these two values are not equal, then the latest calculated values for the water mole fraction and moles flue gas become the next assumed values and the entire procedure begins once again. Knowledge of the water concentration was necessary to convert the emissions measurements (with the exception of hydrocarbons) back to a wet basis. As previously noted these measurements were taken after water removal to a dew point of 10°C. A more detailed mathematical explanation of the iterative procedure is provided in Appendix D.

The addition of thermocouples to measure the refractory temperature gradient will enable the reactor heat losses by conduction and convection, along with the inside reactor temperature (based on the flue gas analysis) to be determined. These calculations will be incorporated into the present computer program as soon as the modifications to the combustor are made.

### C. Limited Systems Study

The complexity of an advanced missile system makes it imperative that consideration of a change in fuel properties and/or combustion characteristics requires an analysis of their potential impacts on the remainder of the system. To address this problem adequately, a team of three subcontractors was assembled, as noted in the introduction, to provide guidance during the course of this program. These subcontractors along with ER&E have the following as their major goals.

A limited study of range improvement achievable in the trade-off between fuel properties and fuel delivery and combustion penalties.

Recommendation of fuel characterization test methods to be utilized during this program.

Establishment of fuel evaluation criteria.

The approach planned for accomplishing these objectives is to meet periodically to discuss the carbon dispersion formulation and combustion properties to enable consideration of their suitability for planned cruise missile engines and airframe designs. Properties of carbon dispersion fuels could have a number of possible impacts which need to be considered such as:

- Fuel tank drainage
- Fuel filtering
- Fuel handling and control devices
- Fuel lubricity
- Pump priming, capacity and power requirements
- Fuel heat exchange capacity
- Fuel ignition and flameout properties
- Techniques/procedures for starting engine
- Fuel injection/atomization systems
- Fuel flameholder devices
- Fuel stability
- Combustor design and materials of construction

The subcontractors were initially provided with anticipated properties of carbon dispersions and later in the program actual laboratory data will be furnished for their consideration of any design or operating procedures which may require changes.

## SECTION IV

### RESULTS

The results reported in this section are summarized in the discussion, tables and figures which follow. Some of the data on formulation has been classified and is included in Part II of this Report. Thus, this section contains coded information on the composition of classified formulations to permit presentation of the data in unclassified form. The results are presented in sections which follow dealing separately with work on formulations and combustion. None of the combustion data has been classified.

#### A. Formulation

As indicated in the previous section the formulation of a useful high density carbon containing fuel should take into consideration the nature of the carbon black, selection of dispersants, method of mixing, two vs three phase systems and ultimately their resultant properties. The results obtained during the initial year of effort on this program are presented below.

##### 1 Carbon Black Selection

A range of carbon black sizes were selected for evaluation varying in size from the smallest available (13 m $\mu$ ) to large sized blacks (300 m $\mu$ ). The properties of the materials selected are given in Table 9. Initially tests were run on a number of different carbon blacks but it was decided to concentrate our detailed studies on Monarch 1300, Sterling R and Statex MT. These were selected because they represent a range of 14 m $\mu$ , 75 m $\mu$  and 300 m $\mu$  sizes. Initial tests on 20-30% formulations indicated the smallest size carbon blacks produced very high viscosity materials which could not expect to be useful. The effect of particle size on viscosity of formulations of similar types of carbon blacks in JP-10 is given in Table 10 and plotted in Figure 13. These data show a significant effect of particle size to about 75 m $\mu$  but little above that size with formulations containing 30 wt % of carbon black. The carbon blacks below 50 m $\mu$  produce very high viscosity formulations. Table 11, which shows the complete data on typical formulations prepared, indicates that blends of small carbon black materials over 30 wt % could not be made fluid enough and had viscosities well over 1000 cp. Much of our effort was concentrated on formulations of Statex MT (300 m $\mu$  size) since this material appeared to offer a reasonable compromise between particle size and other properties of formulation and combustion. Carbon blacks with particle sizes between 75 and 300 m $\mu$  will be obtained for evaluation in future studies.

##### 2 Selection of Dispersants

###### Initial Screening

Based on discussions with internal experts and our consultants eleven different dispersants were used in our initial screening tests at one or more concentrations with a variety of carbon blacks. (See Table 11.)

TABLE 9  
 PROPERTIES OF CARBON BLACKS SELECTED FOR EVALUATION

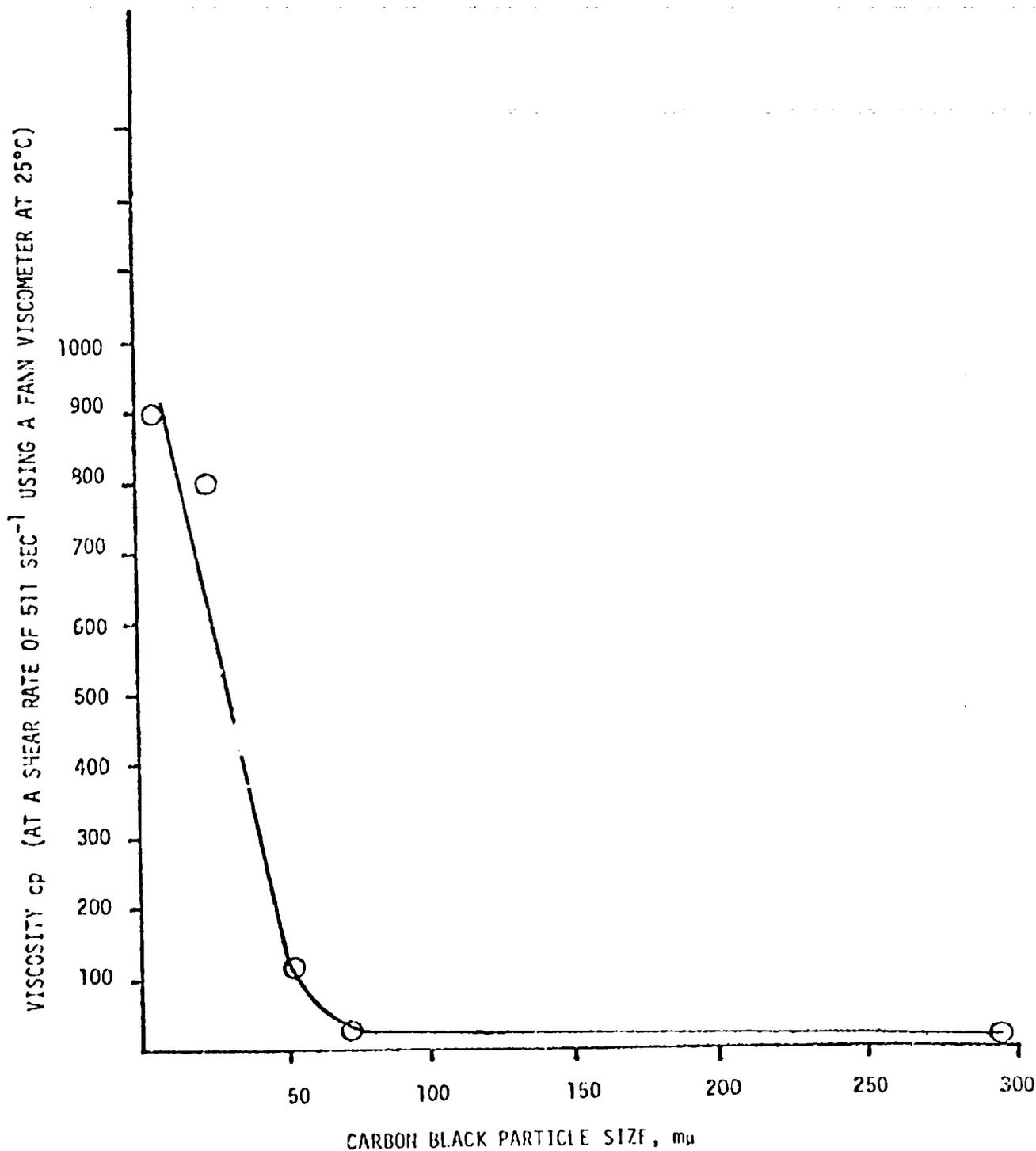
Designation	Supplier	Form	Basic Size $\mu$ y.	Type	Surface Area, Sq. meters/gm.	Gil (DBP) Absorption cc/100 gms.	Volatile Content %	Fixed Carbon %	pH	Apparent Density lbs/cu ft
Monarch 1300	Cabot Corp.	Fluffy	13	Furnace	560	121	9.5	90.5	3.3	18
"	"	Pellets	13	"	"	105	"	"	"	25
Monarch 1100	"	Fluffy	14	"	240	65	2.0	99.0	7.0	15
"	"	Pellets	14	"	"	50	"	"	"	30
Regal 330 R	"	Fluffy	25	"	94	62	1.0	99.0	8.5	19
Regal 330	"	Pellets	25	"	"	70	"	"	"	28
Sterling R	"	Fluffy	75	"	25	71	1.0	99.0	8.5	16
Sterling MS	"	Pellets	75	"	25	70	"	"	"	31
Vulcan 3	"	Pellets	28	"	-	103	2.5	-	-	24
Vulcan 6	"	Pellets	24	"	-	114	2.5	-	-	22
Vulcan 9	"	Pellets	19	"	-	114	3.0	-	-	22
Raven 410	Cities Service Co.	Fluffy	70	"	23	70	0.3	99.7	9.0	17
Raven 410	"	Pellets	70	"	23	70	0.3	99.7	9.0	29
Raven 500	"	Fluffy	54	"	33	75	1.2	98.8	7.0	17
Raven 500	"	Pellets	54	"	33	75	1.2	98.8	7.0	26
Raven 1000	"	Fluffy	29	"	96	61	2.0	98.0	7.0	12
Raven 1000	"	Pellets	29	"	36	61	2.0	98.0	7.0	23
Statex NT	"	Pellets	300	Thermal	10	35	-	-	-	-

TABLE 10

PROPERTIES OF TYPICAL CARBON BLACK FORMULATIONS SHOWING THE EFFECT  
OF PARTICLE SIZE AND CONCENTRATION ON VISCOSITY(1), cp at 23°C

Basic Carbon Black Particle Size, m $\mu$	14	75	300
Concentration in JP-10	Viscosity at Room Temperature(1) cp		
15	11	-	-
20	32.5	9	6
25	108	-	-
30	901	32	12
40		81	17
50			42
60			159
65			234
68			435

(1) Using a Fann Viscometer and a shear rate of 511 sec<sup>-1</sup>



All formulations contained 5 wt % Surfactant A

Figure 13. Viscosity of Carbon Black Formulations (30 wt %) in JP-10 as a function of Particle Size

TABLE 11

## EVALUATION OF DISPERSING AGENTS IN CARBON BLACK FORMULATIONS

Dispersant Used Code No.	Conc., Wt %	Carbon Black Used		Method of Mixing	Viscosity at Room Temp., cp	Appearance
		Type	Conc., Wt %			
A	5	Monarch 1100	15	Colloid Mill	11	Good
A	5	Monarch 1100	20	Waring Blender	18.5/30/12.5/ 17.5/29.0	Good
A	5	"	20	Colloid Mill	31	"
A	5	"	25	"	131/96/96	"
A	5	"	30	Waring Blender	901	Very thick
A	5	Regal 330	30	"	800	"
A	5	Raven 500	30	"	128	Good
A	5	Sterling R	20	"	8.0/9.5	"
A	5	Sterling R	30	"	30.5/36.5/27.5/ 33/28	Good
A	5	"	40	"	78/87	"
A	5	Vulcan 3	30	"	964	Very thick
A	5	Vulcan 6	30	"	2539	"
A	5	Vulcan 9	30	"	1714	"
A	5	Statex MT	20	Colloid Mill	5.5	Very Good
A	5	Statex MT	30	Colloid Mill	11.0/15/24/17 9/0/8.5/10.0/12.5	Good
		"	30	Waring Blender	14	Good
A	5	"	40	Colloid Mill	16.5	"
A	5	"	50	"	39/36.5/49	"
A	2.5	"	50	"	39	"
A	5	"	60	"	87/215/173/ 172.5	"
A	5	"	65	"	203/265	"
A	5	"	68	"	435	Thick

TABLE 11 (CONTD)

Code	Dispersant Used		Carbon Black Used		Method of Mixing	Viscosity at Rot. emp., CP	Appearance
	No.	Conc., Wt. %	Type	Conc., Wt. %			
B	5		Monarch 1100	20	Waring Blender	23	Good
B	5		Statex MT	50	" "	33.5	Good
B	2		" "	60	Colloid Mill	51	"
B	5		" "	60	" "	63.5	"
B	2		" "	65	" "	110	"
B	2		" "	69	" "	Too thick	No Good
C	5		Monarch 1100	20	Waring Blender	18.5	Good
C	5		Statex MT	50	" "	44.0	Good
D	5		Statex MT	30	" "	14.0	Good
E	5		" "	30	" "	11.5	Good
F	5		" "	30	" "	34.0	"
G	5		" "	30	" "	9.5	"
G	5		" "	50	" "	55/54	"
G	2.5		" "	50	" "	50	"
H	2.2		Monarch 1100	63.5	Hobart Mixer	-	Dry
H	2.2		Statex MT	63.5	" "	-	Thick Paste
H	2.2		Raven 410	63.5	" "	-	Grainy
H	2.2		Raven 500	63.5	" "	-	Dry
H	2.2		Raven 1000	63.5	" "	-	Dry
I	5		Monarch 1100	20	Waring Blender	23	Good
J	5		Statex MT	30	" "	8.5	"
J	5		" "	50	" "	30.5/34.5	"
J	2.5		" "	50	" "	25.0	"
K	5		Statex MT	30	" "	9.5	"

1 These codes are identified in Part II (Classified) of this report  
 2 Replicated values are shown which were run on different batches of these formulations  
 (All measurements made using the Fann viscometer generally at a shear rate of 511 sec<sup>-1</sup>)

TABLE 11 (CONTD)

Code No.	Dispersant Used		Carbon Black Used		Method of Mixing	Viscosity at (2)		Appearance
	Conc., Wt %	Type	Conc., Wt %	Room Temp., cp		Room Temp., cp		
B	5	Monarch 1100	20	Waring Blender	23		Good	
B	5	Statex MT	50	"	33.5		Good	
B	2	"	60	Colloid Mill	51		"	
B	5	"	60	"	63.5		"	
B	2	"	65	"	110		"	
B	2	"	69	"	Too thick		No Good	
C	5	Monarch 1100	20	Waring Blender	18.5		Good	
C	5	Statex MT	50	"	44.0		Good	
D	5	Statex MT	30	"	14.0		Good	
E	5	"	30	"	11.5		Good	
F	5	"	30	"	34.0		"	
G	5	"	30	"	9.5		"	
G	5	"	50	"	55/54		"	
G	2.5	"	50	"	50		"	
H	2.2	Monarch 1100	63.5	Hobart Mixer	-		Dry	
H	2.2	Statex MT	63.5	"	-		Thick Paste	
H	2.2	Raven 410	63.5	"	-		Grainy	
H	2.2	Raven 500	63.5	"	-		Dry	
H	2.2	Raven 1000	63.5	"	-		Dry	
I	5	Monarch 1100	20	Waring Blender	23		Good	
J	5	Statex MT	30	"	8.5		"	
J	5	"	50	"	30.5/34.5		"	
J	2.5	"	50	"	25.0		"	
K	5	Statex MT	30	"	9.5		"	

- 1 These codes are identified in Part II (Classified) of this report
- 2 Replicated values are shown which were run on different batches of these formulations (All measurements made using the Fann Viscometer generally at a shear rate of 511 sec<sup>-1</sup>)

Most formulations were prepared initially using a concentration of five (5) wt % dispersant, and those that appeared promising were evaluated at lower concentrations. A complete list of the materials evaluated as dispersants is given in Part II which gives these materials in code. The choice of surfactants to study further was based upon measurement of the viscosity, appearance and stability of finished formulations. The most significant property for initial screening is viscosity, the lower the more effective the dispersant. A review of this data in Table 11 indicates the most promising dispersants are A, B, C, D, E, G and K. For initial screening purposes dispersant A was used. In later work other materials were evaluated in some detail as will be discussed below.

#### Selection by Solubility Parameter Measurements

This method has been described previously (Section III A 1 and 2); the experimental data and results are given in this section. The three carbon blacks, Monarch 1100, Sterling R and Statex MT were evaluated for dispersibility by mixing with the selected reference liquids (Table 7). Dispersion values for each mixture are given in Table 12. The individual values for Statex MT and Sterling R were plotted according to the methods of Hansen (5,6) and Panzer (22) and are shown in Part II. A brief summary of this method is provided in Appendix C. The dispersion values for Monarch 1100 gave a plot which appears to show a mixture of carbon blacks with differing activity.

The solubility parameters for Statex MT and Sterling R and their significance are given in Part II (Classified). This procedure has enabled identification of chemical structures which should be the optimum dispersing agents for these two carbon blacks. However, since these results have only recently been obtained it has not been possible to obtain the compounds identified and evaluate them in formulations.

### 3 Evaluation of Preparation Techniques

Several types of mixers have been evaluated and the results on each follow:

#### Stirrers

Low speed stirrers such as hand mixing, laboratory stirrers and a Hobart mixer (bread or cake type mixer) have proven satisfactory for preliminary mixing of carbon blacks with JP-10 and dispersing agents. Such mixtures separate rapidly when agitation is stopped, and their appearance is nonhomogeneous.

#### High Speed Mixers

A Waring Blender has been successfully used to prepare relatively low viscosity formulations. For preliminary evaluation of small batches a Waring Blender is a useful tool. One disadvantage of this type mixer is the tendency for air entrapment. It was noted that after mixing for one or two minutes, many formulations tended to jell due to air entrapment causing a deep vortex and inefficient mixing. However, on standing the air dissipates resulting in a significant drop in viscosity and more efficient mixing.

TABLE 12

## SOLUBILITY PARAMETER DATA FOR CARBON BLACKS

Reference Liquid	Cohesive Energy Density Parameter, Hildebrand			Dispersion Parameter		
	$\delta_D$	$\delta_P$	$\delta_H$	Stated MT	Monarch 1100	Sterling R
1 Hexane	7.3	0	0	2.035	6.165	5.265
2 Octane	7.6	0	0	2.035	5.685	5.24
3 Dodecane	7.8	0	0	1.87	5.195	5.13
4 Hexadecane	8.0	0	0	1.97	4.105	4.77
5 CCl <sub>4</sub>	8.7	0	0.3	1.965	6.42	6.82
6 Carbon disulfide	10.0	0	0.3	2.325	5.07	5.48
7 Diethylamine	7.3	1.1	3.0	2.17	4.58	4.43
8 Isobutylacetate	7.4	1.8	3.1	--	--	--
9 Cyclohexylamine	8.5	1.5	3.2	1.70	3.875	4.35
10 Anisole	8.7	2.0	3.3	2.365	4.85	5.05
11 Bromoform	10.6	1.5	0.6	3.105	6.455	4.43
12 Dipropylamine	7.5	0.7	2.0	1.83	4.76	4.75
13 o-xylene	8.7	0.5	1.5	1.955	4.82	5.05
14 Chlorobenzene	9.3	2.1	1.0	2.26	5.24	5.78
15 $\alpha$ Bromonaphthalene	10.5	1.2	1.0	2.07	--	6.06
16 Diethylene glycol	7.9	7.2	10.0	1.795	5.09	3.95
17 2 Aminocethanol	8.4	7.6	10.4	1.82	12.34	10.28
18 Formamide	8.4	12.8	9.3	2.055	6.42	4.82
19 Water	7.6	7.8	20.7	1.58	6.965	4.24
20 Acrylonitrile	6.9	7.8	2.8	1.995	5.865	4.41
21 Nitroethane	7.8	7.6	2.2	2.205	6.12	4.13
22 Nitromethane	7.9	9.2	2.5	2.20	4.55	4.78
23 Acetonitrile	7.5	8.3	3.0	2.45	5.58	4.98
24 Propylene carbonate	9.8	8.8	2.0	1.98	5.97	4.47
25 Butyronitrile	7.5	6.1	2.5	2.675	5.61	4.47
26 Nitropropane	7.9	5.9	2.0	2.545	3.75	4.47
27 Methanol	7.4	6.0	10.9	2.025	5.83	5.29
28 Ethylene glycol	8.3	5.4	12.7	1.79	4.635	5.29
29 Glycerol	8.5	5.9	14.3	1.84	4.45	5.78
30 2 Ethylbutanol	7.7	2.1	6.6	1.955	4.91	5.78
31 Cyclohexanol	8.5	2.0	6.6	1.665	4.565	5.78
32 m-Cresol	8.8	2.5	6.3	1.77	4.165	5.78
33 2 Butoxyethanol	7.8	2.5	6.0	2.185	5.51	5.78
34 Methyl salicylate	9.5	2.6	6.0	2.355	4.74	5.78
35 Aniline	9.5	2.5	5.0	2.12	4.475	5.78

TABLE 12 (CONTD.)

## SOLUBILITY PARAMETER DATA FOR CARBON BLACKS

Reference Liquid	Cohesive Energy Density Parameter, Hildebrand			Dispersion Parameter		F = $\frac{\text{vol of dispersed carbon, cc}}{\text{wt of carbon black, gm}}$
	$\delta_D$	$\delta_P$	$\delta_H$	Statex MT	Monarch 1100	
36 Butanol	7.8	2.8	7.7	2.225	5.6	5.22
37 Furfuryl alcohol	8.5	3.7	7.4	2.04	4.84	
38 Trimethyl phosphate	8.2	7.8	5.0	1.60	5.57	5.36
39 Dimethyl sulfoxide	9.0	8.0	5.0	1.395	5.005	
40 Pyridine	9.3	4.3	2.9	1.955	4.835	5.47
41 Nitrobenzene	9.8	4.2	2.0	2.2	4.235	
42 Methylene iodide	11.8	1.7	0.5	3.13	3.72	4.73
43 Acetone	7.6	5.1	3.4	2.745	5.825	
44 n propanol	7.8	3.3	8.5	2.21	5.83	4.94
45 100% ethanol	7.7	4.3	9.5	2.395	5.635	4.54
46 Propionitrile	7.5	7.0	2.7	2.545	5.055	
47 2 furaldehyde	9.1	7.3	2.5	2.785	4.695	
48 Dibutyl phthalate	8.8	1.4	3.4	1.73	5.04	4.83
49 Ethyl cinnamate	9.4	1.4	3.6	1.885	5.02	
50 1 chloro-2 propanol	8.6	2.8	7.2	2.325	5.41	5.03
51 Benzyl alcohol	9.0	3.1	6.7	2.425	5.17	
52 Butyraldehyde	7.1	3.9	4.2	2.35	3.67	4.56
53 Ethyl acetate	7.7	2.6	3.5	2.48	5.7	
54 Tetrahydrofuran	8.2	2.8	3.9	2.74	4.88	5.17
55 Quinoline	10.2	2.7	2.0	1.66	4.66	
56 Methyl iso-butyl ketone	7.5	3.0	2.0	2.395	4.99	4.86
57 Tri (-n butyl) phosphate	7.9	1.7	3.0	1.655	5.35	
58 Bromobenzene	9.6	1.8	1.4	2.80	5.76	6.04
59 Diethyl phthalate	8.6	4.7	2.2	1.725	--	
60 N methyl 2 pyrrolidone	8.8	6.0	3.5	1.415	4.92	
61 Cyclohexanone	8.7	4.1	2.5	1.95	4.50	4.60
62 Diethylene triamine	8.2	5.5	6.0	2.17	4.55	
63 Benzyl ether	9.0	1.8	1.6	1.75	4.67	
64 Isophorone	8.1	4.0	3.6	1.695	3.52	4.52
65 1,1,1 trichloroethane	8.3	2.1	1.0	1.995	5.78	
66 Dimethyl acetamide	8.2	5.6	5.0	1.495	5.40	4.38
67 Methyl acetate	7.6	2.8	5.1	2.30	5.81	
68 Diethyl sulfate	7.7	5.3	3.5	1.57	5.22	5.62
69 2 propanol	7.7	3.0	8.0	2.045	6.02	

TABLE 12 (CONTD.)

## SOLUBILITY PARAMETER DATA FOR CARBON BLACKS

Reference Liquid	Cohesive Energy Density Parameter, Hildebrand			Dispersion Parameter	
	$\delta_D$	$\delta_P$	$\delta_H$	$F = \frac{\text{vol of dispersed carbon, cc}}{\text{wt of carbon black, gm}}$	
				Statex MT	Monarch 1100 Sterling R
70 2 methoxyethanol	7.9	4.5	8.0	2.37	5.13
71 Allyl alcohol	7.9	5.3	8.2	2.385	4.56
72 1 chloropropane	7.8	2.9	1.4	2.34	5.74
73 Ethyl formate	7.6	4.1	4.1	2.345	5.58
74 Diacetone alcohol	7.7	4.0	5.3	1.94	5.28
75 Isobutyl isobutyrate	7.4	1.4	2.9	1.94	4.81
76 Butyl sebacate	8.3	0.9	3.4	1.85	5.04
77 Isobutanol	7.4	2.8	7.8	1.93	5.72
78 Methylene chloride	8.9	3.1	3.0	2.44	5.49
79 1-octane	7.0	0	0	1.87	6.09

## Colloid Mill

The Greerco Colloid Mill proved a versatile tool for preparation of most carbon black formulations. Mixtures containing up to nearly seventy (70) wt % carbon black were successfully prepared. Some difficulties were encountered in circulating very thick systems in this mill, but for practical purposes this is not a problem since such thick formulations would probably not be useful. Air entrapment was not a problem, but the speed of mixing was regulated and baffles used to minimize such difficulties.

## Roll Mill

A three roll mill was evaluated as a means of reducing the viscosity of high concentration carbon black formulations. The results varied with different formulations, and excessive milling resulted in a viscosity increase as shown in Table 13. Based on these results it appears that one or two passes through the roll mill can be beneficial in reducing viscosity, but the same benefits can be obtained by proper choice of dispersing agents and preparation in a colloid mill. The differences between the formulations designated #697-84-2 and #697-153-2 [noted in Table 13] is in the type of surfactant used. The latter formulation could not be improved by further processing in a roll mill, whereas the formulations of #697-84-2 Batches 3 and 4 responded well. The reasons for the differences in behavior have not been determined but the following may be postulated.

1. The decrease in viscosity resulted from improved mixing and more uniform dispersion of the particles.
2. The increased viscosity is caused by the shearing action of the roll mill upon the carbon agglomerates resulting in a smaller average particle size. The smaller the particle size, the higher the viscosity (see Figure 13 above).

Some tests were also run on higher concentration (65-70 wt %) formulations, but these could not be processed satisfactorily on the mill. The reasons for this are not fully understood, but it was observed these high concentration formulations had a very strong affinity for metal surfaces and stuck to the rolls. In addition, there appeared to be a loss of JP-10 probably caused by local overheating due to the high shear even though the rolls of the mill are water cooled.

## Ball Mill

Ball milling appeared to provide some reduction in viscosity of carbon dispersions in JP-10. For example, using a blend containing 60 wt % carbon black (300 m $\mu$ ) with an initial viscosity of 54 cp, by ball milling for 60 minutes the viscosity was reduced to 47.5 cp. While this reduction is of some benefit the roll mill or longer milling on a colloid mill is preferred to achieve the same results. Ball milling is a time-consuming, batch operation which is not generally a desirable process for such systems.

TABLE 13

## EFFECT OF ROLL MILLING ON VISCOSITY OF CARBON DISPERSION (1)

Blend No.	Carbon Black		Viscosity, cp <sup>(2)</sup>		Viscosity after Passing thru the Roll Mill, cp			
	Type	Conc., Wt %	Initial		1 time	2 times	3 times	4 times
697-84-2 (Batch 4)	Statex MT	60	173			102	112	
697-84-2 (Batch 3)	"	60	174				101	113
697-153-2	"	60	110		183			

(1) Test formulations were made initially in a colloid mill and subsequently passed through the roll mill.

(2) Using a Fann Viscometer at room temperature (23°C) and a shear rate of 511 sec<sup>-1</sup>.

## 4 Formulation Characteristics

Carbon dispersions prepared to date have been evaluated mainly by their rheological and stability characteristics. Other tests have been run on a few selected blends. The results obtained are given below.

### Viscosity Increases with Carbon Loading

Data on the viscosity (as measured by a Fann Viscometer) versus percent carbon in JP-10 (from Table 10) are plotted in Figure 14 for three different sized carbon blacks. These data show a nearly linear relationship from 20-50 wt % carbon and then the viscosity increases rapidly above 50 wt % for the largest sized carbon black tested (300 m $\mu$ ). The smaller blacks produce a much more rapid increase. Another plot of these data is given in Figure 15 for the largest sized carbon black which shows the log of viscosity to be a linear function of the weight percent in JP-10.

### Viscosity Variation with Temperature

Preliminary experiments have been run on several high concentration carbon black formulations to determine the viscosity change with temperature in the range of (20 to -50°C). Figure 16 shows data on several formulations containing 60 wt % of carbon black. The data were plotted on standard ASTM Viscosity Temperature Charts (D-341). Based on these preliminary data surfactant type and concentration appear to be significant. Upon extrapolation to -51.1°C (-60°F) there would seem to be an advantage for the higher concentration of surfactant B at the lower temperature range. This is an interesting phenomenon and needs further study. Actual viscosity data at lower temperatures will be run in the future. The extrapolated values for the best formulation gave a viscosity at -51.1°C (-60°F) of about 560 cSt (733 cp).

### Rheology of Carbon Black Formulations

The rheological properties of several carbon black formulations have been characterized in preliminary tests to get an indication of the nature of their flow properties. These tests were run on the Fann Viscometer which is capable of operating over a shear rate of about 180 to 510 sec<sup>-1</sup> with a shear stress for these systems ranging from about 100 to 1400 dynes/cm<sup>2</sup>. Typical flow curves for four important flow models: (A) Newtonian, (B) Bingham Plastic, (C) Pseudoplastic and (D) Dilatent are given in Figure 17. Data on formulations of different size carbon blacks are given in Figure 18. These data indicate the large carbon black formulations (Sterling R and Statex Mt) are essentially Newtonian and the small carbon black blend (25 wt % Monarch 1100) shows Dilatent flow. The rheological properties of these systems need to be studied in further detail by more sophisticated techniques before a final judgment is made on their flow properties.

### Stability

Static stability of formulations has been tested to obtain a preliminary evaluation of the tendency for carbon black and oil to separate. Typical data are given in Table 14. As might be expected

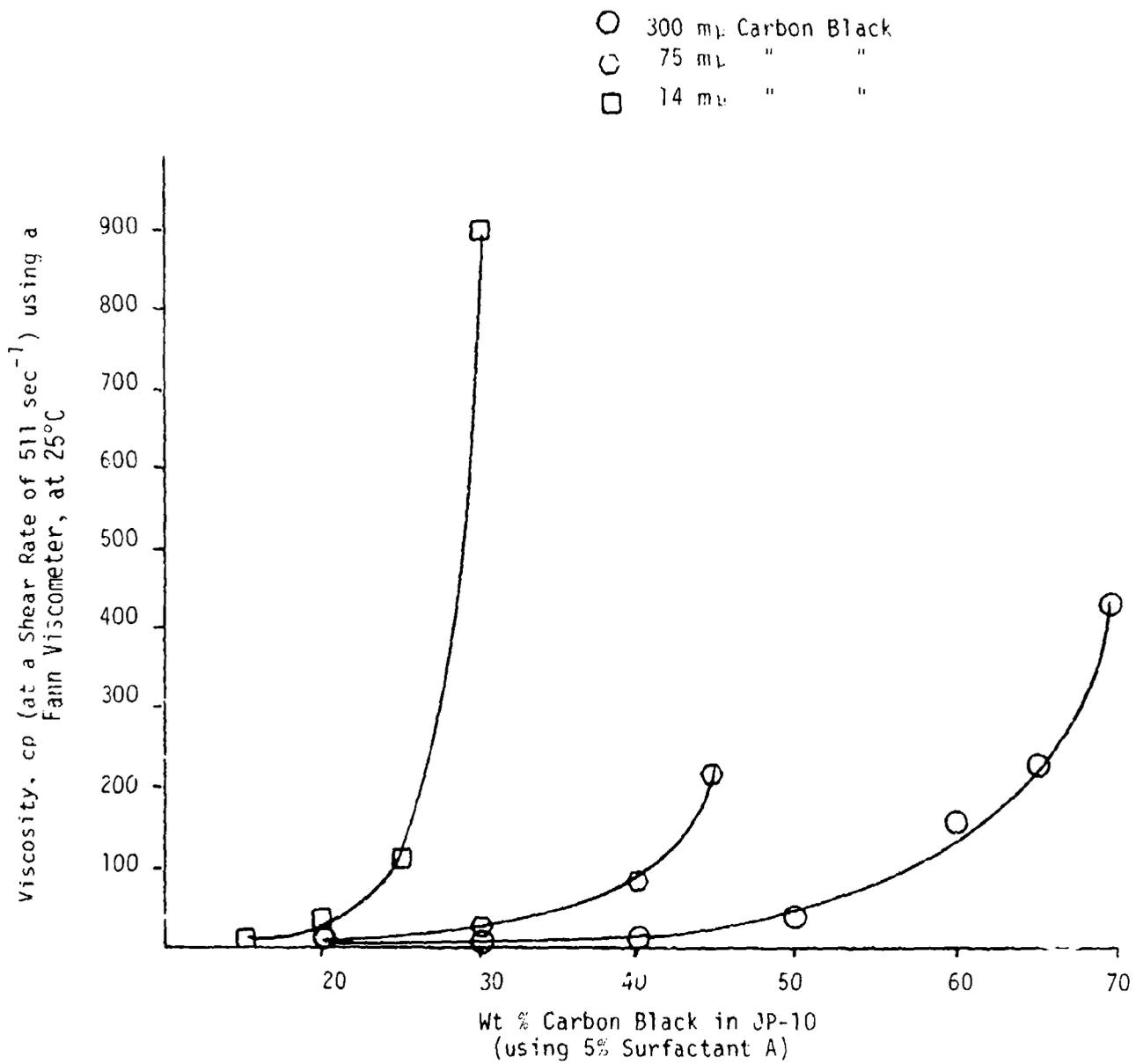


Figure 14. Effect of Carbon Loading on Formulation Viscosity

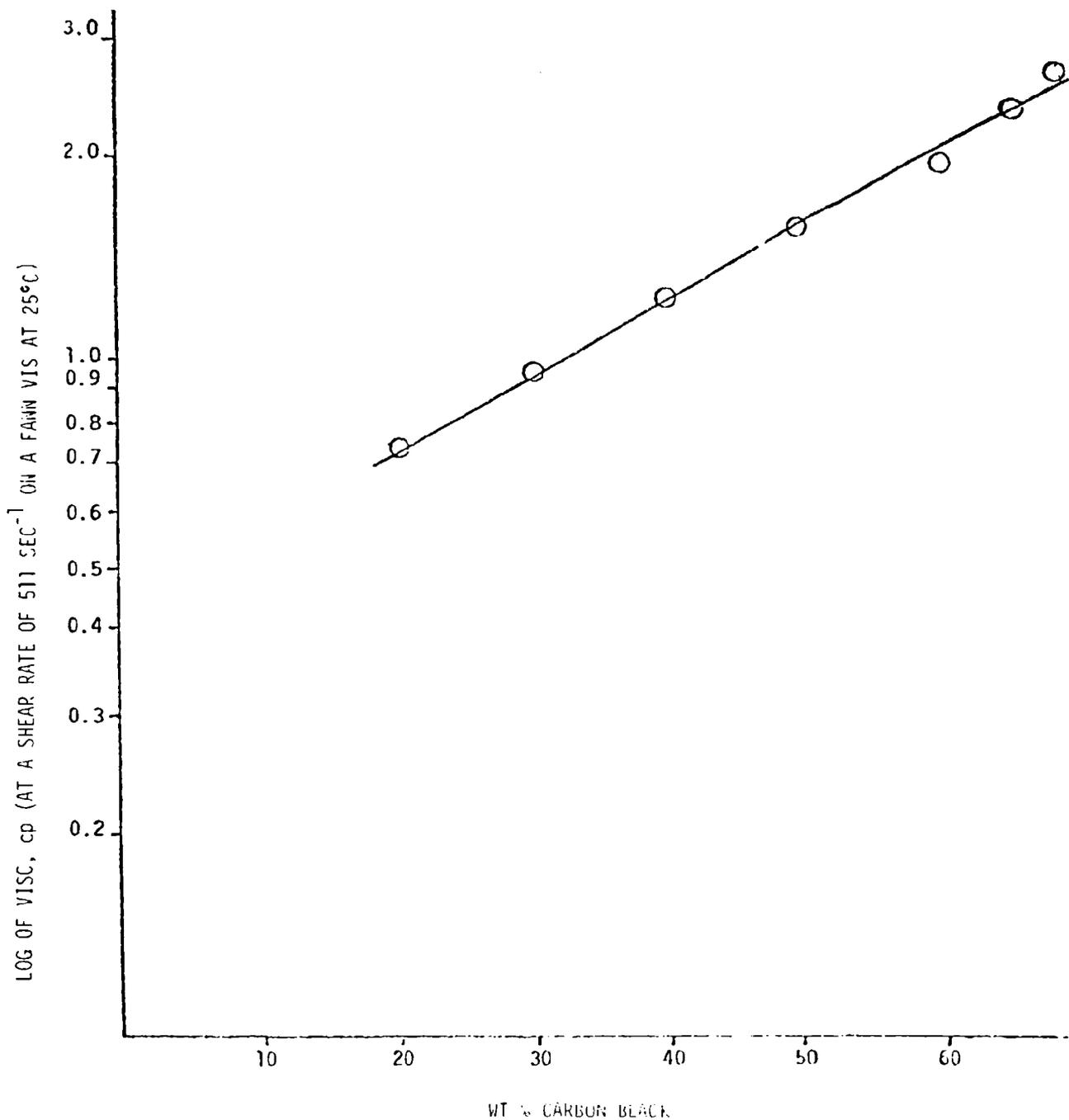


Figure 15. Viscosity of Formulations in JP-10 vs Carbon Black Loading (300 m $\mu$  Basic Particle Size Carbon Black Formulations Containing 5 wt % Surfactant A)

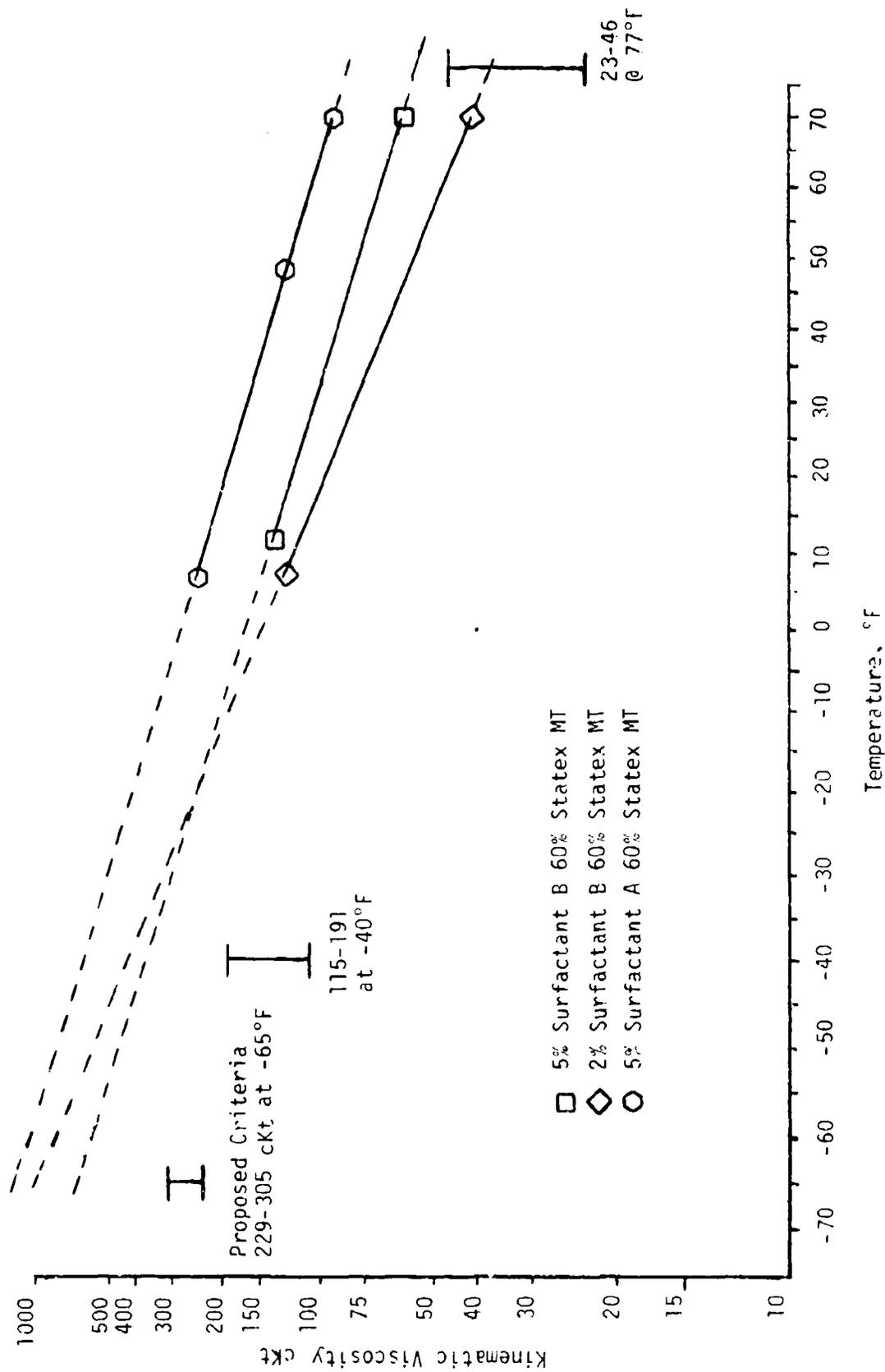


Figure 16. Viscosity-Temperature Curves for Carbon Dispersions  
(Plotted on ASTM Standard Viscosity-Temperature Chart  
for Liquid Petroleum Products, D-341)

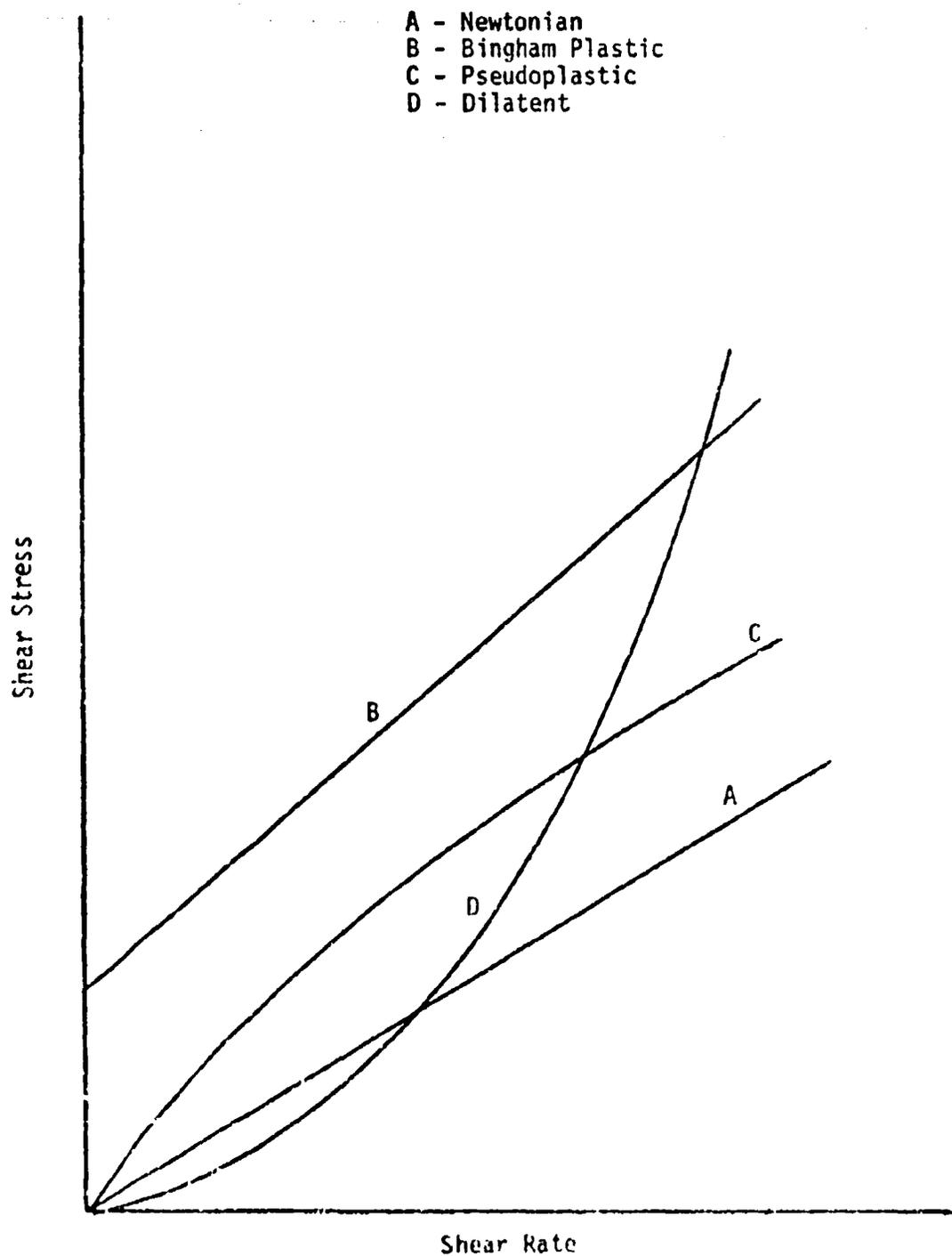


Figure 17. Typical Flow Curves for Four Important Flow Models.

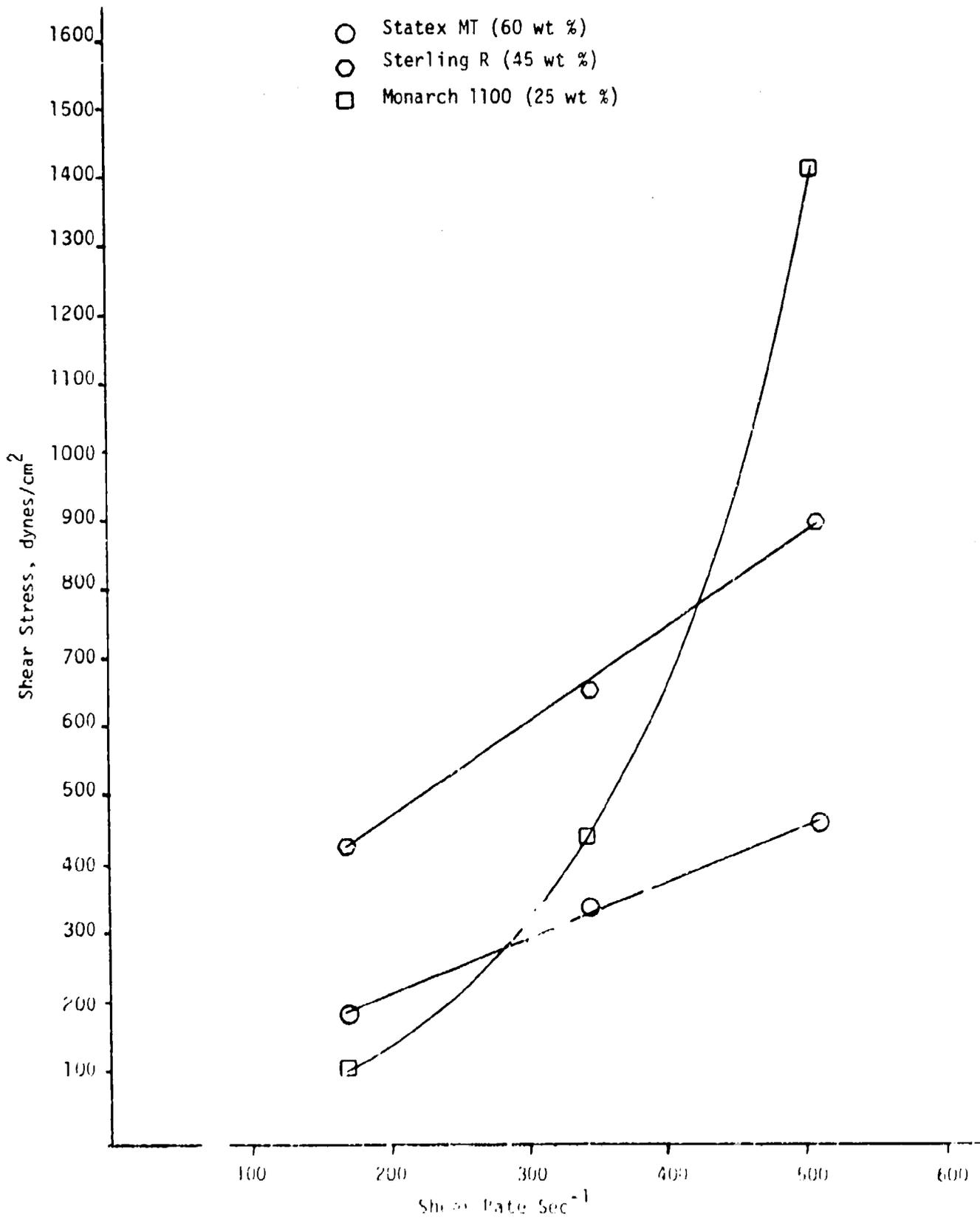


Figure 2. Rheological Properties of Carbon Black Formulations.

TABLE 14

## STATIC STABILITY OF TYPICAL CARBON BLACK FORMULATIONS (AT ROOM TEMPERATURE)

Basic Carbon Black Particle Size, $\mu$	14			75			300					
	20	30	40	20	30	40	20	30	40	50	60	65
Concentration in JP-10 with 5 Wt % Surfactant A	0	0	0	0	0	0	0	0	0	0	0	0
Volume Percent Carbon Black Separated After												
1 day	0	0	0	0	0	0	0	0	0	0	0	0
1 week	0	0	0	3(1)	0	0	4(2)	6(2)	6(1)	0	0	0
1 month	0	0	0	0	0	0	4(2)	6-(2) 10	6(1)	0	0	0
2 months	0	0	0	(Some oil)	0	0	0	0	0	0	0	0
3 months	0	0	0	0	0	0	0	0	0	0	0	0
4 months	0	0	0	0	0	0	0	0	0	0	0	0
5 months	0	0	0	0	0	0	0	0	0	0	0	0
6 months	0	0	0	0	0	0	0	0	0	0	0	0

(1) Difficult to redisperse on shaking.  
 (2) Easily redispersed on shaking.

the small particle size carbon black formulations tend to be stable with little or no settling of carbon black in the time period tested (up to 5 months). However, some oil separation was noted. With the largest size carbon black, the low concentration materials tend to separate out rapidly but as the concentration is increased the stability also increases. These observations are typical Stokes law phenomenon, and thus the higher viscosity formulations (small size or high concentration compositions) may be expected to be stable. Under longer storage times and more severe test conditions (temperature cycling and dynamic testing) it is expected more formulations would tend to separate. As noted in Table 14 even the material which separated out in some cases was readily redispersed with mild agitation.

#### Solubility Parameter Determinations

The test results on the three carbon blacks evaluated by this technique were given in Table 12. The F values were then plotted by the previously noted method of Hansen and centroid coordinates obtained. These plots, centroid coordinates, and interpretations of these data are given in Part II of this report (Classified). The materials identified in Part II for two of the carbon blacks are, according to this approach, the best dispersants for the respective carbon blacks. Plotting the data for Monarch 1100 has not yet resulted in a clear-cut selection of centroid coordinates and is currently being examined further. Not all substances are amenable to this type analysis and it may not be possible to interpret the Monarch 1100 data. This may not be a serious loss since Monarch 1100 would be extremely difficult to formulate at high concentrations even using this approach because of its very small particle size and resulting high viscosity of formulations even at 20-25 wt % in JP-10.

The surfactants identified for Statex MT and Sterling R are on order and have not yet been tested in laboratory formulations.

#### 5 Three Phase Emulsion Systems

Preparation of a three phase emulsion system containing carbon black in JP-10 as an internal two phase mixture and a hydrophile as the external third phase has been described in Section III A. This type of system requires proper selection of dispersants and emulsifying agents to connect the various interfaces noted in Figure 7. Our laboratory efforts to prepare a three phase system started prior to completion of solubility parameter measurements and thus the HLB method was used in an attempt to select the proper surfactants. In addition, the methods and formulations provided in the Exxon Patent (U.S. #3,732,084, Ref. 10) were utilized.

From this latter work it was determined that a combination of surfactants with an HLB (Hydrophilic/Lipophilic Balance scale developed by Atlas Chemical Industries Division of ICI) value of 12 was optimum for emulsifying a dispersion of carbon dispersed in JP-4 with formamide plus water. Since the current system of interest is somewhat different we explored surfactants above and below HLB 12 in an attempt to identify a satisfactory system. We initially evaluated JP-10 alone and then progressed to JP-10 carbon dispersion systems. These experiments are summarized below for several different hydrophiles (i.e., water and formamide).

The procedure used was to titrate the JP-10 (with or without carbon) into a specified weight (50 gms) of hydrophile with stirring. Various surfactant combinations were evaluated. The system was tested after each addition of 50 gms JP-10 (w or w/o carbon black) to determine whether it was an oil-in-water (O/W) or water-in-oil (W/O) emulsion (by adding a drop separately both to water and oil in a vial and noting whether it was soluble or insoluble). In addition, the higher concentration O/W emulsions were tested for viscosity. The results for the systems tested follow.

#### Emulsions of JP-10

This is the simplest system and the results shown in Table 15 indicate that O/W emulsions were formed over a range of HLB values from 6-10. (The HLB materials used are commercially available blends of surfactants.)

TABLE 15  
TEST RESULTS IN EMULSIFICATION OF JP-10  
IN SEVERAL HYDROPHILES

Surfactant added to Hydrophile at 5 wt %	O/W Emulsion Formed in Hydrophiles					
	Water			Formamide		
	6 HLB	8 HLB	10 HLB	6 HLB	8 HLB	10 HLB
65	Yes	Yes	Yes	Yes	Yes	Yes
72.2	"	"	"	"	"	"
75	"	"	"	"	"	"

#### Emulsions of JP-10 Containing Surfactant A

This is the system in which most of the carbon black formulations have been made. Table 16 gives the results of emulsification trials using formamide as the hydrophile. Successful emulsion formulations were made containing up to 86 wt % of the lipophile (JP-10 with surfactant A) in formamide with HLB 10-16. The HLB 8 surfactant system inverted to a W/O emulsion at the 86% level. Viscosities are shown for the highest concentrations made and range from a low of about 100 cp for the HLB 10 to 150-200 cp for the other surfactants. These results indicate an HLB range of 10-12 appears optimum.

#### Emulsions of JP-10 with Carbon Black

Initial trials were made with a 30 wt % Statex MI formulation in JP-10 as shown in Table 17. These results indicate a shift in HLB requirement to about HLB 16 from the optimum of 10-12 for the JP-10 system without carbon black. The maximum concentration for an O/W emulsion was 86% by weight with a viscosity of 81 cp at room temperature (26°C).

TABLE 16

TEST RESULTS ON EMULSIFICATION OF JP-10 CONTAINING SURFACTANT A

Lipophile		JP-10 WITH 5% SURFACTANT A										
Hydrophile		-----FORMAMIDE-----										
Surfactant Added to Hydrophile (5 wt %)	Wt % Lipophile Added	HLB-8	HLB-10	HLB-12	HLB-13	HLB-14	HLB-16	HLB-8	HLB-10	HLB-12	HLB-13	
		O/W Emul.	O/W Emul.	O/W Emul.	O/W Emul.	O/W Emul.	O/W Emul.	O/W Emul.	O/W Emul.	O/W Emul.	O/W Emul.	O/W Emul.
67		Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
83		" (104) <sup>1</sup>	"	"	"	"	"	"	"	"	"	"
86		No	" (99)	" (164)	" (205)	" (205)	" (170)	"	"	"	"	"

1. Viscosity, in cp, of this blend using a Fann Viscometer R-1, B-1, F-1 at 300 RPM at 26°C, shear rate of 511 sec<sup>-1</sup>.

TABLE 17

TEST RESULTS ON EMULSIFICATION OF JP-10 CONTAINING  
30% STATEX MT AND SURFACTANT A

Lipophile JP-10 WITH 30 WT % STATEX MT AND 5 WT % SURFACTANT A  
 Hydrophile -----FORMAMIDE-----

Surfactant Added to Hydrophile (5 wt %)	HLB-6	HLB-14	HLB-16
Wt % Lipophile Added	<u>O/W Emul.</u>	<u>O/W Emul.</u>	<u>O/W Emul.</u>
67	Yes	Yes	Yes
75	No	Yes	Yes
80	"	" <sup>1</sup> (90)	"
83	"	No	"
86	"	No	(81)

1. Viscosity, in cp, of this blend using a Fann Viscometer, R-1,  
B-1, F-1 at 300 RPM @ 26°C, shear rate 511 sec<sup>-1</sup>.

## High Concentration Carbon Black/JP-10 Emulsions

Table 18 summarizes the laboratory results and shows that the maximum concentration achieved was an emulsion of a 60% Statex MT dispersed in JP-10 at the 80 wt % level in 20 wt % formamide and surfactants. This final emulsion contains nearly 50 wt % carbon black in the total formulation. The viscosity of this highest concentration formulation was 107 cp using HLB 14 as the emulsifier and Surfactant A as the dispersant. The other data indicate that HLB 14 appears to be optimum for emulsifying these systems.

These results are not optimized formulations and further formulation and testing of such systems is currently underway.

### B. Combustion

Work during the first year included developing the Liquid Fuel Jet Stirred Combustor and studying carbon burnout as a function of

- Equivalence Ratio
- Residence Time
- Catalyst Type and Concentration
- Carbon Loading
- Particle Size

Each of these areas is discussed in detail below.

#### 1 Liquid Fuel Jet Stirred Combustor Development

During the past year the Liquid Fuel Jet Stirred Combustor (LFJSC) has been conceptually designed, constructed, and is now operational. The combustor design employs features from stirred-combustor devices which have been utilized by Essenhigh at Ohio State to study pulverized coal combustion and by Putnam at Battelle Columbus Laboratories to study gaseous fuel combustion stability. Discussions with each of these individuals proved helpful in developing the LFJSC and their assistance is greatly appreciated.

Prior to the initial start-up of the LFJSC, a shakedown of the facility was conducted during January and February. It was during this period that all the individual pieces of equipment and subsystems were extensively tested and necessary modifications made to the system. Once the shakedown phase was completed, an internal safety inspection of the facility was conducted. The unit, having successfully passed this inspection, was then ready for initial start-up in March.

Ethylene was used for initial combustion tests since it is an easy fuel to combust. No complications resulted during the ignition or combustion of this fuel. After this phase of testing was completed, attention of the next few months was focused on operating the reactor on liquid and then finally on carbon slurry. The unique requirements for combusting carbon slurries have led to the development of a water-cooled fuel nozzle. In most experiments, slurry was only combusted through the front nozzle while JP-10 was introduced through the rear

TABLE 18  
 TEST RESULTS ON EMULSIFICATION OF STATEX MT DISPERSED IN JP-10  
 USING FORMAMIDE AS THE HYDROPHILE

Lipophile	Blend 82-3 40% Statex MT in JP-10			Blend 84-1 50% Statex MT in JP-10			Blend 84-2 60% Statex MT in JP-10			Blend 84-4 65% Statex MT in JP-10		
	HLB-12	HLB-14	HLB-16	HLB-12	HLB-14	HLB-16	HLB-14	HLB-16	HLB-14	HLB-16	HLB-14	HLB-16
Surfactant Added to Hydrophile (5 wt%)												
Wt Lipophile Added to Hydrophile												
67	Yes	Yes	Yes									
75	46	68.5	-	75	71	45	36	46.5	No	-	-	206
80	44	121	44.5	No	91	116	107	164.5	-	-	-	No
83	No	210	No	49	168	No	No	No	-	-	-	No
88	No	-	-	-	No	-	-	-	-	-	-	-

Farr Viscoseter, F-1, B-1, F-1 at 300 RPM at 26°C

nozzle. Successful combustion of a 30% carbon slurry for continuous periods of over three hours has been achieved while operating in this manner. In addition, the LFJSC has also operated on slurry alone (no JP-10 flow through the rear nozzle) for a period of about 30 minutes during September and October.

## 2 Experimental Results

Combustion experimentation during the first year has focused on studying carbon burnout as a function of equivalence ratio, residence time, catalyst type and concentration, carbon loading, and particle size. Complete data computer printouts are given in Appendix D.

Prior to obtaining the above data, tests were conducted with a Statex MT 30% carbon slurry (300  $\mu$  basic particle size) to verify that carbon burnout efficiency at a constant equivalence ratio was independent of the ratio of slurry flow (front nozzle) to JP-10 flow (rear nozzle). Establishing this relationship is essential if a valid comparison of carbon burnout data obtained for different slurry flow rates is to be made in the future. Experiments were performed at an equivalence ratio of 0.85, temperature of 1700°C, and residence time of 6 ms for four slurry rates ranging from 5.2 to 10.5 g/min. Corresponding JP-10 rates ranged from 8.9 to 4.2 g/min. The results of this test indicated that there was essentially no difference in the carbon burnout efficiency for the different slurry rates. Results are summarized in Table 19.

### a. Equivalence Ratio

Carbon burnout was investigated at equivalence ratios of 0.65 to 1.5. A Statex MT 30% carbon slurry was combusted with 25% oxygen enriched air. For mixture ratios less than 1.0, the slurry rate to the front nozzle was held constant while the operating conditions were established by adjusting the JP-10 flow to the rear nozzle. Above a mixture ratio of 1.0, the slurry rate had to be increased to achieve the proper conditions since the maximum JP-10 flow rate had already been achieved. Slurry rates varied from 5.8 to 13.4 g/min, while JP-10 rates ranged from 4.8 to 11.5 g/min. The oxygen and air rates were maintained at 10.6 and 178.8 g/min throughout the entire experiment. These conditions corresponded to an overall residence time of 6 ms.

The carbon burnout increased from an initial value of 93.7 at an equivalence ratio of 0.65 to 96.5 at a ratio of 0.85. This gradual increase can be attributed to the increasing combustion temperature (1500 to 1650°C). After reaching this peak, the burnout percent decreased sharply to a minimum of 85.7 at a ratio of 1.52. This rapid dropoff after 0.85 illustrates the strong dependence of carbon oxidation on oxygen availability. A dropoff in temperature from 1710 to 1540°C was also observed as the equivalence ratio was increased to 1.52. In addition, the carbon monoxide, hydrogen and unburnt hydrocarbon concentrations increased with decreasing oxygen availability. Increased levels of these species in the exhaust stream indicate inefficient utilization of fuel energy. Overall combustion efficiency, which is a quantitative measure of energy utilization, decreased from 98.5 to 91.4 as the equivalence ratio was increased to 1.0. It appears

TABLE 19

CARBON BURNOUT PERCENT AS A FUNCTION OF SLURRY FLOW RATE  
AT AN EQUIVALENCE RATIO OF 0.8,  $\tau=6$  ms

<u>Slurry Flow Rate (g/min)</u>	<u>JP-10 Flow Rate (g/min)</u>	<u>Temperature °C</u>	<u>Carbon Burnout (%)</u>
5.2	8.9	1690 <sub>±</sub> 5	96.0
5.8	8.0	1690 <sub>±</sub> 5	96.1
7.9	6.1	1725 <sub>±</sub> 5	94.9
10.5	4.2	1720 <sub>±</sub> 10	95.7

TABLE 20

CARBON BURNOUT AND COMBUSTION EFFICIENCIES AS A FUNCTION  
OF EQUIVALENCE RATIO FOR STATEX MT 30%; 25% ENRICHED AIR  $\tau=6$  ms

<u>Equivalence Ratio</u>	<u>Temperature (°C)</u>	<u>Carbon Burnout (%)</u>	<u>Combustion Efficiency*</u> (%)
0.65	1500 <sub>±</sub> 40	93.7	98.5
0.75	1580 <sub>±</sub> 15	95.7	98.6
0.85	1650 <sub>±</sub> 15	96.5	98.3
0.95	1690 <sub>±</sub> 10	95.6	96.1
1.05	1710 <sub>±</sub> 20	94.9	91.4
1.28	1655 <sub>±</sub> 10	89.8	--
1.52	1540 <sub>±</sub> 10	85.7	--

\* Combustion Efficiency values for equivalence ratios greater than 1.0 are not meaningful since it is stoichiometrically impossible to completely combust the fuel to CO<sub>2</sub> and H<sub>2</sub>O.

from these initial findings that carbon burnout and combustion efficiency are favored at an equivalence ratio of 0.85 and high temperatures. Therefore additional efficiency determinations were concentrated at these conditions. The results are summarized in Table 20 and plotted in Figure 19.

#### b. Residence Time

Carbon burnout for Statex MT 30% was also studied for residence times ranging from 4.0 to 10.0 msec. These tests were conducted at an equivalence ratio of 0.85 and a temperature of approximately 1700°C. This particular time range represented the physical limitations of the present combustion system. Since carbon oxidation is the slowest step in the overall combustion process of a carbon slurry fuel, burnout efficiency should increase with increasing residence time. The results do show this, however, only to a slight extent. Carbon burnout values increased from 95.5 to 96.3. Unrealistically longer residence times would have to be utilized if higher efficiencies (99+) are to be achieved with this particular carbon particle size. The more fruitful approach involves study of smaller carbon particles and catalytically accelerating carbon oxidation. The results are summarized in Table 21 and plotted in Figure 20.

#### c. Catalysts

The effect of homogeneous catalysts on carbon oxidation was next examined. Statex MT 30% without catalyst was compared to Statex to which the following catalysts had been added.

- (1) 100 ppm Mn as methylcyclopentadienyl manganese tricarbonyl (MMT).
- (2) 1000 ppm Mn as MMT.
- (3) 1000 ppm Fe as ferrocene.
- (4) 1000 ppm Pb as lead acetate.
- (5) 1000 ppm Zr as zirconium octoate

The experimental procedure was to first obtain a carbon burnout value for the uncatalyzed Statex and then combust the catalyzed Statex. In this manner, the catalysts were directly compared to the base fuel under similar operating conditions. Despite the fact that the uncatalyzed Statex values are lower than those previously reported, when same day comparisons are made for all three catalysts the results show that at these concentrations no significant improvement in carbon burnout was achieved. It should be emphasized that our hope was for a major difference in carbon burnout (i.e. an increase close to or greater than 99%). The results clearly do not show such improvement. In the case of MMT, increasing the catalyst concentration from 100 to 1000 ppm had no effect. A direct comparison of catalytic ability of the three metals was not possible since the Statex values were not the same each day. The carbon burnout values for the Pb and Zr tests were lower than normally

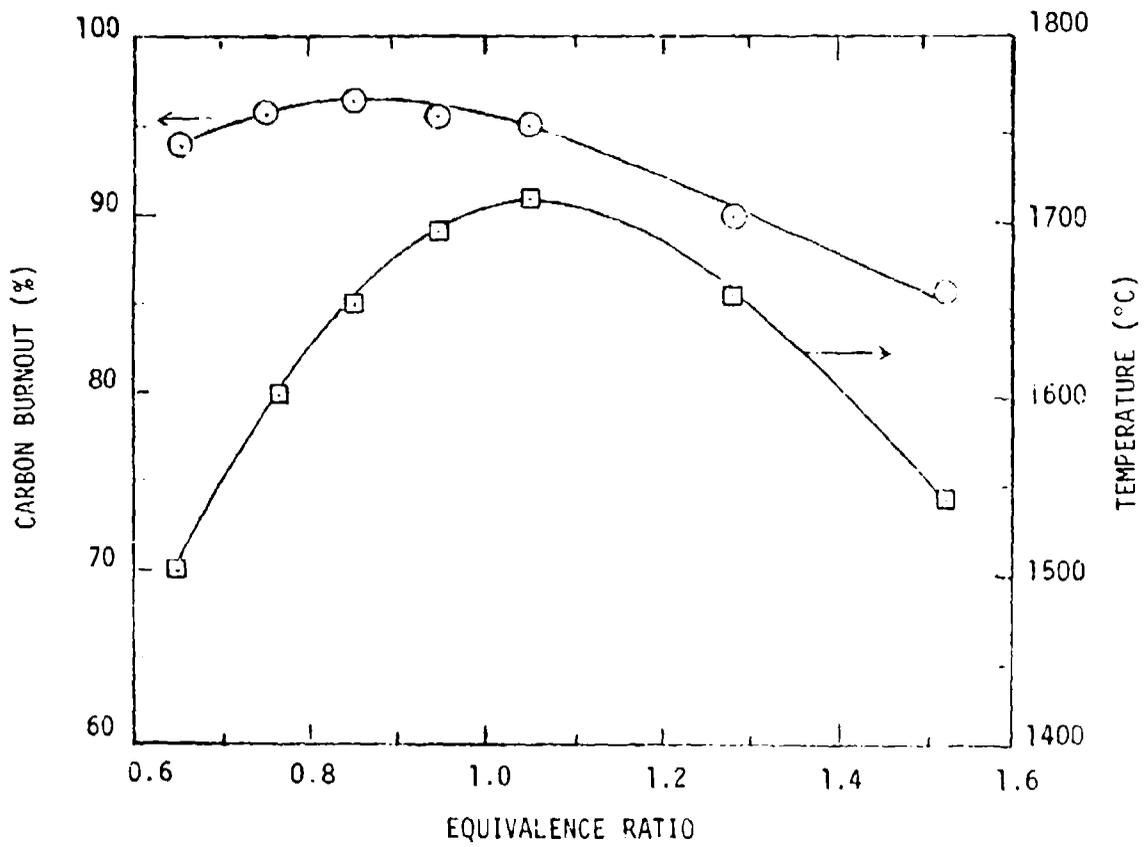


Figure 19. Effect of Equivalence Ratio on Carbon Burnout Percent For Statex MT 30%; 25% Enriched Air,  $\tau=6$  ms

TABLE 21

EFFECT OF RESIDENCE TIME ON CARBON BURNOUT PERCENT  
FOR STATEX MT 30% AT AN EQUIVALENCE RATIO OF 0.85

Residence Time (msec)	Temperature °C	Carbon Burnout (%)
4	1690±10	95.5
6	1700±10	96.0
8	1700±15	96.4
10	1700±20	96.2

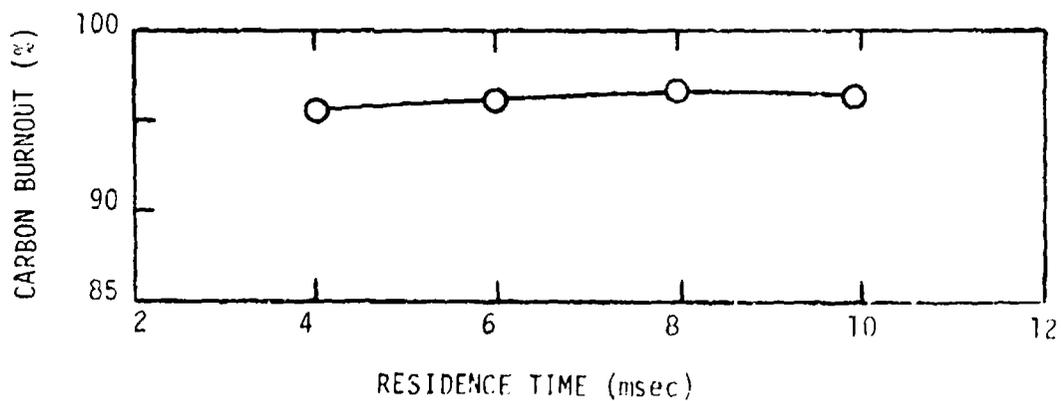


Figure 20. Effect of Residence Time on Carbon Burnout Percent for Statex MT 30% At An Equivalence Ratio of 0.85; Temperature of 1700°C

expected for these conditions. A spare fuel nozzle was used for these tests and a change in the fuel spray characteristics may be the reason for the lower values. It appears that carbon oxidation enhancement will only be realized by incorporating the catalyst on the individual carbon particles. Results are summarized in Table 22.

TABLE 22

EFFECT OF HOMOGENEOUS CATALYST ON CARBON BURNOUT PERCENT  
AT AN EQUIVALENCE RATIO OF 0.85; 25% ENRICHED AIR,  $\tau=6$  ms

<u>Fuel</u>	<u>Temperature °C</u>	<u>Carbon Burnout (%)</u>
Statex MT 30%	1650 $\pm$ 20	95.5
Statex MT 30% with 100 ppm Mn	1630 $\pm$ 40	95.0
Statex MT 30%	1690 $\pm$ 10	95.3
Statex MT 30% with 1000 ppm Mn	1690 $\pm$ 10	95.0
Statex MT 30%	1690 $\pm$ 10	94.3
Statex MT 30% with 1000 ppm Fe	1690 $\pm$ 10	93.8
Statex MT 30%	1720 $\pm$ 10	92.7
Statex Mt 30% with 1000 ppm Pb	1680 $\pm$ 10	91.8
Statex MT 30%	1680 $\pm$ 10	91.4
Statex MT 30% with 1000 ppm Zr	1670 $\pm$ 10	91.9

Note: Mn added as Methylcyclopentadienyl Manganese Tricarbonyl (Mn)  
Fe added as Ferrocene  
Pb added as Lead Acetate  
Zr added as Zirconium Octoate

#### d. Carbon Loading

The effect of carbon loading on carbon burnout was also examined. Statex MT carbon slurries of 30 and 50% carbon by weight were compared at an equivalence ratio of 0.85 and residence time of 6 ms. The results showed that increasing the carbon mass loading does not decrease the burnout efficiency. A slightly higher value was reported for the 50% slurry and this can be attributed to the higher combustor temperature. Again the spare fuel nozzle was used for this and subsequent experiments and may be the reason for the lower burnout values than previously reported. Results are summarized in Table 23.

#### e. Particle Size

Particle size was studied to determine whether reduced size could improve carbon burnout. This test was conducted at an equivalence ratio of 0.85 and a residence time of 6 ms. Comparison of two slurries (Sterling R, 20% with a 75  $\mu$ m mean particle size and Monarch 1100, 20% with 14  $\mu$ m particle size) with Statex MT 30% was planned; however, the Monarch 1100 posed pumping problems due to its high viscosity and data was not obtained. A Sterling R 30% also posed pumping problems. It was found that the smaller particle size of the Sterling R increased the carbon burnout. A value of 97.1 was recorded for the 75  $\mu$ m material as compared to 93.8% for the 300  $\mu$ m slurry. Results are summarized in Table 24.

#### f. Operating LFJSC on Carbon Slurry Alone

The LFJSC was successfully operated on carbon slurry alone on two occasions. The first occurred when a total loss of JP-10 flow to the rear nozzle left the combustor running strictly on slurry. The slurry flow rate was 5.8 g/min. No soot measurements or gaseous emissions data were obtained since this was not a planned experiment. However, combustion was very stable with a temperature of  $1300 \pm 10^\circ\text{C}$ .

After having established that operating on slurry alone was possible, an experiment was planned to compare the carbon burnout efficiencies obtained for slurry alone with that for slurry and JP-10. The combustor was first operated on both fuels to obtain a carbon burnout measurement at an equivalence ratio of 0.85 and a residence time of 6 ms. Once this was completed, the JP-10 flow from the rear nozzle was gradually reduced while the slurry rate from the front nozzle was increased. This continued until the combustor was running solely on slurry (flow rate of 15.8 g/min). All other conditions were maintained as they had been while operating on both fuels. Combustion was again very stable. This part of the experiment was also to have been conducted at an equivalence ratio of 0.85; however, due to an error in the slurry pump calculation curve, the actual equivalence ratio was 0.95. Despite the slightly different experimental conditions, the results indicated that high carbon burnout efficiencies can be obtained while operating the LFJSC in either of these two modes. The results are summarized in Table 25.

TABLE 23

EFFECT OF CARBON LOADING ON CARBON BURNOUT PERCENT FOR STATEX MT  
AT AN EQUIVALANCE RATIO OF 0.85; 25% ENRICHED AIR,  $\tau=6$  ms

<u>Carbon Loading (%)</u>	<u>Temperature °C</u>	<u>Carbon Burnout (%)</u>
30	1735+5	93.8
50	1790+10	94.8

TABLE 24

EFFECT OF PARTICLE SIZE ON CARBON BURNOUT PERCENT AT AN  
EQUIVALENCE RATIO OF 0.85; 25% ENRICHED AIR,  $\tau=6$  ms

<u>Fuel</u>	<u>Particle Size (mi.)</u>	<u>Temperature °C</u>	<u>Carbon Burnout (%)</u>
Statex MT 30%	300	1735+5	93.8
Sterling R 20%	75	1790+5	97.1

TABLE 25

RESULTS OF OPERATING LFJSC ON 30% STATEX MT  
30% ALONE; 25% ENRICHED AIR,  $\tau=6$  ms

<u>Slurry Flow Rate</u>	<u>JP-10 Flow Rate</u>	<u>Equivalence Ratio</u>	<u>Carbon Burnout (%)</u>
5.8	8.0	0.85	92.7
15.8	0.0	0.95	92.7

### C. Limited Systems Study

To accomplish the objectives of this effort (see Section III C) several meetings were held with our three subcontractors to discuss the proposed criteria for carbon dispersion fuels (Table 26) and to determine the possible impact of these properties on engine and air-frame design, and missile performance. As noted below it was indicated in early discussions that the potential improvement for ramjet powered missiles was minimal; therefore, most of our subcontractor effort was concentrated on turbine powered missiles. The results may be summarized as follows:

#### 1 Range Improvement Study (by Boeing Military Airplane Division, Seattle, Washington)

A sensitivity study of system performance of carbon slurry fueled subsonic and supersonic missiles was performed using baseline missions chosen after consultation with ASD/XR's Advanced Technology Cruise Missile (ATCM) Program Manager. Both the supersonic ramjet and the subsonic cruise missile were launched at low altitude at 0.55 Mach number. The cruise missile remained at low altitude flying a medium range mission, while the ramjet missile made a steep climb to an initial altitude of 70,000 feet and thereafter flew a cruise climb profile at 4.0 Mach number to a relatively long range.

A series of constant missile volume performance calculations were made for each of the vehicles, using percent carbon loading as the independent variable, and range as dependent variable. Parameters were percent usable fuel (reflecting fuel trapped through clingage to tank walls and piping) and missile dry weight (reflecting special items needed to pump the fuel, such as positive expulsion systems). Engine performance estimates were reviewed with the engine subcontractors, while aerodynamic estimates and performance calculations were provided by Boeing's missile systems organization.

The results of the study are presented in Figures 21 and 22; for security reasons, the range results have been nondimensionalized using as a basis the range of a 100% JP-9 fueled vehicle. Both vehicles are very sensitive to percentage increments in unexpended fuel, and somewhat less sensitive to vehicle dry weight. The following remarks are specific to each vehicle.

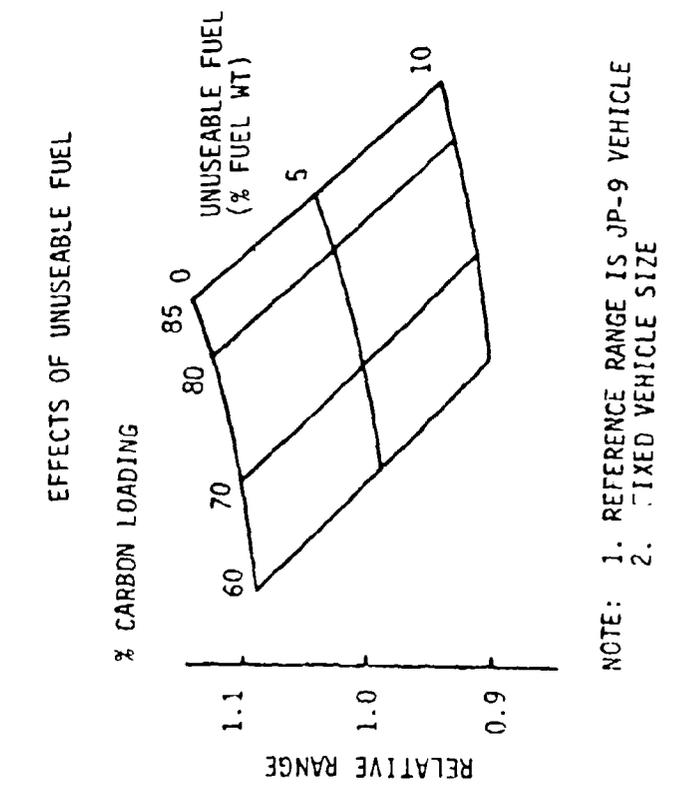
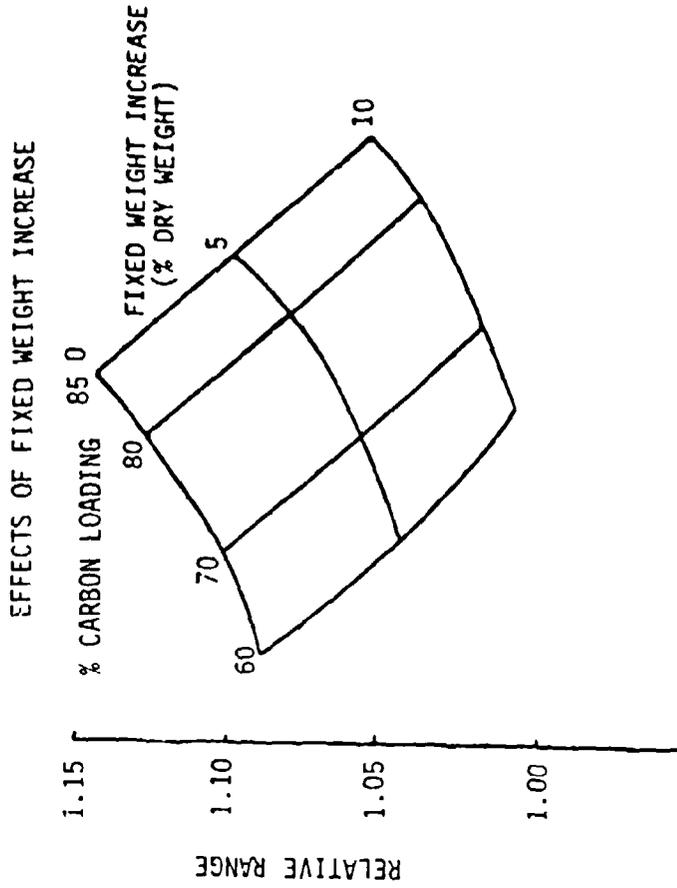
The ramjet vehicle range improvement is smaller than anticipated (less than 15%) due to the fact that the more dense fuel must be accelerated and lifted to high altitude early in the mission. Combustion efficiency was also found to strongly influence range; a 10% decrease (such as might result from incomplete carbon combustion) reduces range by 14%.

The turbine powered cruise missile, flying at essentially launch altitude, shows from 20 to 30% range benefits from use of carbon slurry fuels.

TABLE 26

## PROPOSED CRITERIA FOR CARBON DISPERSION FORMULATIONS

Btu Content, lbs/gal, min.	180,000
Pour Point, °F, max.	-65
Viscosity @ 77°F cp	30-60
@ -40°F cp	150-250
@ -65°F cp	300-400
Yield Stress @ -65°F, max.	340 dynes/cm <sup>2</sup>
$\frac{\text{Shear Stress}}{\text{Shear Rate}}$ @ 0°F, max.	50 dynes/cm <sup>2</sup>
$\frac{\text{Shear Stress}}{\text{Shear Rate}}$ @ -65°F, max.	500 dynes/cm <sup>2</sup>
Clingage, max, wt%	0.5
Stability Tests	
- Static Storage	OK for 5 years
- Freeze Thaw	OK after 10 cycles @ -65 to 140°F
- Vibration Test	OK after 1 hour
- Thixotropy	Not to exceed 500 dynes/cm <sup>2</sup> after 1 yr.
Pump Test (Type ?)	OK after once through
Nozzle Test	Produces a satisfactory pattern for combustion
<u>OTHER</u>	

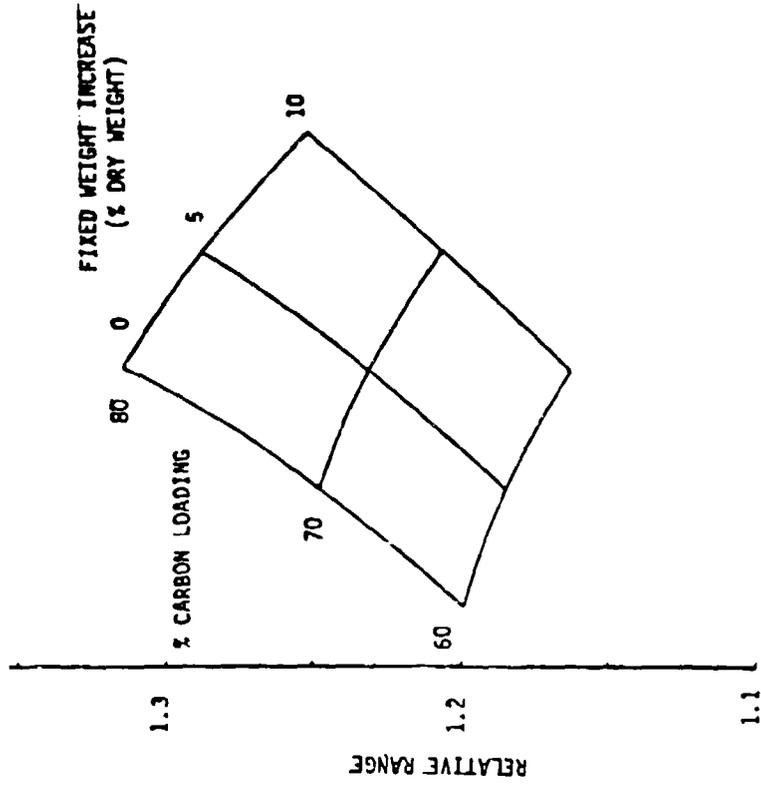


NOTE: 1. REFERENCE RANGE IS JP-9 VEHICLE  
 2. FIXED VEHICLE SIZE

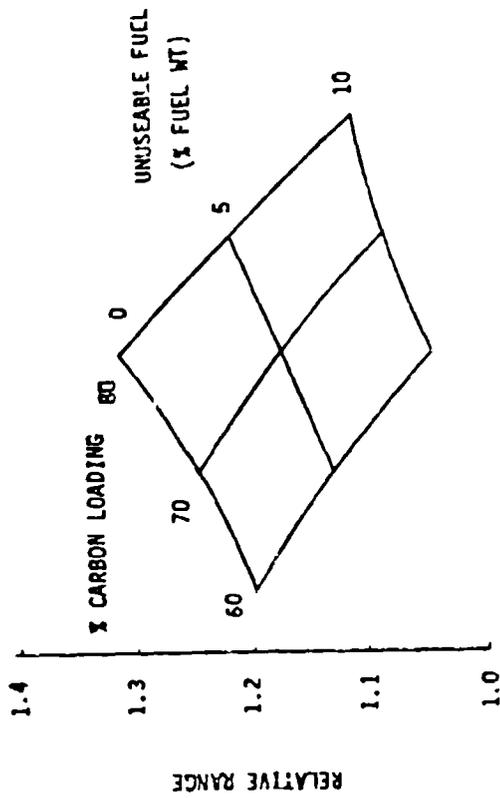
Figure 21. Supersonic Vehicle

Approved for Release by NSA on 05-08-2014 pursuant to E.O. 13526

EFFECTS OF FIXED WEIGHT INCREASE



EFFECTS OF UNUSEABLE FUEL



NOTE: 1. REFERENCE RANGE IS JP-9 VEHICLE  
2. FIXED VEHICLE SIZE

Figure 22. Subsonic Vehicle

A brief comparison of pumped vs. positive expulsion systems was also completed. At this time, Boeing has a clear preference for pumped systems on the basis of volumetric efficiency (fuel volume/available fuel system volume), a view concurred in by AFAPL/RJA.

2 Turbo-Fan Engine System Investigation for Carbon Dispersion Fuel Program (by General Electric Aircraft Engine Group, Lynn, Massachusetts)

The General Electric investigation into the potential impact of carbon slurries can be summarized within four broad categories:

Fuel handling and control  
Fuel injection/atomization  
Combustor design - life considerations  
Techniques/procedures for starting engine

The results of the studies are given below.

Fuel Handling and Control

Wide variation in fluid properties with temperature and shear rate are expected. It is not possible to pump and meter by conventional methods with this type of fluid. As a result, a new state of art fuel control concept must evolve to handle the proposed materials. Methods now under consideration involve use of variable speed positive displacement pumps to move, pressurize, and meter the fluid. Control intelligence will be gathered and processed by digital electronics to produce the proper controlling functions. The entire process is expected to take advantage of the latest technology called FADEC (Full Authority Digital Electronic Control). FADEC is being applied to new GE products.

Engine piping is expected to be several times normal diameter to minimize the effect of line loss and may require a prefilled or primed system to eliminate fill lag during the start sequence. A primed system will need to be hermetically sealed until launch, and will require explosive valves to allow quick initiation of the start sequence.

Priming fuel is not necessarily carbon slurry. It can be varied to accomplish various ignition window requirements. This technology has already been demonstrated from the late 1950's on the J-85 powered GAM-72 decoy missile.

Fuel Injection/Atomization

Fuel injectors will require a significantly larger flow capacity than is normal, to minimize restriction pressure at cruise fuel flow levels. As a result, each injector may require a pressurizing valve to minimize head effect at minimum fuel flow.

Tests accomplished at G.E. in the past year indicate that current state of art blast atomizers can successfully handle and atomize viscous fluids up to 1100 centistokes, which is believed to cover the required range of fuel properties. The upper limit of viscosity has yet to be determined.

The injection scheme that was investigated here is based on an existing General Electric small production engine design which is known to be successful in burning a wide range of fuels down to  $-53.9^{\circ}\text{C}$  ( $-65^{\circ}\text{F}$ ) fuel temperature. Successful experience has been obtained on Jet A, Marine Diesel, JP-4, JP-5, JP-8, JP-9, and JP-10. Burner tests in the fuel viscosity range of two (2) to forty (40) centistokes have been carried out under a separate USAF contract, and have demonstrated negligible discernible difference in flammability over that range.

This technology is available now and will be demonstrated in a few months in cruise missile size engines.

#### Combustor Design - Life Considerations

A cruise missile size annular combustor has recently been demonstrated at G.E. employing the above-described fuel injectors. The combustor is about three inches long and currently meets all combustion test requirements for a cruise missile turbofan engine burning the liquid fuels described above. This combustor will be on engine test by the end of 1979.

The combustor is currently made of Hastelloy X sheet stock.

It is believed that carbon slurry fuels, if burned in this combustor, will produce a significant increase in flame radiation producing shell temperatures as much as  $800^{\circ}\text{F}$  above current observations. Hastelloy X is incapable of meeting this requirement. New alloys are available which may be able to help overcome this problem. One such material is MA-956, an oxide dispersion strengthened (ODS) material which can take temperatures as high as  $2200^{\circ}\text{F}$  while maintaining acceptable structural properties. It is available in thin sheets which can be formed into a combustor. This material is also being evaluated on other AEG combustion system components. Thermal barrier coatings are also available to provide considerable additional relief, especially where higher radiation loads are expected.

Cooling improvements are available, if required. The present cruise missile combustor is predominantly film cooled - impingement/film cooling is available for additional cooling. Several of these concepts have been demonstrated on other AEG products. Other materials will soon be available offering additional design margin. Ceramics are under consideration and being run on combustion tests within General Electric.

The very small surface area of the very short straight through annular approach at General Electric makes the cooling job significantly easier. This technology is demonstrable in 1-3 years.

## Engine Starting Techniques/Procedures

Ignition limits with carbon slurries are currently unknown and will require investigation on an aircraft engine combustor. In the event that excessive ignition limitations exist, it is possible to overcome such difficulties with a priming fuel that has broad ignition boundaries. Since a carbon slurry fueled engine will require priming to eliminate fill time lag, the use of a hydrocarbon such as JP-4, JP-10 or a high altitude ignition fluid such as ethylene oxide is possible.

The sequence of launch will probably be:

- Firing of cranking cartridge
- Firing of explosive valves
- Admission of priming fuel
- Firing of torch igniters
- Partial acceleration of the engine on priming fuel
- Smooth transition to carbon slurry
- Complete acceleration to full power

Timing of this sequence will be controlled to match specific engine dynamics.

It is also planned to demonstrate a starting procedure on a cruise missile engine in the first half of 1980.

## APPENDIX A

### PROPERTIES OF CARBON BLACK

#### I. Introduction

An annotated bibliography comprising a comprehensive sample of the extensive literature and numerous patents on carbon black has been prepared in support of the current studies of carbon-enriched slurry fuels. Specific topics covered from 1960 to date include particle size and structure; surface area, porosity and activity; adsorption phenomena; superficial oxidation; and the rheology of suspensions of carbon black. References to raw materials, manufacture and uses (except in coatings and inks) are omitted. The state-of-the-art of slurry fuels and the combustion of carbon black are considered elsewhere.

The bibliography is prefaced by the following brief overview in which the topics are discussed in the same sequence as in the bibliography. Copies of many of the articles and patents are available as noted.

When reviewing the literature on carbon black, the more recent citations should be examined first. This minimizes the chance of being misled by concepts that have since been deprecated. The appraisal of structure by X-ray diffraction and earlier estimates of porosity are cases in point. Also, since the organization of the bibliography is necessarily only approximate, subjects in addition to the one of apparent immediate interest should be scanned.

#### II. Abstract

The literature on the properties and some of the uses of carbon black has been reviewed and an annotated bibliography has been completed.

Some physical and chemical properties are notable. Particles of carbon black are extremely small, ranging from 5 to 500 nanometers, and can be seen only with the electron microscope. Their shape varies from spheroidal to complex; and the particles tend to clump together--indeed, dispersion of the particles is a major problem in the use of carbon black. Surface area is typically in the neighborhood of 100 m<sup>2</sup>/g, with extremes from perhaps 5 to 950 m<sup>2</sup>/g, and 0 to 35% porosity. The surface is usually active with a tendency to react with oxygen and some other substances to form surface groups that influence wettability and pH, which varies from acid to alkaline. There is also some free surface energy that draws the particles together. The rheology of suspensions of carbon black is strongly influenced by these surface characteristics and the suspensions are usually non-Newtonian. Viscosity, for example, is a function of shear history. The technology of carbon blacks in coatings and inks entails the adaptation of the peculiarities of carbon black to the preparation of the stable suspensions required in these industries.

### III. General Characteristics

The general characteristics of carbon black may be summarized as follows. Specific properties are considered in subsequent sections.

Carbon black is mostly carbon, of course, with small amounts of other elements. The numbers vary:

C	84-99.7%	Lower levels contain more oxygen
O	0.1-11.0	Higher levels are due to oxidation during manufacture or subsequently
H	0.1-0.5	Largely aromatic
S	0.01-1.5	From feedstock
Ash	0.0-1.0	Mostly from quench water, especially in furnace blacks
Tar	<0.1-1.0	Origin uncertain

Some other characteristics of carbon black are summarized in Table A-1. Again, the rather wide spread in the numbers is notable. The volatile matter and the variable pH are largely due to the oxygen-containing surface groups.

Table A-1\*

#### Typical Characteristics of Carbon Blacks Made by Various Methods

		<u>Partial Combustion</u>			<u>Thermal Decomposition</u>	
		<u>Lamp Black</u>	<u>Channel</u>	<u>Furnace</u>	<u>Thermal</u>	<u>Acetylene</u>
Surface Area, BET	m <sup>2</sup> /g	20-50	100-950	20-550	6-15	~65
Particle Size	nm**	50-120	5-30	10-80	120-500	35-42
Volatile Matter	%	2-10	4-20	1-6	0.5-1.0	0.5-2.0
pH		6-9	3-5	6-10	7-9	5-8

\* Adapted from Ref. 356

\*\* Nanometers

#### IV. Inspections and Standards (Ref. 1)

ASTM standards for carbon blacks are listed in Ref. 1. References to other less official tests are scattered through the articles cited (e.g., 350) including a number relevant to specific uses, notably rubber manufacture.

#### V. Carbon Black in Pigments, Coatings and Inks (Ref. 2-48)

The technology of carbon black in pigments, coatings, and inks entails the preparation of a stable dispersion of carbon black in a liquid medium. Garrett (18) states this objective more explicitly as follows:

"Attainment of suitable pigment dispersion requires a process that encompasses incorporation (or wetting), deagglomeration, and stabilization (electrostatically and sterically). In order to do this, by definition, one must displace the adsorbed contaminants (air, gases, or water) from the pigment surface (along with subsequent attachment of the resinous medium), supply sufficient mechanical energy to disrupt the pigment agglomerates, and expose the surface of the particles to the polymer to effect the necessary permanent particle separation required for stability."

Some of the concepts thus developed by the pigment users are more broadly applicable to other carbon black/liquid systems.

Carbon black properties considered particularly important include particle size, surface area, structure (measured by DBP\* adsorption) and surface chemistry. These and other properties of the carbon black interact in rather complex ways. The finer blacks are more difficult to disperse but form more stable suspensions; area increases with decreasing particle size and with oxidation; and high DBP numbers (high structure) are often preferred.

Surface chemistry is perhaps most important because the kind and quantity of surface groups and unsatisfied surface bonds on the particles influence their tendency to stick together. This mechanism is operative either directly, or indirectly by reaction of the surface groups with the liquid vehicle and/or dispersant added to it. Oxygen groups formed by oxidation are mentioned most frequently. Incidentally, heating to 35°C facilitated deagglomeration in one system examined (40c) (because of reduced viscosity?).

It is customary when using carbon black as a pigment to first prepare a paste which is then "let down" by addition of diluent. It is

\* Dibutyl phthalate

crucial that the paste be carefully made, and it is also most important that the dilution be properly accomplished to avoid "shock out" of the pigment.

The technology seems to be quite artsy.

#### VI. Toxicology (Ref. 49-50)

Except for some chronic nonspecific inflammation of the respiratory tract following prolonged exposure (49, 350), carbon black seems to be nontoxic. Traces of carcinogenic hydrocarbons on some blacks have not been shown to be active in laboratory animals (50). No adverse effects of severe exposure incidental to the manufacture of carbon black has been noted.

#### VII. Structure (Ref. 51-80)

Carbon black is formed by the thermal decomposition of hydrocarbons in a reducing or oxidizing (partial combustion) environment. The fine mechanism is not known. However, it seems likely that at an early stage small spherical particles form as a consequence of dispersion of a liquid feed and/or by nucleation and condensation from the vapor phase. These particles carbonize to solid microspheres.

Sometimes depending largely on the manufacturing process, it appears that the freshly formed particles collide with one another while they are still tacky and stick together. This results in a branched beaded structure referred to as an aggregate.

Both microspheres and aggregates comprise concentric uniformly spaced graphitic planes of carbon atoms. The planes are not fully continuous. They tend in the center to surround the nuclei, and near the outside they follow the external contour. This means that an individual aggregate is, in fact, a coherent particle--not simply a group of microspheres superficially stuck together.

Evidently, the ordering of carbon atoms is greater near the surface than within the particles because oxidants attack the interior first. The "graphitic" planes in carbon black are typically more than 344 picometers apart, which is the maximum spacing below which graphitization can occur. Hence, carbon black is not usually graphitizable. Nevertheless, the term "graphitized" is still applied to carbon blacks that have been heated to a high temperature, say 3000°C.

The individual particles of carbon black--microspheres or aggregates--tend to form clumps that may be remarkably stable. Presumably surface forces are operative in causing individual particles to stick together. In any case, because the particles are so very small, it is difficult to establish the shear gradient necessary to separate them in a liquid suspension. For these reasons it isn't easy to achieve and sustain a suspension of isolated individual particles in a gas or liquid.

Liquid suspensions of carbon black are non-Newtonian and are said to be "structured" (see Rheology of Dispersions, Sec. XVI). It

appears that the aforesaid clumps sometimes tend to form larger, less stable groups of clumps, or flocs.

It is interesting to note that despite the frequent references to adhesion and grouping of particles, bulk carbon black is mostly space. As produced, actual solids volume may be as little as 2%. Even in pellets, solids volume is typically little more than 30%, and extremely high pressures are required to increase it much more.

Void volume is considered an important attribute of carbon black by coating manufacturers. It is often measured by noting the quantity of dibutyl phthalate (DBP) taken up by carbon black up to the point at which an abrupt increase in viscosity of the mix occurs.

#### VIII. Surface Area (Ref. 81-96)

Several procedures have been used to estimate the surface area of carbon black.

The BET nitrogen absorption method is often used in the laboratory and occasionally in the field. Iodine absorption was used for many years as a measure of surface area, but it has limited utility-- surface oxides, for example, interfere--and it is now used primarily for production control. A variety of other substances and adsorption techniques have been used or considered as indicated in the literature cited.

The electron microscope also is employed to estimate the surface area of carbon black, particularly since the procedure has been facilitated by automation. The electron microscope is not well adapted to field use and is limited almost exclusively to the laboratory.

There has been much debate regarding the relative merits of these several methods and how total area should be corrected for porosity (note comments on porosity, Sec. IX). At the moment, BET nitrogen adsorption, CO<sub>2</sub> adsorption, and the electron microscope seem to be favored.

Most carbon blacks do not have a notably high surface area although a few oxidized blacks do approach 950 m<sup>2</sup>/g (Table 1, p. 3). ASTM surface area limits for various classes of carbon black are shown in Table A-2, following.

#### IX. Porosity (Ref. 97 to 111)

Until recently measurements of the porosity of carbon black were questioned because of a suspicion that interparticle capillary condensation was included in the apparent porosity (99). Lamond (99,100) resolved this problem and reported 28-32% porosity for fluffy blacks, 0-26% for pelletized blacks, and 0-5% for rubber grade furnace blacks.

Evidently, carbon black is not usually a very porous substance. There is some thought, incidentally, that oxidation may increase porosity, in addition to selectively burning out the interior of the particles.

Pore shape and size remain uncertain.

Table A-2\*

ASTM Designation and Surface Area Limits for Commercial Blacks

ASTM designation	Older type	SA limits m <sup>2</sup> /g	ASTM designation	Older type	SA limits m <sup>2</sup> /g
N 110	SAP	125-155	S 301	MPC	105-125
N 219	ISAF-LS <sup>a</sup>	105-135	N 440	PF	43-69
N 220	ISAF	110-140	N 550	FEP	36-52
N 242	ISAF-HS <sup>b</sup>	110-140	N 601	HMF	26-42
N 285	IISAF-HS <sup>b,c</sup>	100-130	N 660	GPF	26-42
N 326	HAF-LS <sup>a</sup>	75-105	N 770	SRF	17-33
N 330	HAF	70-90	N 774	SRF-NS <sup>c</sup>	17-33
N 347	HAF-HS <sup>b</sup>	80-100	N 880	FT	13-17
S 300	EPC	95-115	N 990	MT	6-9
N 339	HAF-HS(NT) <sup>b,c</sup>	90-105			

<sup>a</sup>LS = low structure.

<sup>b</sup>HS = high structure.

<sup>c</sup>IISAF = "Intermediate" intermediate super abrasion black.

<sup>d</sup>NT = new technology.

<sup>e</sup>NS = nonstaining.

\* Reference #352

## X. Particle Size (Ref. 112-115)

The average size of the ultimate grains of carbon black varies with the method of manufacture but in all cases is extremely small. Size distribution also varies. Finest carbon blacks are on the order of 5-10 nm, while the coarsest blacks range up to 500 nm, (Table A-1, p. 91) with a more or less gaussian distribution in all cases.

Particle size (and shape and area) is measured with the electron microscope. Earlier estimates based on X-ray diffraction are now suspect.

## XI. Surface Groups (Ref. 116-182)

Carbon blacks have on the surface functional groups containing oxygen, hydrogen and to a lesser extent sulfur and nitrogen. These groups affect surface energy and activity. The tendency of the particles to stick together is reduced and wettability may be increased as a consequence of the presence of the surface groups, which, in turn, facilitates dispersion. Thus, oxidized blacks are hydrophilic and disperse spontaneously in water.

Contrary to earlier views, the surface groups seem to be chemically bonded--not simply adsorbed--on the surface. Oxygen groups formed by oxidation that have been identified include carboxyl, phenol, quinone, and lactone, plus possibly anhydride, ether and others that are less certain. Aromatic hydrogen also is present.

The pH of carbon black varies from 3 to 10 and is dictated by the nature of the surface groups. Oxidation lowers pH and heating, which evidently decomposes the acidic groups preferentially, increases it.

Heating decomposes and drives off the surface groups primarily as CO, CO<sub>2</sub>, and H<sub>2</sub>. The oxygen compounds are evolved at 400 to 1200°C, but 1500°C with vacuum is needed to drive off hydrogen and sulfur. Dissipation of the surface groups leaves some transient, unsatisfied bonds which can subsequently in the presence of an oxidant reform oxygen groups, or the free bonds may cause the carbon black particles to stick together. As noted below, heating also alters the structure of the black.

## XII. Heat Treatment (Ref. 183-192)

Heating drives off surface groups, as noted above, and initially increases surface area. Area reaches a maximum at about 700-900°C, then at higher temperatures decreases to values that may be less than the original. As noted in Section VII, carbon black is not considered graphitizable because the carbon atom planes are too far apart. However, heating to 2500-3000°C does improve symmetry and extent of the planar structure.

## XIII. Grinding (Ref. 193-196)

Mixtures of carbon black and vehicle intended for coatings and inks are first ground for the purpose of dispersing the black. Evidently, individual particles are not usually much affected by this treatment.

Devices used include the three roll mill, steel ball mill, carborundum stone mill, sand mill, and high speed impeller (18).

Prolonged grinding of dry carbon black in a steel ball mill breaks up some of the particles. The new surface thus created is extremely active, to the extent that the ground black is pyrophoric (194). Evidently, free ions are formed when the particles are crushed.

#### XIV. Oxidation (Ref. 197-257)

The superficial oxidation of carbon black may be accomplished with any of a number of gaseous or liquid reagents including air, ozone, hydrogen peroxide, carbon dioxide, nitric acid and many others. Initially the oxidation occurs primarily within the particle; the outer surface is not much affected. This results, therefore, in the formation of a shell with a burned out interior.

As would be expected, oxidation alters the several properties of carbon black. Area is increased. Oxygen content (oxygenated surface groups) also is increased, and as noted above dispersability is thus improved. The kind and degree of the side effects of oxidation vary depending on the oxidant used.

Carbon black itself has some activity as an oxidation (and reduction) catalyst, and carbon black and some other forms of carbon are used as catalyst supports (351,352). Oxidations promoted by carbon black include ethylene to water and CO<sub>2</sub>, ethanol to acetic acid, hydrogen sulfide to sulfur, and ferrous to ferric ion. Carbon black also has some activity in alkylation, halogenation, hydrolysis, isomerization and polymerization reactions, and decomposition of peroxides. Carbon supported metal catalysts have been used for several procedures including olefin oxidation, hydrogenation and paraffin isomerization.

#### XV. Densification (Ref. 258-260)

Carbon blacks are routinely pelletized for convenience in handling. This reduced void volume from better than 90% to approximately 70% and may reduce surface area. Pressures up to 10000 psi and above further reduce void volume, but the individual particles are remarkably stable; porous blacks may be partially fractured but nonporous black particles are largely unaffected by this severe treatment. There is some thought, however, that pressing carbon black so there is substantial particle-to-particle contact causes chemical bonding. This could be due to the interaction of free radicals on the surface of the carbon (259).

#### XVI. Rheology of Dispersions (Ref. 261-329)

The rheology of dispersions of carbon black in liquids is complex. It is subject to a number of physical and chemical variables including: particle size, shape, area, porosity, pH, surface activity and surface groups; particle aggregation; quantity of black in the suspension; viscosity, polarity, pH and chemical composition of the liquid; the presence of dispersants, etc. It is not surprising, therefore,

that carbon black dispersions are usually thixotropic, with hysteresis, and a "memory" of recent shear experience.

Except at very low loadings of carbon black with vigorous shear (achieved with ultrasound, for example), the individual particles tend to form clumps--the slurry is said to have structure. Fine particles, in particular, are difficult to disperse; and the viscosity of dispersions of fine particles is higher than the viscosity of coarser particles. Mixing or grinding reduces but does not necessarily eliminate clumping, and the individual particles are not usually affected. One concept advanced is that when mixing is stopped a continuous network of carbon black clumps forms. With mild agitation (or simply on standing?), this structure reverts to discrete flocs (groups of clumps).

The properties of carbon black dispersions are strongly influenced by the surface groups on the particles. Thus, as noted, oxygen groups seem to enhance and stabilize the dispersion, and adsorbed dispersants added for the purpose can be effective. Water also may be a factor inasmuch as vigorous desiccation has a negative effect on stability (294). More broadly, the properties of the particle surface and the liquid and/or dispersant--acidity, polarity, stereochemistry, etc.--must be carefully balanced. The references cited include more detailed comments.

#### XVII. Reviews (Ref. 330-363)

Several reviews of some spectral and properties of carbon black and more general coverage are cited. An extensive article by Medalia and Rivin, 1976 (Ref. 351) and a book by Donnet and Voet, 1976 (Ref. 352) are particularly relevant. Excerpts from the tables of contents of these references are included in the bibliography.

## Review of Carbon Black Literature

### ATTACHMENTS

#### I. Bibliography

- II. Characterization of Powder Surfaces with Special Reference to Pigments and Fillers, G. D. Parfitt, K.S.W. Sing edit.; Academic, 1976; Carbon Blacks, A. I. Medalia, D. Rivin; pp. 379-351 (Ref. No. 351)

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W. F. Rollman:sns  
July 26, 1979

ATTACHMENT I

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## APPENDIX B

### Combustion of Carbon Slurry Fuels

The subject of carbon slurry combustion is exceedingly complex. Superimposed upon the already intricate processes involved in the combustion of gaseous or liquid fuels is the heterogeneous oxidation of carbon particles which are large compared to soot particles. The discussion in this section reviews the nature of combustion systems which would utilize these new fuels, offers a brief summary of the events occurring during the combustion of practical liquid hydrocarbons, and then considers the complications which arise due to the inclusion of carbon particles in the fuel. Since the oxidation of carbon particles is expected to lag the consumption of the hydrocarbon component of the fuel, methods to promote carbon oxidation are discussed in a final subsection.

### Gas Turbine and Ramjet Combustion Systems

This subsection describes the nature of combustion systems in engines which are candidates for cruise missile propulsion systems, gas turbines and ramjets. It should be noted that mission differences drastically influence whether the gas turbine or ramjet engine is selected and affects the nature of the engine being designed. For example, low subsonic speed applications clearly favor the selection of a turbine while high speed applications favor the ramjet. The description which follows intends not to focus on a specific application but rather to provide general background on the types of systems which will utilize future slurry fuels.

### Gas Turbine Combustors

The gas turbine employs the Brayton thermodynamic cycle--adiabatic compression, constant pressure heat addition, and adiabatic expansion. The function of the combustion system is to accomplish the heat release with complete combustion and minimum pressure loss and to satisfy numerous engine operational requirements. It must provide for the mixing of fuel and air within the proper environment to ensure their nearly complete reaction to desirable combustion products. Operation of the combustors in small gas turbines used in cruise missile systems is adequately described through consideration of Figure B-1. In the "primary zone", fuel and oxidizer are mixed, usually in slightly fuel-rich proportions. Approximately 90 percent of the fuel is burned in this zone. Fuel oxidation is completed in the "secondary zone". In modern engines, turbine inlet temperatures are close to the temperature at which significant chemical reactions cease ( $\sim 1600^{\circ}\text{K}$ ) and no dilution is required. However, older designs with reduced turbine inlet temperature utilize a "dilution zone" to further reduce temperature. No significant reaction occurs within this zone.

The fuel-air ratio typically required for the combustor temperature increase is less than one-third the stoichiometric quantity--that resulting in complete  $\text{O}_2$  consumption upon fuel conversion to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The equivalence ratio parameter,  $\phi$ , defined as the ratio of the actual fuel-air mixture strength to that required for stoichiometric combustion, provides a convenient way of describing mixture variations through the combustor. Equivalence ratio values less than 1.0 correspond

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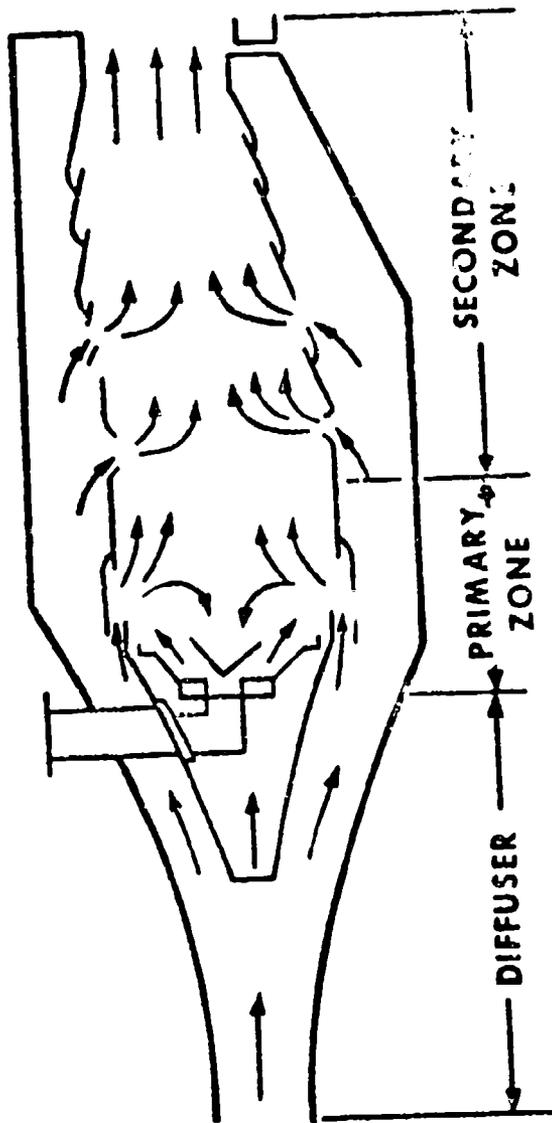


Figure B-1. General Schematic of a Gas Turbine Combustion System

to fuel lean operation while those values greater than 1.0 indicate fuel rich operation. Current primary zone equivalence ratios are about one whereas combustor exit values are less than one-third.

The purpose of the primary zone is to stabilize combustion. High temperatures resulting from stoichiometric operation promote rapid fuel consumption reactions. Primary zone flow is dominated by a strong recirculation region (established by swirling the air entering the head end or dome of the burner) which furthers combustion stability. The requirement to ensure an adequate residence time for completion of chemical reactions is satisfied by limiting combustor reference velocity (the average cold-flow velocity just behind the primary zone) to about 25 m/sec.

In practically all current gas-turbine combustors, the fuel is injected as a liquid. The formation of a well distributed dispersion of small droplets is desirable to promote rapid evaporation of the fuel and intimate mixing of the fuel and air. Three general categories of fuel injectors are currently employed. Pressure atomizers utilize a large fuel pressure drop (greater than 100 psi) across a nozzle to create a finely dispersed spray of small (<50 $\mu$ ) fuel droplets which quickly vaporize. Airblast atomizers create strong swirling motions of a small portion of the combustor air flow into which fuel is introduced. The severe shearing motion of the air disperses the fuel and results in small fuel droplets. The slinger design, although a pressure atomizing type, is the third type. It is very different from the conventional fuel nozzle in that the fuel is injected through small holes in the rotating turbine shaft. The high centrifugal force imparted to the fuel provide atomization. Slinger systems are used in several small engine combustors of interest to this program--the WR19 is one such system.

The secondary zone introduces additional air to provide for the chemical reactions which consume the products of incomplete combustion passing from the primary zone. Air participating in these chemical reactions is introduced normal to the main flow direction. The remaining air enters parallel to the main flow at the combustor walls to provide a film of cool air which protects the combustor liner and to tailor the temperature profile exiting the combustor. Design of the combustor liner hole pattern to accomplish this requirement traditionally involves a costly development effort to avoid a number of possible detrimental effects. Excessive addition of air may result in quenching chemical reactions (especially carbon monoxide and soot oxidation) essential in reducing emissions. Air introduction must be accomplished in a manner which results in the correct temperature profile entering the turbine; a 25 K increase in temperature at a critical region of a turbine blade can result in a four-fold decrease in blade life. These design objectives must be met within a prescribed combustor length. Although increasing combustor size might facilitate the design task, this would cause undesirable increases in engine length, main shaft size, bearing requirements and engine weight.

## Ramjet Combustors

The ramjet is the simplest of all air breathing engines. Air enters a diffuser where it is decelerated from a supersonic condition to a Mach number of about 0.3. This results in substantial compression prior to fuel introduction and combustion. The hot combustion products are then expanded through a nozzle to a high exhaust velocity resulting in the generation of substantial thrust. A simplified schematic of a ramjet engine is included in Figure B-2.

Ramjet combustors may be of the type depicted in the schematic--a design very similar to the turbojet afterburner. A more modern design which is of primary importance to the subject program is the "dump combustor". This configuration employs the flow of a premixture of fuel and air into a sudden duct expansion (see Figure B-3). The recirculation zones created by the "dump" stabilize the combustion process by providing a continuous ignition source for the incoming fuel-air flow. The predominant combustion processes occur within the turbulent reacting shear layer at the boundary between the inflow and the recirculation zone. The dump combustor has gained prominence because of its ability to accommodate the rocket/ramjet principle. In this configuration, the initial use of the engine involves operation as a rocket with the solid rocket propellant packing the volume of the dump combustor; subsequent propulsion is achieved in the ramjet mode.

Key combustion aspects which must be considered in evaluating the utility of fuel candidates in ramjets are ignition, stability, and combustion efficiency. It should be noted that ramjet combustion efficiencies are typically 75-95% much less than the corresponding values for gas turbines operating at cruise operating conditions.

### Representations of Combustion Processes in Gas Turbines and Ramjets

The characterization of fuel behavior in combustion systems can be considered by evaluating the performance of fuel candidates in small-scale, well-characterized combustion simulation devices. In this connection, turbine and ramjet combustors can each be described as combinations of such devices, which collectively perform in the same manner as the entire combustion system.

Gas turbine combustors are often modeled as a combination of a well-stirred system which represents the primary zone and a plug flow in series with the stirred system, representing the secondary and dilution zone. The fuel vaporization, initial combustion (pyrolysis or breakdown of larger molecules), stabilization processes, CO formation, and soot production take place primarily in the well-mixed zone. CO and unburned hydrocarbon (fuel) burnout and, most importantly, soot and fuel carbon burnout take place in the plug flow region which represents the secondary zone.

Ramjet dump combustors would be represented by well-stirred and plug flow zones in an analogous way. The recirculation zones are represented by well-stirred regions, while the turbulent reacting flow along the centerline is represented by plug flows.

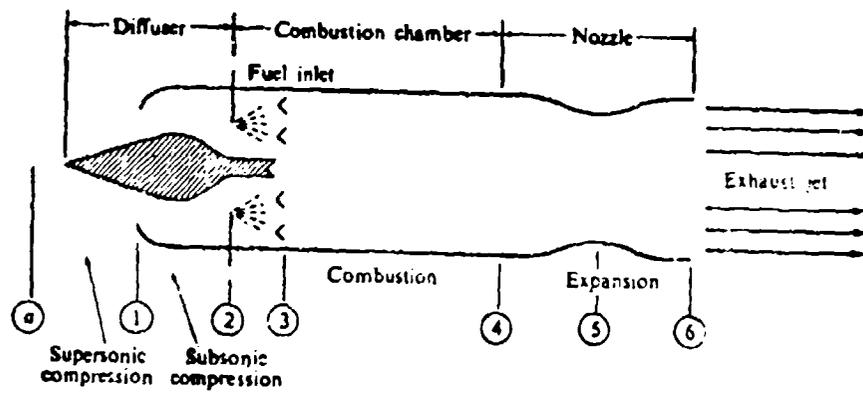


Figure B-2. Schematic Diagram Of A Ramjet Engine  
(from Reference 1)

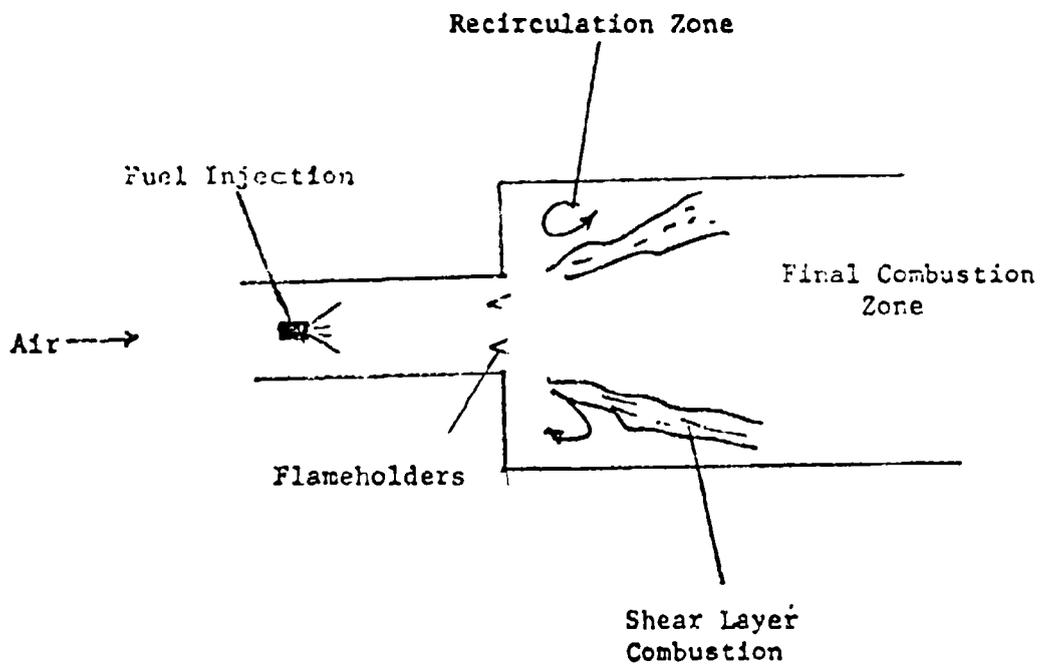


Figure B-3. Ramjet Dump Combustor Schematic

These well-characterized combustion simulations provide the means to screen carbon slurry fuel candidates and to investigate the parametric influences of slurry properties on various performance aspects. Because of the convenience of these experimental tools, a large number of candidates can be examined and the parametric variations can be thoroughly studied.

### Hydrocarbon Combustion

An appreciation for hydrocarbon combustion processes must be in hand if carbon slurry fuel combustion is to be understood. Major aspects of hydrocarbon combustion chemistry involve hydrocarbon pyrolysis and partial oxidation to H<sub>2</sub> and CO, soot formation, chain branching, reactions resulting in H<sub>2</sub> consumption, CO oxidation by radicals generated during chain branching, and soot oxidation. Each of these reaction steps is schematically illustrated in Figure B-4. Note that the chronology of these processes is indicated here by the flow from left to right through the reaction steps. Each process is individually described below.

### Pyrolysis and Partial Oxidation

Pyrolysis is the term given to the process by which fuel molecules are broken into smaller fragments due to excessive temperature and partial oxidation. This molecular destruction is accomplished during the first phase of the combustion process. The predominant resulting products are hydrogen and carbon monoxide. Little detailed information is available concerning the chemistry of these processes for practical fuels--large hydrocarbons with molecular weights of 50 to 200. It is well-recognized that hydrocarbon structure and its influence on the pyrolysis chemistry affects the early stages of combustion process. For example, the ignition delay characteristics of various hydrocarbons differ significantly.

Edelman(2) has developed a single-step quasi-global model to characterize the pyrolysis and partial oxidation of any practical hydrocarbon fuel. His approach is to characterize the kinetics of the numerous complex chemical reactions resulting in production of H<sub>2</sub> and CO by a single reaction step. An Arrhenius type expression has been fitted to experimental data involving variations in temperature and pressure as well as fuel and oxygen concentration. Edelman's result is:

$$\frac{d[C_{nH_m}]}{dt} = \frac{5.52 \times 10^8 T}{P^{.825}} [C_{nH_m}]^{1/2} [O_2] \exp(-24,400/RT) \quad (1)$$

where concentrations are expressed in moles/cc, T in °K, and P in atmospheres. The activation energy of 24,400 is in the units cal/g mole°K.

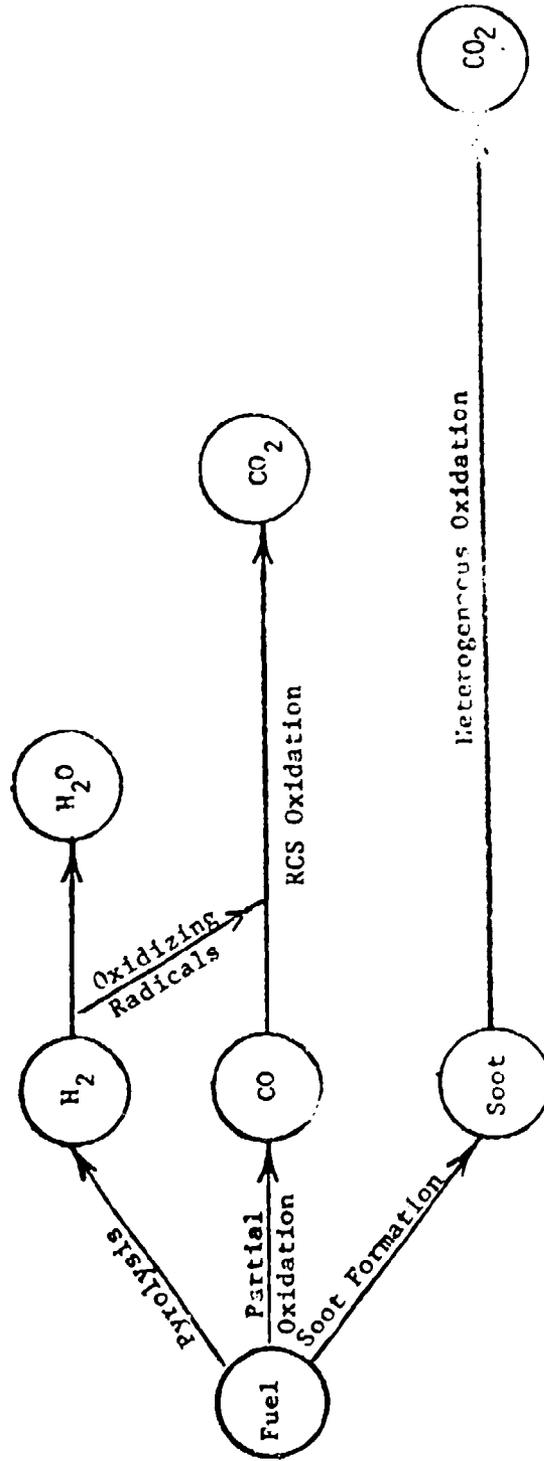
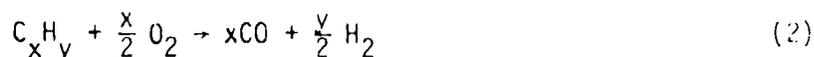


Figure B-4. Hydrocarbon Combustion Chemistry Schematic

Knowledge of hydrocarbon combustion pyrolysis processes is of prime importance to the understanding of slurry fuel combustion. The factors which influence ignition delay and stability in liquid hydrocarbons (those that govern Equation 1) will be the same with slurry fuels since the liquid hydrocarbon will still govern the process. However, as will be discussed in carbon slurry combustion section, the presence of the solid carbon material can be expected to influence commonly encountered combustion behavior.

### Soot Formation

The predominance of fundamental research on soot formation has involved laminar premixed flames. Street and Thomas' work published in 1955 is extremely thorough in experimental detail and breadth of hydrocarbons examined; it has become the classical paper in the field.<sup>(3)</sup> Other key publications are References 4-23. These investigations have universally confirmed that soot formation is a kinetically controlled process. Equilibrium calculations indicate that soot should not be present at fuel-air mixture conditions where the oxygen-to-carbon atomic ratio (O/C) is greater than one. That is, the general chemical equation



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

Another very important premixed flame experiment conducted by MacFarlane and Holderness at the British National Gas Turbine Establishment (NGTE) attempted to evaluate the effect of pressure on soot formation.<sup>(18)</sup> Most previous work with premixed flames has concerned atmospheric or subatmospheric conditions. The combustion system employed at MacFarlane and Holderness took special precautions to prevent flashing back to upstream locations, an additional difficulty associated with the high pressure operation. In addition to sooting limits, the amount of soot formed was determined and expressed as a "soot formation ratio" (the percent of fuel carbon evident as soot). The index of the soot quantity was found to increase with the cube of pressure. Very useful plots of pressure versus equivalence ratio for various values of soot formation ratio were presented. Examples are shown in Figure B-5 for cyclohexane, cyclohexene, and benzene. Gas phase species were also determined during this testing and it was concluded that H<sub>2</sub>O and CO<sub>2</sub> (oxygenated compounds not predicted by equilibrium for the system  $C_xH_y + \frac{x}{2} O_2 \rightarrow xCO + \frac{y}{2} H_2$ ) are formed in substantial quantities and deplete the system of oxygen prior to consumption of all fuel. Later work by this same organization<sup>(19)</sup> has indicated that the hydrocarbon pyrolysis product plus soot formed was dependent on fuel-air ratio and roughly independent of other variables. Differences in soot formed (e.g. with increasing pressure) represent a more effective conversion of the pyrolysis product to carbon particulate.

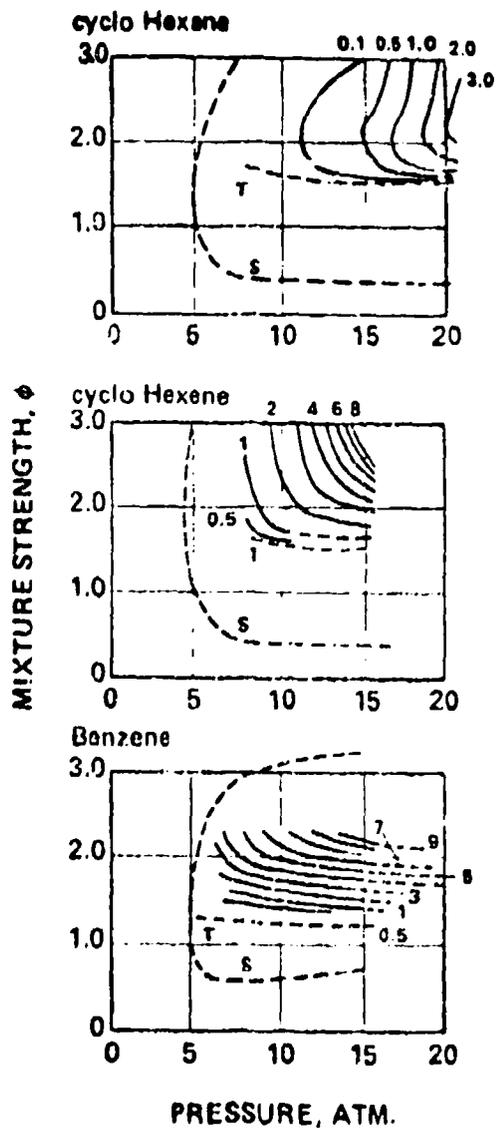


Figure B-5. Pressure and Mixture Ratio Effects on Soot Formation (from Reference 18)

Wright's work at ER&E involving soot formation in the jet stirred reactor(24,25) is probably of greatest interest to this discussion--it is a combustion process similar to that at which soot forms in the recirculation zone of an actual aeropropulsion combustion system. As in the previously mentioned studies, it was determined that soot forms at O/C >1 but the strong backmixing of the jet stirred reactor did seem to afford some broadening of the soot-free O/C ratio. In addition to the establishment of sooting limits, as determined by the color of the flame (luminous yellow versus blue), Wright determined the concentrations of soot formed for some limited conditions of O/C below the soot limit. No analysis of this "yield" data to determine soot formation kinetics was undertaken but it is recognized that more such data might provide the basis for global carbon formation chemical models.

Soot formation processes may be of interest in carbon slurry combustion if solid carbon is produced which is more difficult to burn out than is the carbon in the slurry. It is unlikely that this will be the case as soot particles would be much smaller than those of the slurry, thus requiring less burn time. Secondly, the amount of soot resulting from a combustion process is usually less than 2% of the fuel carbon--a small amount compared to the carbon particles present in the slurry. Consequently, a relatively small inefficiency penalty would result even if soot production was high and the soot was not oxidized in the combustor.

#### Carbon Monoxide Oxidation

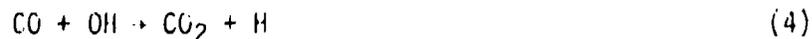
The products of pyrolysis are reduced state compounds (RSC). Oxidation of these species is better understood than their formation. The important oxidation reactions for the reduced state compounds are of the general form:



where RSC = reduced state compound  
OR = oxidizing radical  
OSC = oxidized-state compound  
RR = reducing radical

The rate of oxidation of the RSC may be assumed to be given by the appropriate Arrhenious controlled mechanism.

Carbon monoxide consumption is controlled by the following RSC reaction:



Since the activation energy of the reaction indicated by Equation 4 is generally low (only a few kcal/g-mole), the carbon monoxide oxidation rate is predominantly influenced by OH concentration. As previously noted, this quantity is controlled by the chain branching mechanism. Nevertheless, a common method of approximating radical concentration in a RSC reaction involves assuming local or partial equilibrium. This

type of approach has been used in CO oxidation studies by Howard, et al. (26) Because the functional relationship between equilibrium OH concentration and temperature is exponential, an Arrhenius like dependence can be written for a quasi-global  $O_2 + CO$  reaction in the presence of  $H_2O$ . Howard, et al determined:

$$\frac{-d[CO]}{dt} = k_0 [CO][O_2]^{1/2} (e)^{\frac{-30,000}{RT}} \quad (5)$$

where  $k_0$  is a constant =  $1.3 \times 10^{14}$  cc/mole sec.

This information is of importance to carbon slurry combustion because of the need to utilize the chemical energy in CO within the combustor. Any CO present in the exhaust beyond the equilibrium amount corresponding to the exhaust temperature represents an inefficiency which compromises the benefits gained from using the carbon slurry fuel and reduces vehicle range.

#### H<sub>2</sub> Oxidation

While reactions of the nature described by Equation 3 play a role in consuming the  $H_2$  formed during the pyrolysis process, many gross characteristics of hydrocarbon combustion are a result of other chemical reactions which involve chain branching. This type of reaction sequence involves the production of additional radical species during the process. In the case of the  $H_2$  oxidation process, the important chain branching reactions are:



Note that in either reaction a single radical (O or H) results in the production of two radicals (H + OH or OH + O). This type of reaction has the potential of producing large quantities of radical species. In portions of the combustion zone having high  $H_2$  concentration, radical species can reach levels far in excess of equilibrium. During this process, OH radicals also participate in RSC reactions (Equation 3) to produce  $H_2O$  from  $H_2$ .

#### Soot Oxidation

The small carbon (<.05 $\mu$ m) soot particulates which are formed during the early stages of the combustion of a hydrocarbon fuel may be oxidized in the latter portions of the process. Correct conditions of mixture ratio, temperature, and residence times can optimize the rate of the soot burnout process. (27-36) Radcliffe and Appleton have investigated the consumption of soot under conditions corresponding to the gas turbine engine. (35) Appleton points out that the surface oxidation rates for soot and pyrolytic graphite are the same and that the rates are predictable by an expression developed by Nagle and Strickland-Constable. (26)

Their results, illustrated in Figure B-6, indicate optimum consumption of particles at  $\phi = 0.75$ .\* Their particle surface consumption rates of 1-20 $\mu\text{m}/\text{sec}$  indicate that particles whose initial diameter is less than 0.04 $\mu\text{m}$  will be consumed in a typical residence time of five ms. Additional detail on carbon particle oxidation will be given below, which focuses on carbon slurry combustion.

Soot burning times are likely to be much less than the time required for slurry carbon particle consumption. Nevertheless, the above discussion provides an idea of the relevant background information available on carbon particle oxidation under combustion conditions. This information will be of value in our consideration of slurry particle burning times as discussed below.

### Carbon Slurry Combustion

The size of the carbon particles incorporated into the liquid hydrocarbon carrier to produce a slurry fuel can vary significantly. It is possible that micro-fine particles--roughly the size of soot particles--might be utilized. In this case, it would seem that burning times of carbon particles would be on the order of 5-10 milliseconds. It should be noted, however, that the carbon slurry must burn a substantial portion of its carbon content to achieve the equivalent temperature conditions at which soot produced from a hydrocarbon flame is oxidized in 5-10 ms. Consequently, much of the carbon will be oxidized at lower temperature conditions where consumption times may be much longer than 5-10 ms. This current program will investigate a number of methods to accelerate carbon burnout to allow effective utilization of slurry carbon in times which are characteristic of aeropulsion devices.

It may also be found that it is necessary to utilize larger particles (up to 1.0 $\mu\text{m}$ ) to improve fuel rheological properties or that the micro-fine particles agglomerate to a larger diameter during the formulation process. In either case, oxidation of the carbon particles will require much more time than that for soot oxidation which is the slowest process in normal hydrocarbon combustion. However, it must be noted that even at 1.0 $\mu\text{m}$  diameter, the rate of carbon particle consumption is controlled by surface oxidation kinetics rather than oxygen diffusion to the surface. Figure B-7 illustrates the combustion time required for particles of various diameters burned in the stoichiometrically correct ratio (i.e.  $\phi = 1.0$ ). The band of required times at lower diameters is due to data variation for different types of carbon tested. An abrupt change in the slope of the combustion time/diameter characteristic is apparent at about 10 $\mu\text{m}$ . This corresponds to the transition between diffusional and surface kinetic control of the particle oxidation rate. At the diameters of interest to carbon slurries (<1.0 $\mu\text{m}$ ), the process is definitely kinetically controlled. The substantial difference between the extrapolation of

\*The parameter  $\phi$  represents the equivalence ratio  $\phi = (f/a)_{\text{stoich}} / (f/a)$ . For fuel rich mixtures the fuel-air ratio exceeds the stoichiometric value and  $\phi > 1$ . In the case of fuel lean mixtures,  $\phi < 1$ .

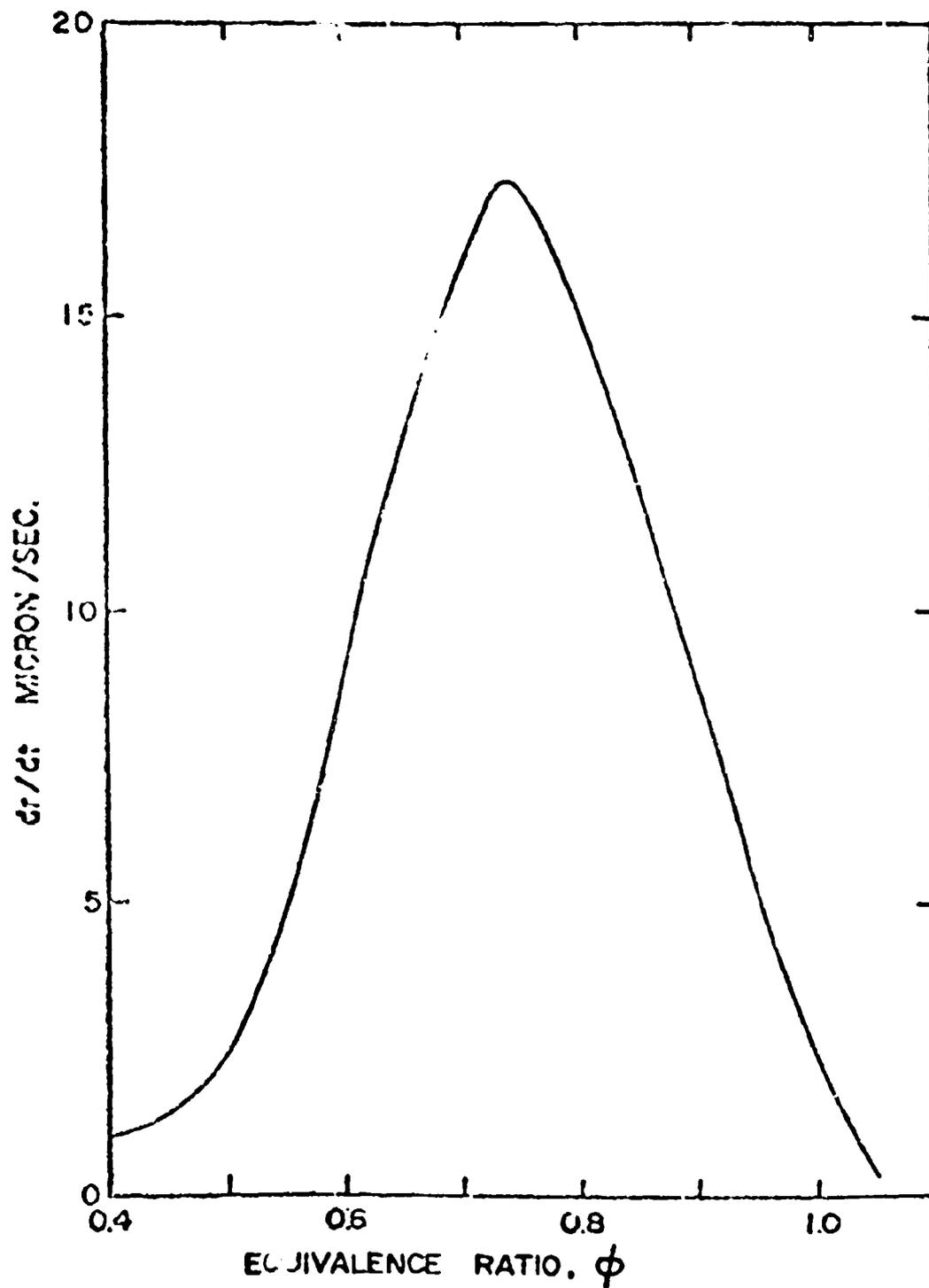


Figure B-6. Dependence Of Surface Oxidation Rate On Equivalence Ratio  
(from Reference 35)

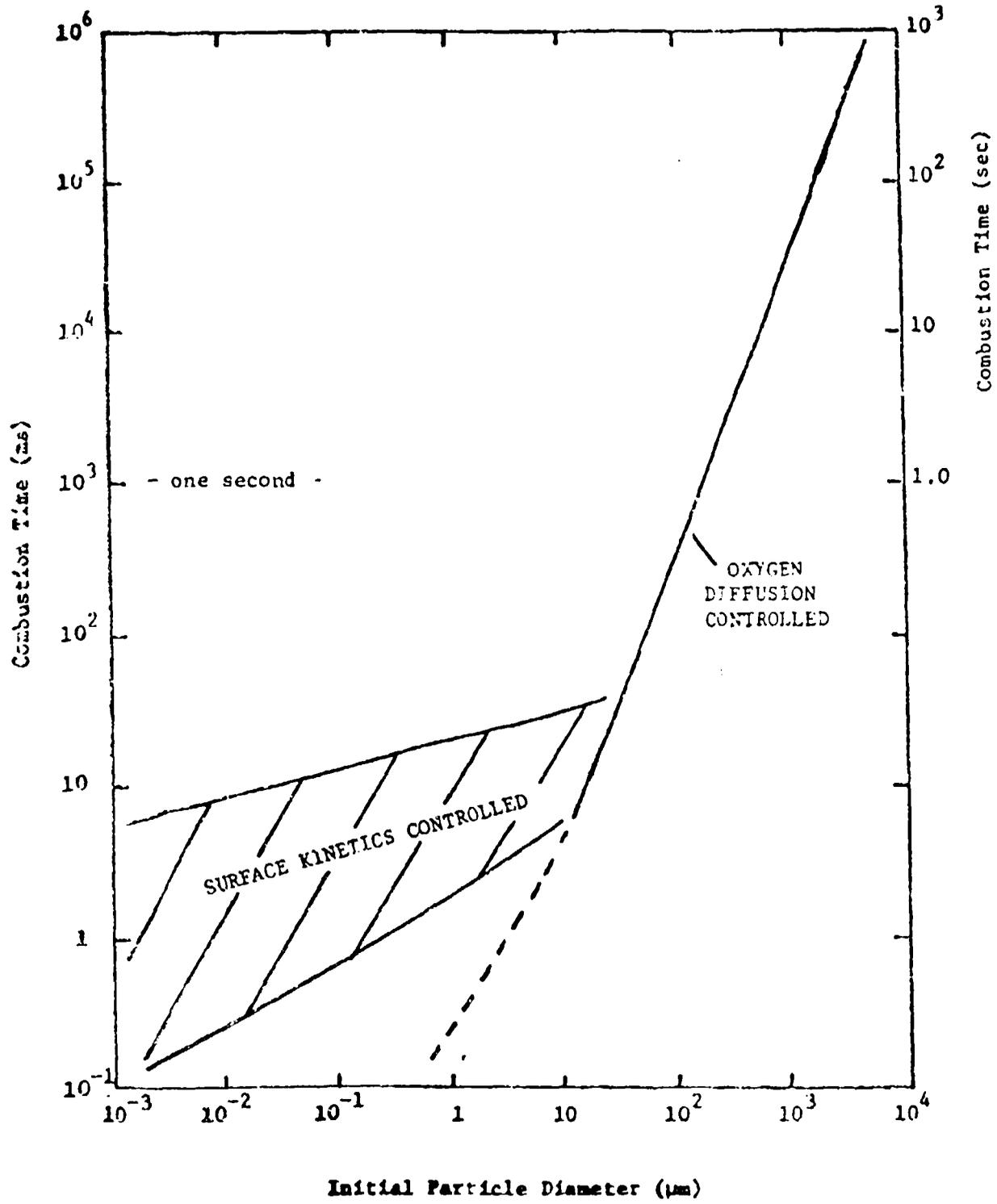


Figure B-7. Dependence Of Carbon Particle Combustion Time On Particle Diameter

the diffusion controlled behavior and the observed carbon burning times at small diameters indicates that much is to be gained by consideration of methods for acceleration of carbon particle surface kinetics (i.e. selection of the proper carbon type and catalysis). Consideration of improvements in carbon slurry combustibility by carbon type selection and catalysis will be discussed in the next section.

Figure B-8 describes the overall combustion process for a carbon dispersion fuel. Volatilization of the slurry produces a gaseous hydrocarbon vapor and carbon particles. The hydrocarbon vapor then undergoes a complex process of pyrolysis and partial oxidation. In simplified terms, the principal products of these reactions can be considered to be hydrogen, carbon monoxide and soot. The  $H_2$  then undergoes chain branching reactions which provide free radicals (H, O, and OH) and termination of the process results in the final combustion product  $H_2O$ . These radicals participate in and often dominate, other chemical processes occurring within the combustion process. The pyrolysis process is influenced by those species, and CO disappearance is actually controlled by oxidation by OH. These gas phase processes are very rapid at the temperatures of interest in aer propulsion application ( $>2000K$ ) and near complete oxidation is possible in less than 2 ms. However, soot oxidation requires heterogeneous oxidation which is slower than that occurring in the gas phase. Figure B-8 shows this time requirement as  $t_1$ .

Combustion of the carbon portion of the slurry also requires a heterogeneous reaction. The time required for complete burnout, designated  $t_2$  in Figure B-8, depends upon particle size and combustion conditions. Carbon black of smaller size than soot is not available. Therefore, the release of the carbon's heating value will require more time than would be the case for a 100% liquid fuel. Consequently, the carbon oxidation process will lag the consumption of the hydrocarbon portion of the fuel.

Since carbon oxidation is likely to be the limiting step in the complete combustion of carbon slurry fuels, our current emphasis in slurry formulation has been on the use of sub-micron carbon particles (0.01-0.3 $\mu$ ) which would be expected to have short burnout times. The slurry enters the combustion system as liquid droplets containing approximately 60% by weight of this very small particle size carbon. Depending on the injection technique utilized, the average droplet diameter may range from about 50 to 150 $\mu$  and, therefore, each drop contains millions of small carbon particles.

The vaporization of the slurry droplet must be such that the carbon particles enter the gas phase individually or in small groups. If agglomeration occurs--all the liquid is removed without causing the carbon particles to disperse--a large, 40-120 $\mu$  mass of carbon will remain, as shown in Figure B-9. The burning rate of such a large diameter particle would be diffusion rate controlled. In this case the combustion benefits of providing the small particle size will be lost. In fact, if the agglomeration problem cannot be avoided, the practicality of combusting the slurry carbon content in the short time available (1-5 ms) will be in serious doubt.

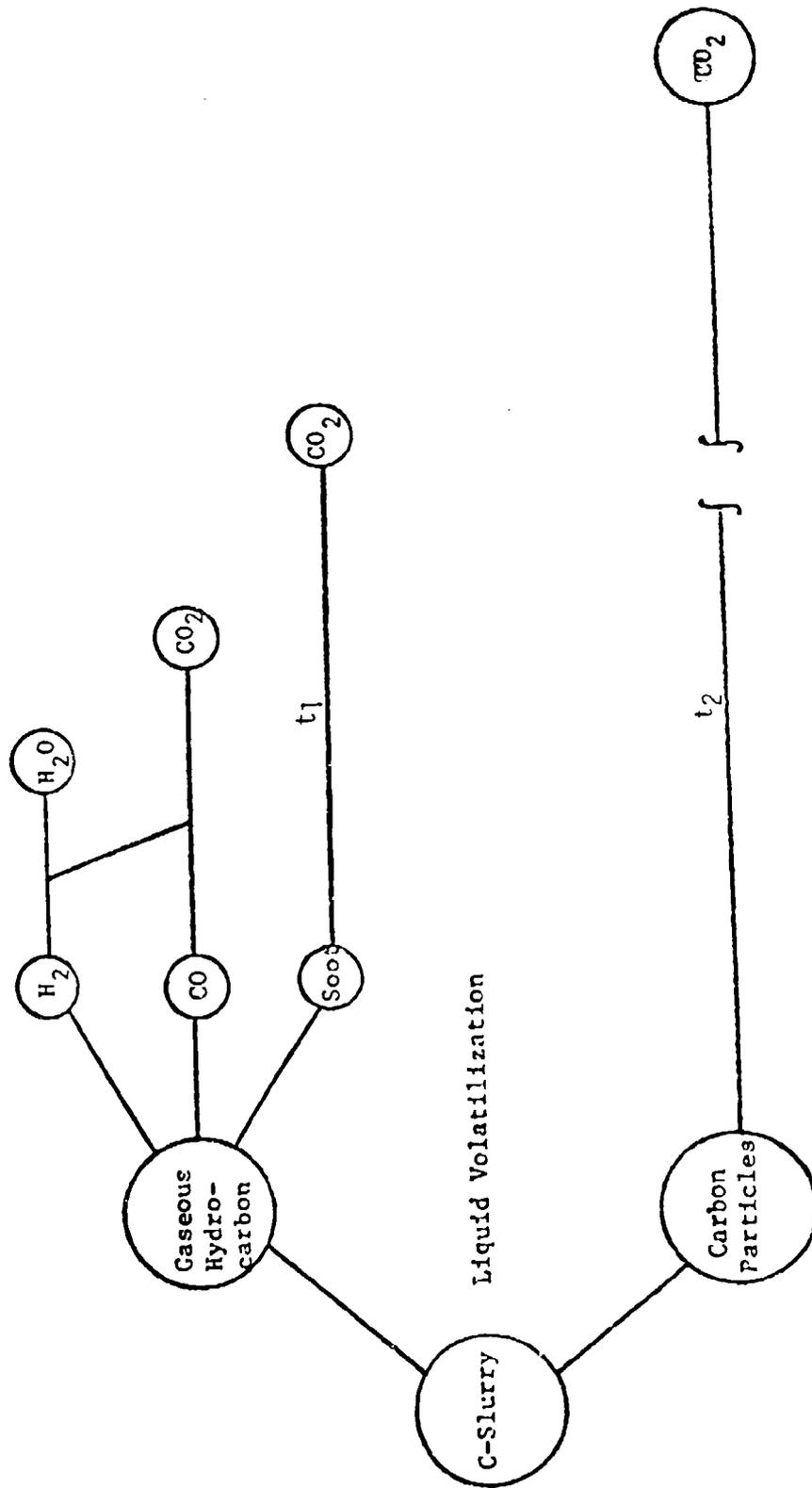
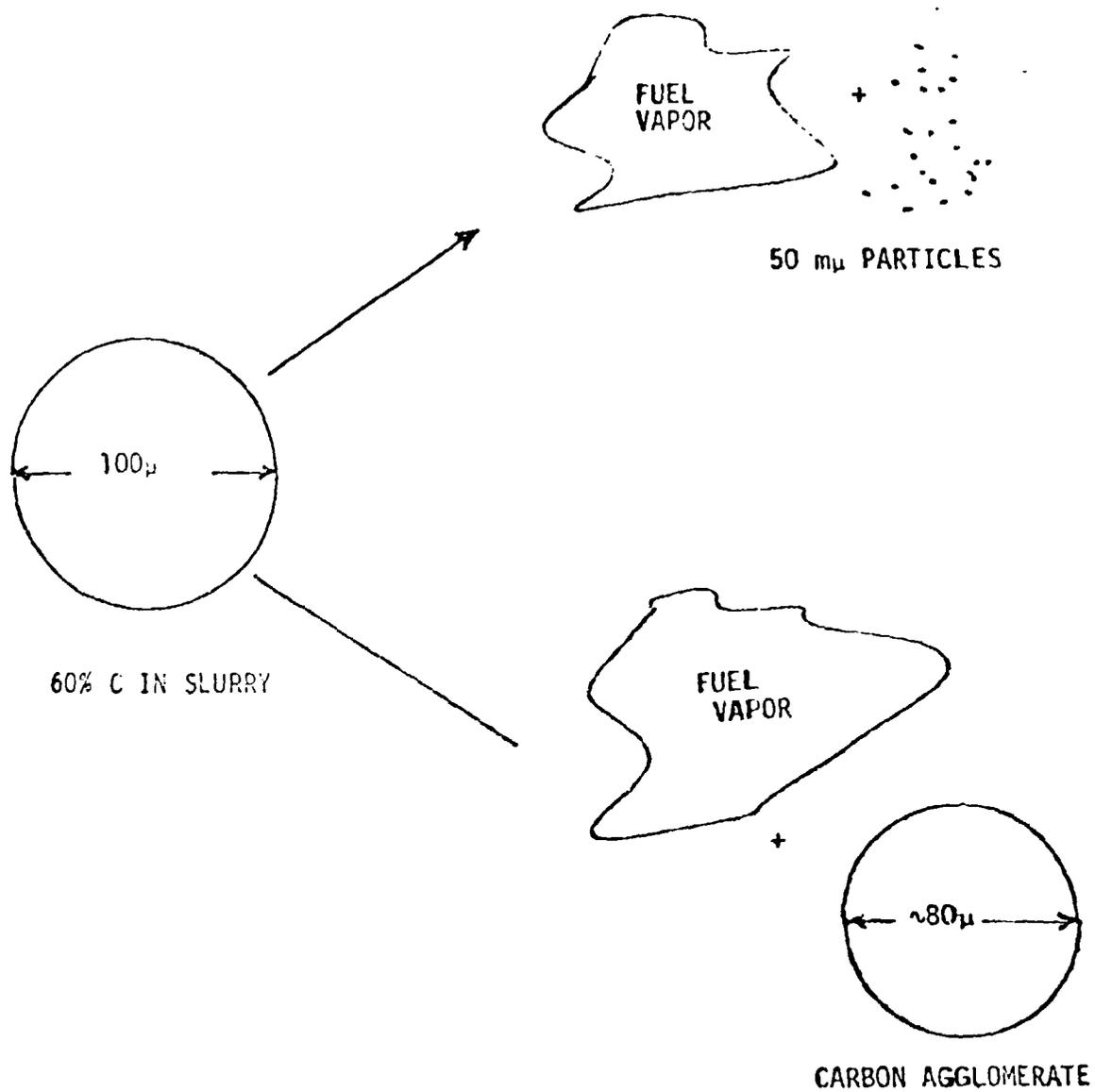


Figure B-8. Carbon Slurry Combustion Chemistry Schematic



CARBON AGGLOMERATE BURN TIME WOULD BE > 1s

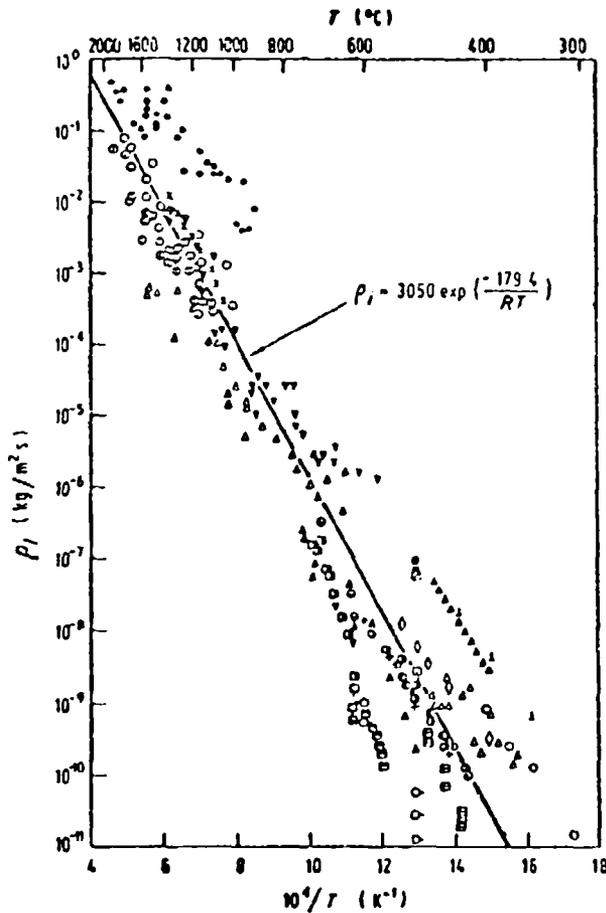
Figure B-9. Vaporization Process for A Carbon Slurry Fuel Droplet

One approach for solving this problem is to maximize the volatility difference between the internal (high density hydrocarbon) and external (hydrophile) phases of the carbon slurry emulsion. This would result in a droplet fragmentation process which forces individual or groups of carbon particles to separate from the parent droplet. Other approaches might involve some treatment of the carbon particles to result in repulsive forces upon heating or even a modified fuel injection technique. In any case, it is important to be able to observe the droplet vaporization process so that an understanding of these approaches may be gained and correlations for formulating slurries which minimize agglomeration may be developed.

Two unique types of fuel injection problems are encountered when using carbon dispersion fuels. The first involves the potential prevaporization of the hydrocarbon component of the fuel within hot fuel lines or the fuel nozzle. When 60% of the fuel is solid carbon, loss of even a small amount of liquid carrier will result in immediate plugging. Consequently, special care must be taken to insure against the fuel lines or nozzles reaching temperatures where prevaporization can take place. Further, the initial flow of slurry into the fuel lines and nozzle must occur with cold hardware and shut down must not allow the fuel to remain in hardware which becomes hot (i.e. it must be burned). In this case, deposition of carbon near the hot wall would result and this may eventually result in plugging. This phenomena is analogous to, but much more dramatic than, the afterburner spray bar plugging problem which occurs due to high temperature instability of liquid jet fuels.

The second problem involves deposition of carbon within the combustion system after injection. If the liquid fuel impinges on a hot surface, the liquid portion of the fuel will flash vaporize leaving a deposit of carbon behind. In addition, if the carbon in the combustion zone (after vaporization) is allowed to come close to a colder surface within the combustor, the carbon will be attracted to and deposit on the surface. In either case a substantial carbon deposit can build up distorting the aerodynamics of the combustion process and/or the hardware cooling scheme. Further problems can result if the carbon breaks away from the deposit site in masses large enough to erode downstream engine components. Deposits of soot in combustion systems have been shown to destroy turbine hardware in this manner.<sup>(37)</sup> These problems will require special attention in systems which utilize low pressure air atomization fuel injection methods. Prevention of carbon deposition on air swirling devices will be especially difficult.

Many of the postulated problems concerning the combustion of carbon slurries could be at least scoped if we had a dependable means of predicting carbon particle oxidation rates. However, the overall picture now extant of carbon particle and soot oxidation leaves much to be desired. A comparison study of the literature which includes measurements of soot oxidation as well as various forms of carbon particles, reveals that the range of burning time is quite large, encompassing several orders of magnitude (see Figure B-10). Even for a specific type of carbon, such as graphite, there is a range of almost two orders of magnitude. Clearly oxidation rates are in serious disagreement; there are virtually no conditions under which we can assume accurate knowledge of the time for carbon burnout.



### Key to Symbols in Figure

Ref. No.	Symbol	Material
5	●	Petroleum coke
(a)	▲	
6	■	
2	△	Brown-coal char
7	○	Lignite char
5	○	Anthracite
8	▲	
1	○	Semi-anthracite
5,9	▽	Bituminous-coal char
6	□	Metallurgical coke
10	x	Soot
6	⊗	Pitch coke
11	○	Pitch resin
12	⊕	Nuclear graphite
13	△	
14	○	
15	+	
15	⊥	Cracker carbon (uncatalysed)
15	⊥	Cracker carbon (catalysed)
16, (a)	⊕	AGKSP graphite
16, (b)	△	
17	○	AGKSP graphite
18	○	AUF
19	⊕	SPI
20	⊕	
19	⊕	SPI
21	⊕	Spectroscopic graphite
22	△	
(a)	○	Graphon
20	○	
20	○	
14	○	Purified carbons
20	○	Sterling FC
23	▽	Acheson F.C
23	▽	Acheson AFC4

(a) Tyler (personal communication, 1974)

(b) Wouterlood (personal communication, 1969)

Figure B-10. Variability in Available Data on Carbon Oxidation Rates  
(Reference 38)

Table B-1 provides carbon burnout time information for the conditions of interest to cruise missile combustion systems. Information was extracted from data or correlations were applied for conditions of 2000K and an oxygen partial pressure of one atmosphere. Some of this background information recognizes the influence of fuel-air ratio on burnout, but much assumes the carbon burning in a non-depletable atmosphere of oxygen--i.e. very fuel-lean. Such information under predicts the actual required time for burnout. It is evident that the disagreement for carbon burnout time among these previous works exceeds an order of magnitude. And the range of uncertainty, from less than one millisecond to ten, spans time requirements at which efficient slurry combustion would certainly appear to be feasible to times at which application of the concept is in serious doubt.

It should be noted that the possibility that burnout times may be on the order of one millisecond is extremely encouraging. If burnout time were on this order, the "lag" expected for carbon burnout may be negligible and the combustion process of a slurry may become very much like that of a liquid. Consequently, even if a burnout time for carbon of 2-3 ms were determined, motivation to increase the rate of burnout would remain with the overall objective of making the slurry behave as much like a liquid as possible. It is evident that the objective of developing an optimum carbon slurry fuel will be substantially enhanced by additional study of carbon oxidation chemistry. Oxidation kinetics of the actual carbon being utilized in slurry formulations should be established and the impact of various fuel formulation variables (especially catalyst behavior) evaluated.

The two phase combustion (rapid hydrocarbon oxidation and particulate consumption) of carbon dispersion fuels has four important implications. First, it is imperative that the combustion system provide sufficient residence time to consume the carbon particles. Since the carbon particles might comprise more than 50% of the fuel heating value, they must be efficiently consumed to realize the benefits of higher volumetric energy content. Secondly, the time delay experienced between energy release due to hydrocarbon oxidation and that due to consumption of the carbon will affect normally encountered combustion characteristics. Third, the presence of the carbon particles may alter the chemistry of the hydrocarbon pyrolysis process. Finally, the radiative characteristics of flames utilizing carbon slurries are expected to be substantially altered from those normally encountered.

Whether sufficient residence time for carbon particle consumption can be achieved is dependent on the type of system being considered and the fuel itself. Table B-2 lists the important combustion inlet temperatures, pressures and velocities as well as the stoichiometry considerations for the airbreathing engine systems of interest. Substantial variations are evident. Generally speaking, the carbon particle oxidation process is assisted by high temperature (near stoichiometric operation) and increasing pressure and lean mixture ratios (high oxygen partial pressure).

TABLE B-1

## CALCULATED CARBON BURNOUT TIMES

Researcher(s)	Type of Information	Burn Time for 300m $\mu$ Particle* (ms)
Essenhich (30)	Analytical Model of Carbon Oxidation	<1
Mulcahy and Smith (40)	Correlation of Data for Coal, Char Graphite, and Carbon Black	$\sim$ 2
Lee, Thring, and Beer (31)	Equation Based on Data for Oxidation of Soot	2.3
Bryant and Burdette (41)	Graphite Particles ( $\sim$ 5 $\mu$ ) Burning in a Flat Flame	0.9
Radcliff and Appleton (35)	Calculated from Soot Burnout Information at Gas Turbine Conditions	$\sim$ 8
Park and Appleton (34)	Shock Tube Measurements of Carbon Black ( $\sim$ 18m $\mu$ ) Oxidation	$\sim$ 10
Bradford and Bernard (42)	Carbon Black (100-200m $\mu$ ) Oxidation in Laboratory Burner	$\sim$ 5
Cassel (43)	Graphite (3-6 $\mu$ ) Oxidation in Laboratory Burner	$\sim$ 1

\* Where possible, information was extracted or correlations were applied for conditions of 2000K, P<sub>O<sub>2</sub></sub> = 1 atm.

TABLE B-2

## SUMMARY OF AEROPROPULSION COMBUSTION CONDITIONS

System	Inlet Conditions				
	Temperature (K)	Equivalence Ratio	Velocity (m/sec) or Mach Number	Pressure (X Ambient)	Air Condition
Mainburners	400-920	0.1-0.4	16<V<31	2.5-20	Non-vitiated
Ramjet	420-870	0.22-1.0	100<V<500	3.7	Non-vitiated

The rather obvious fuel parameters affecting consumption efficiency are carbon loading and particle size distribution. Inter-particle effects would increase and the temperature at the completion of combustion of the hydrocarbon portion of the fuel would decrease as the weight fraction of carbon in the fuel increased. Particle size can generally be considered as proportional to required burn time, as the surface kinetics require a reaction rate ( $\text{gm cm}^{-2} \text{sec}^{-1}$ ) which is independent of particle diameter. However, the influence of particle size distribution in a system with minimal excess air (say  $\phi > 0.7$ ) is significant. A frequently used example to illustrate the effect of distribution in pulverized coal combustion involves the case where a monosize distribution of particles is divided into two portions and one portion is further pulverized to develop monosize particles one half of the original size. While the first inclination would be to respond that overall burning time of the new fuel is decreased, more detailed examination indicates an increase in required residence time. The smaller particles are consumed first and produce an environment for completion of combustion of the larger particles which, relatively speaking, are starved in oxygen; the result is an overall longer total burning time. Consequently, minimization of the maximum particle size provides the most meaningful reduction in time for complete oxidation. Similar particle distribution characteristics must also be considered in developing carbon slurries for aeropulsion applications.

The types of combustion characteristics which can be altered by the presence of solid carbon in the fuel include the stability limits. Figure B-11 illustrates the shift in lean and rich stirred reactor blow out limits which might be expected. Because of the significant time lag associated with the carbon oxidation process, stability will be governed primarily by the heat release occurring during hydrocarbon oxidation. This shifts the stability maximum to a condition corresponding to stoichiometric based on hydrocarbon only, far richer than stoichiometric when the entire fuel is considered. Similar changes would be expected in ignition behavior and stirred reactor loading for optimum heat release rate.

The presence of the solid carbon may alter the pyrolysis process itself and/or the particulates may serve as nucleation sites for additional soot formation and agglomeration. This, of course, would cause additional difficulties in consumption of carbon and may lead to lower combustion efficiency (i.e., poor fuel utilization). However, it is unlikely that this affect would be significant since soot formation normally consumes less than 2% of the fuel carbon leading to only small decreases in combustion efficiency.

Because of the effectiveness of carbon particles as radiators of energy, the radiation field within the combustion device burning a carbon slurry may approach that of a black body radiator. This has a significant impact on the system hardware and may require improved cooling schemes to be applied in the case of a turbine engine. In the case of a ramjet dump combustor the protective ablating liner would receive increased heat flux and additional material might be required. The extent of modification required and the increase in system volume and weight must be considered in evaluating the net benefit of the slurry in extending system range.

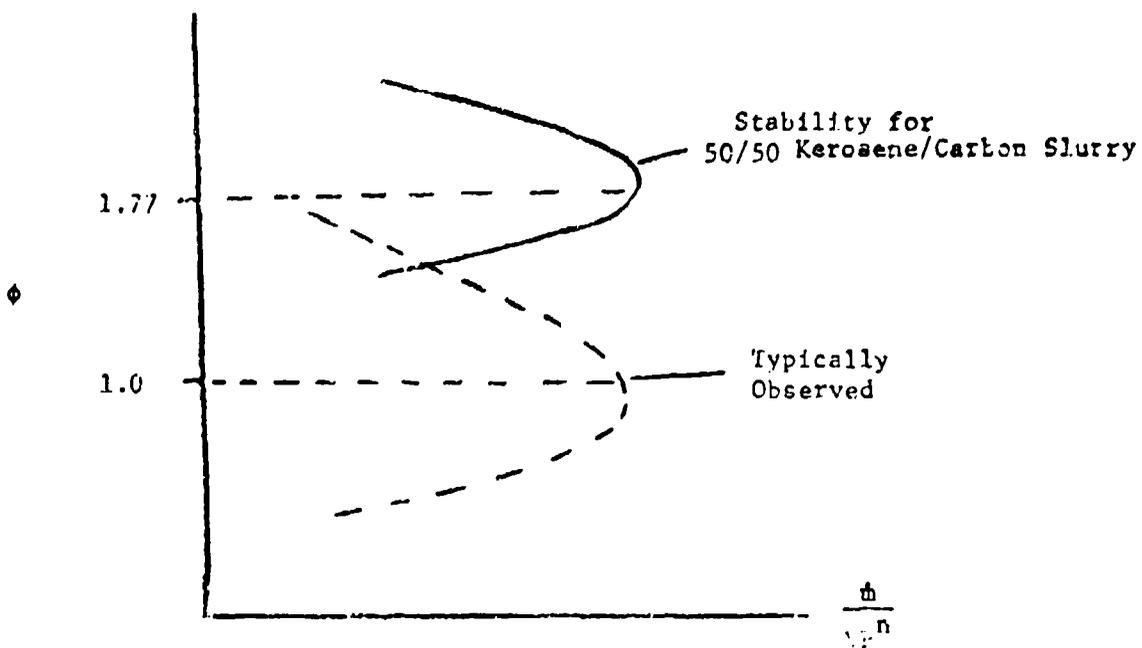


Figure B-11. Stability Considerations In Carbon Slurry Combustion

An additional consequence of incomplete combustion of carbon particles relates to their effect of the presence in the exhaust plume. The plume signature from a device not efficiently consuming carbon would be clearly distinguishable from that of a hydrocarbon burning system. Increased total radiation would result from the carbon particles which behave as "blackbody" radiators and the radiation would be broader than the CO<sub>2</sub>-band infrared plume radiation normally encountered. In addition, the plume would become visible allowing detection by a normal optical means. Obvious implications with respect to systems intended to defend against cruise missiles are apparent from this discussion.

#### Acceleration of Carbon Particle Oxidation

In addition to designing the combustion system to provide temperature, and oxygen concentration conditions to optimize the consumption of carbon particles, the process might benefit through the proper selection of the components of the "fuel package". The size distribution and type of carbon utilized may have a substantial effect and the use of certain metallic elements known to have smoke abatement potential can accelerate the carbon oxidation process.

The results of Magnussen<sup>(32)</sup> illustrate the importance of selecting the proper type of carbon for the slurry application. He points out that the surface reaction rates for soot are more than two orders of magnitude less than that for "carbon". As previously indicated, Appleton was successful in using pyrolytic graphite oxidation data to correlate soot consumption. One possible explanation for this contradiction given in Appleton's paper<sup>(27)</sup> is that the "carbon" data used by Magnussen was for the much more reactive isotropic forms of graphite (such as Reactor graphite).

Carbon appears in an almost infinite spectrum of shades of structural perfection and frequently samples cut from the same specimen exhibit significant differences in their reactivity. This difficulty applies to catalyzed and noncatalyzed reactions alike. Differences in reactivity have been related to surface structure. Isotropic forms of graphite appear to provide a large number of carbon atoms in "edge" positions in the more reactive prismatic plane. Pyrolytic graphite would have carbon atoms embedded within the basal plane of the particle surface. Investigation of these characteristics to select the carbon type which optimizes slurry burning rate is an absolutely essential element of this program.

The catalysis of the soot oxidation process by various metals including Mn, Fe, Co, Ni, and Ba is well known and some of these compounds are currently marketed (usually in the organometallic form) as smoke abatement additives for industrial gas turbine engines burning conventional liquid fuels. Significant reductions in gas turbine smoke visibility have been achieved using small concentrations of these compounds (50 ppmw of metal in the fuel). Use of metal containing additives in aviation turbines has been very limited due to the impact of metal deposition on the turbine after long periods (>50 hrs) of use. In the case of cruise missile ramjets or turbine engines using high density fuels, the short system life may allow additive utilization without significant impact on engine performance.

Some question regarding the additive mechanisms remains.<sup>(44,53)</sup> Claims that the additive affects the chemical processes leading to formation of ions which play a role in soot formation are supported by the known strong influences of electric fields on flames. The view that additives like Mn actually accelerate carbon oxidation, however, is supported by AFAPL experimental results<sup>(53)</sup> which illustrate that smoke emission can be significantly reduced while primary zone flame radiation (primarily due to luminous radiation from soot) is unaffected. It is likely that various additives function with different mechanisms. Naturally, this program is concerned only with those which catalyze soot oxidation and the Exxon approach will be to focus on such metallic elements.

Table B-3 illustrates data from which the acceleration effect of manganese might be calculated. These data were acquired using a T56 combustion rig<sup>(53)</sup> operated at inlet temperatures of 662 and 773K and an exhaust temperature of 1200K. JP-4 with a hydrogen content of 14.5 and a JP-4/xylene blend with a hydrogen content of 13.3 were the test fuels. Smoke emission was determined for the fuel without additive and with 50 ppmw manganese as CI-2, a commercially-marketed smoke abatement organometallic. Reductions in soot emissions of 80% or more were observed.

It is difficult to predict the effectiveness of these additives in accelerating the carbon oxidation of a slurry fuel. In the slurry fuel case particles may be an order of magnitude larger and present in much higher concentrations--only about 2% of the fuel carbon is converted to soot in a relatively smoky flame while the slurry can have 50% or more of its carbon as particulates. It should be noted, however, that additional methods for incorporating the smoke additives into slurries can be envisioned. One particularly attractive method considered in the Exxon approach is the incorporation of metals into the carbon particles themselves which may provide advantages relative to the concentration of catalyst near the carbon surface.

A number of workers have investigated, some qualitatively and some quantitatively, the relative activities of various catalysts for accelerating the oxidation of carbon. These relative activities are by no means universal but depend strongly on the particular experimental conditions used. Besides the all important condition of temperature, the experimental conditions determine such important parameters as size and porosity of catalyst particles (and thus their surface area), chemical state of the catalyst, intimacy of contact between catalyst and carbon surface, and relative amounts of catalyst on the carbon basal plane and prismatic faces.

The particular anion associated with a metal catalyst added in the form of salt can also have an important effect on the case of carbon oxidation. For example, Nebel and Cramer<sup>(54)</sup> give a relative activity series for lead salts, added in the amount of 0.2 mole %, in reducing the ignition temperature of carbon in air as follows:  $\text{CH}_3\text{COO}^- > \text{basic bromide} > \text{Br}^- > \text{monoxide} > \text{basic sulfate} > \text{NO}_3^- > \text{SO}_4^{2-} > \text{PO}_4^{3-}$ . The organic salts gave the greatest catalysis and the phosphate acted as an inhibitor.

TABLE B-3

EFFECT OF MANGANESE ON SOOT OXIDATION

	Combustor Inlet Temperature (°K)	Combustor Exhaust Temperature (°K)	Without Additive		With 50 ppm Mn		Reduction in Soot Mass (%)
			SN*	Mn in exhaust	SN*	Mn in exhaust	
JP-4 (H Content = 14.5%)	{ 662 773	1200	60.5	50	32.6	10	80
			49.3	27	24.5	6	81
JP-4 + Xylene (H Content = 13.3%)	{ 662 773	1200	70	85	39.2	15	82
			59	46	18.6	4	91

\* SAE Smoke Number from Reference 2-53.

\*\* At STP. Determined from SN using Champagne's correlation (2-54).

This extensive combination of parameters makes it virtually impossible to a priori select the optimum catalyst type/method of preparation/carbon type/carbon particle size. Further, it is not possible to experimentally evaluate the effectiveness of a formulation without a test at combustion conditions. Consequently, it is necessary to conduct the combustion testing simultaneously and iteratively with formulation work. The Exxon approach is to utilize small scale, well-characterized combustion devices which allow the accomplishment of such a program.

The above brief discussion of the possible catalytic effects in carbon oxidation shows that there is significant potential in this area to accelerate carbon particle oxidation. As a result of our preliminary review of the catalysis of carbon oxidation and our extensive expertise in combustion and catalysis, we will have, at our disposal, an extremely useful approach to accelerate the oxidation of carbon particles.

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## APPENDIX C

### PREPARATION OF HANSEN PLOTS

(1) The first step is to mark off a piece of graph paper to simulate a three dimensional cube corner opened out along the  $\delta_D$  axis. Paper ruled every 1/4 in. in pale blue is quite satisfactory. The center of the coordinate system is located about 1/3 of the way up and right from the lower left corner. The  $\delta_D$  scale is marked on both the left and lower axes, usually at the rate of one unit per inch. The  $\delta_P$  and  $\delta_H$  scales are put on the left and top axes, respectively, at twice the rate of  $\delta_D$  - usually 2 units per inch. (The basis for this is that  $\delta_D$  seems to interact twice as strongly as the others in most cases. The reason probably is that the London forces are omni-directional and insatiable, while the others are more selective so their energy ( $V\delta^2$ ) with a solid or another liquid is only about  $(1/2)^2$  or 25% that of the vapor-liquid interaction by which  $\delta$  is defined.) The effect is that most systems plot as circles in the three quadrants, representing the projections of a spherical shell dividing the strongest from the weaker interactions.

(2) The second step is to divide the data into ranking groups. The strongest interaction is assigned a conspicuous symbol, and should be applied to about 10% of the data. The weakest interaction should then have a symbol which is conspicuously different, this be applied to about 25% of the data. The three intermediate levels assigned other symbols, taking care to make the second-strongest distinctive from the strongest.

(3) Start plotting the strongest points, as follows: Locate  $\delta_D$  on the bottom axis, go right to the  $\delta_P$  value and mark. Then go up to the  $\delta_H$  and mark it. Last, go left to the  $\delta_D$  value and mark that. There will now be a mark in each of the active quadrants, the lower left being the inactive one. This process is repeated for each of the strongly interacting points. By now, it should be possible to visualize circles that will contain all the points, but do not mark them yet.

(4) Repeat the process with the weakest interaction points. These are the ones which define the area outside the circles, but it is no cause for concern if one or more falls right in the "strong" area on one of the quadrants. That merely means it is in the line-of-sight with the spherical surface in that one direction. The circles may be lightly drawn in with a compass, remembering that they must all have the same radius and that the centers must behave as if they were the parameters of a single probe liquid - that is, consistent across all the axes. It is all too easy to overlook an inconsistency on  $\delta_D$ .

(5) Continue to plot in the intermediate levels, pausing at each stage to consider changing the circles to avoid violations and reduce the radius. Unless this is done stepwise, the final plot may be confusing because it has so much information.

(6) After the last points are added, it may be desirable to put the job aside for a few hours, then resume with rested mind and eyes. The best possibility may then be drawn in fairly firmly. It is important that the circle exclude all but the two strongest classes. However, a few violations can be attributed to experimental error, defects in the parameter tables (not all liquids have been equally studied), or to specific interactions of an irreversible nature.

(7) If all efforts to resolve the data into a sphere fail, the possibility of a bimodal system must be considered. These arise in mixtures, some gross as with two powders but others as fine as a copolymer. Such a case may require two circles, but if the centers are close together an ellipse. Since the circles tend to differ in diameter, the "ellipse" may prove to be pear-shaped.

## APPENDIX D

### COMPUTER DATA REDUCTION PRINT-OUTS OF LFJSC EXPERIMENTAL RUNS

Computer print-outs of the first year's experimental data are presented in this appendix. An explanation of the run number indexing is given below.

<u>Run No.</u>	<u>Title</u>
100	Slurry Rate Experiments
110	Equivalence Ratio Experiments
120	Residence Time Experiments
150	Catalyst Experiments - 100 ppm Mn
160	Catalyst Experiments - 1000 ppm Mn
170	Catalyst Experiments - 1000 ppm Fe
180	Catalyst Experiments - 1000 ppm Pb
190	Experiments with Only Carbon Slurry
200	Particle Size Experiments
210	Carbon Loading Experiments
220	Catalyst Experiments - 1000 ppm Zr

Note: A and B denote duplicate runs.

I. Detailed mathematical explanation of iterative calculation of total moles flue gas produced and hydrogen mole fraction

Definition of symbols:

AFG	-	Assumed Mole of Flue Gas
$AXH_2O$	-	Assumed Mole Fraction of Water
$CH_2$ or HC	-	Total Hydrocarbons
$CX(I)$	-	Mole Fraction of Species (I) in Flue Gas Corrected to a Wet Basis
Delta	-	Percent Difference between Calculated and Assumed Values
Keq	-	Equilibrium Constant
MCFR	-	Moles Carbon from Fuel Mass Rates
MCFG	-	Moles Carbon from Flue Gas Analysis
MHFR	-	Moles Hydrogen (H) from Fuel Mass Rates
MHFG	-	Moles Hydrogen (H) from Flue Gas Analysis
MNFR	-	Moles Nitrogen ( $N_2$ ) from Mass Rates
MNFG	-	Moles Nitrogen ( $N_2$ ) from Flue Gas Analysis
MW	-	Molecular Weight
MUBC	-	Moles of Unburnt Carbon
$X(I)$	-	Mole Fraction of Species (I) in Flue Gas
$W(I)$	-	Fuel Elemental Weight Fraction for Species (I)
Z	-	Wet Flue Gas Analysis Correct Factor

Step 1: Assume values for moles flue gas (AFG) and mole fraction of water ( $AXH_2O$ )

$$\begin{aligned} AFG &= \text{total moles of air, oxygen, nitrogen, and fuels} \\ AXH_2O &= 0.07 \end{aligned}$$

Step 2: Determine wet flue gas analysis correction factor

$$Z = \frac{(\text{moles flue gas after water trap})}{(\text{moles flue gas before water trap})}$$

$$Z = 1 - AXH_2O + \text{humidity of air at } 10^\circ\text{C}$$

$$Z = 1.0124 - AXH_2O$$

Step 3: Convert dry basis mole fractions (X(I) to wet basis mole fractions (CX(I)

$$\begin{aligned} CXCO &= (XCO) (Z) \\ CXCO_2 &= (XCO_2) (Z) \\ CXO_2 &= (XO_2) (Z) \\ CXNO &= (XNO) (Z) \\ CXNO_2 &= (XNO_2) (Z) \\ CXH_2 &= (XH_2) (Z) \end{aligned}$$

Step 4: Calculate the CO mole fraction (CXCO) based on a carbon material balance only if the CO analyzed maximum concentration is exceeded.

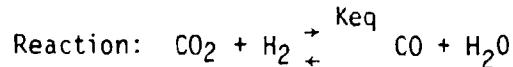
$$\text{Moles carbon from Fuel rates (MCFR)} = \text{Moles carbon from flue gas analysis (MCFG)}$$

$$MCFR = \frac{(\text{JP-10 mass rate}) (\text{WC in JP-10}) + (\text{slurry mass rate}) (\text{WC in slurry})}{\text{MW carbon}}$$

$$MCFG = (CXCO + CXCO_2 + XCH_2) (AFG) + MUBC$$

$$\therefore CXCO = \frac{MCFR - MUBC - AFG (CXCO_2 + XCH_2)}{AFG}$$

Step 5: Calculate the hydrogen mole fraction (CXH<sub>2</sub>) from the water-gas shift equilibrium reaction only if a measured value was not obtained



$$K_{eq} = \frac{(CXCO) (AXH_2)}{(CXCO_2) (CXH_2)} \quad \text{Where } K_{eq} = 4.80$$

$$\therefore CXH_2 = \frac{(CXCO) (AXH_2)}{(CXCO_2) (K_{eq})}$$

Step 6: Calculate the water mole fraction (XH<sub>2</sub>O) from a hydrogen balance

$$\text{Moles hydrogen (H) from fuel rates (MHFR)} = \text{Moles hydrogen (H) from Flue gas analysis (MHFG)}$$

$$MHFR = \frac{(\text{JP-10 mass rate}) (\text{WH in JP-10}) + (\text{slurry mass rate}) (\text{WH in slurry})}{\text{MW hydrogen}}$$

$$MHFG = 2(CXH_2) + XH_2O + XCH_2 (AFG)$$

$$\therefore XH_2O = \frac{MHFR - (2) (AFG) (CXH_2 + CH_2)}{(2) (AFG)}$$

Step 7: Percent difference between calculated water mole fraction (XH<sub>2</sub>O) and the assumed value (AXH<sub>2</sub>O)

$$\Delta H_2O = \text{Absolute value of } \left( \frac{XH_2O - AXH_2O}{XH_2O} \right)$$

Step 8: Compare calculated delta (H<sub>2</sub>O) with minimum acceptable data

If the calculated delta  $X_{H_2O}$  is greater than the acceptable delta, the calculated mole fraction ( $X_{H_2O}$ ) becomes the next assumed mole fraction ( $AX_{H_2O}$ ) and the iteration is repeated from step 2. If calculated data  $X_{H_2O}$  is less than or equal to the acceptable delta, this part of the iteration has converged.

Step 9: Calculate nitrogen mole fraction ( $X_{N_2}$ ) in flue gas

$$X_{N_2} = 1 - (CXCO_2 + CXCO + CXO_2 + XCH_2 + CXNO + CXNO_2 + CXH_2 + XH_2O)$$

Step 10: Calculate flue gas moles (FG) from a nitrogen ( $N_2$ ) balance

$$\text{moles nitrogen } (N_2) \text{ from flow rates (MNFR)} = \text{moles nitrogen } (N_2) \text{ from flue gas analysis (MNFG)}$$

MNFR = moles nitrogen from nitrogen mass rate + moles nitrogen from air mass rates +

$$\left( \frac{(\text{JP-10 mass rate}) \text{ WN in JP-10} + (\text{slurry mass rate}) \text{ (WN in slurry)}}{\text{MW Nitrogen } (N_2)} \right)$$

$$\text{MNFG} = (X_{N_2} + 0.5 (CXNO + CXNO_2)) \text{ FG}$$

$$\therefore \text{FG} = \frac{\text{MNFR}}{X_{N_2} + 0.5 (CXNO + CXNO_2)}$$

Step 11: Percent difference between calculated moles flue gas (FG) and the assumed value (AFG)

$$\text{Delta FG} = \text{Absolute value of } \left( \frac{\text{FG} - \text{AFG}}{\text{FG}} \right)$$

Step 12: Compare calculated delta FG with minimum acceptable delta

If the calculated delta FG is greater than the acceptable delta, the calculated values for moles flue gas and water mole fraction become the next set of assumed values and the iteration is repeated from step 2. If calculated delta FG is less than or equal to the acceptable delta, the entire iteration has converged.

LIQUID FUEL JET STIRRED COMBUSTOR DATA OUTPUT

DATE : OCT 2, 1979  
 RUN NUMBER: 100-A  
 FRONT FUEL: STATEK MT 30K  
 REAR FUEL : JP-10

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 312.0  
 REAR FUEL 534.0

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 10044.0  
 REAR FUEL 9436.9

CARBON MATERIAL BALANCE

96.9

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 4099.0  
 REAR COMBUSTION AIR 4098.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 3137.1

OXYGEN MATERIAL BALANCE

101.4

NITROGEN FLOW RATES (GRAMS/HR)

FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC FUEL TO OXIDANT RATIO 0.322  
 F FUEL 0.304  
 R FUEL 0.099  
 OX OVERALL 0.270  
 FUEL TO OXIDANT RATIO OVERALL 0.31  
 F FUEL 0.54  
 R FUEL 0.87  
 OX OVERALL 0.83

BASED ON MASS FEED RATES  
 FUEL TO OXIDANT RATIO OVERALL 0.31  
 F FUEL 0.54  
 R FUEL 0.87

BASED ON FLUE GAS ANALYSIS  
 FUEL TO OXIDANT RATIO OVERALL 0.258  
 FUEL TO OXIDANT RATIO OVERALL 0.83

WET FLUE GAS ANALYSIS (MOLE PERCENT)

TOTAL GH-MOLES/HR 422.4  
 CO 0.37  
 CO2 14.03  
 HC 0.0007  
 O2 4.08  
 NO 0.0  
 NOX 0.0  
 N2 71.02  
 H2O 10.48

SOOT MEASUREMENT (GRAMS/HR)

3.8

COMBUSTION TEMPERATURE (K)

1943.121 5.01

RESIDENCE TIME (MILLISEC)

6.3

EFFICIENCIES  
 CARBON EFFICIENCY 96.0  
 COMBUSTION 98.1

LIQUID FUEL JET STIRRED COMBUSTION DATA OUTPUT

DATE : OCT 2, 1979  
 RUN NUMBER: 100-B

FRONT FUEL: STATIX MT 30%  
 REAR FUEL: JP-10

CARBON MATERIAL BALANCE

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL REAR FUEL

96.9

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL REAR FUEL

534.0

9436.9

OXIDANT FLOW RATES (GRAMS/HR)

FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 762.0  
 FRONT COMBUSTION AIR 4094.0  
 REAR COMBUSTION AIR 4094.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 3137.1

OXYGEN MATERIAL BALANCE

101.4

NITROGEN FLOW RATES (GRAMS/HR)

FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 164.0  
 TOTAL 164.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC BASED ON MASS FEED RATES  
 FUEL TO OXIDANT RATIO EQUIVALENCE RATIO  
 F FUEL P FUEL OVERALL F FUEL R FUEL OVERALL

0.322 0.304 0.009 0.170 0.270 0.31 0.56 0.87 0.258 0.83

BASED ON FLUE GAS ANALYSIS

FUEL TO OXIDANT RATIO EQUIVALENCE RATIO

WET FLUE GAS ANALYSIS (MOLE PERCENT)

TOTAL GM-MOLES/HR		COMBUSTION TEMPERATURE (K)				RESIDENCE TIME (MILLISEC)				SOOT MEASUREMENT (GRAMS/HR)	
422.4	0.17	14.03	0.0007	4.04	0.0	0.0	71.02	0.0146	10.48	3.7	
		CO	CO2	HC	NO	NOX	N2	H2	H2O		

1963.12( 5.0)

1963.12( 5.0)

6.3

EFFICIENCIES  
 CARBON EQUIPMENT COMBUSTION

94.1

94.3



LIQUID FUEL JET STIRRED COMBUSTOR DATA OUTPUT

DATE 1 OCT 2, 1979  
 RUN NUMBER: 101-B  
 FRONT FUEL: STATEK MT 308  
 REAR FUEL: JP-10

CARRON MATERIAL BALANCE

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 440.0  
 REAR FUEL 440.0

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 10044.0  
 REAR FUEL 9436.9

91.7

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 4008.0  
 REAR COMBUSTION AIR 4098.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 11371.1

OXYGEN MATERIAL BALANCE 96.3

NITROGEN FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC BASED ON MASS FEED RATES  
 FUEL TO OXIDANT RATIO FUEL TO OXIDANT RATIO FUEL TO OXIDANT RATIO  
 F FUEL H FUEL OVERALL F FUEL H FUEL OVERALL F FUEL H FUEL OVERALL

0.272 0.304 0.111 0.157 0.264 0.34 0.59 0.85 0.251 0.81

NET FUEL GAS ANALYSIS (MOLE PERCENT)

TOTAL GM-MOLES/HR 416.5

CO	CO2	H2	H2O	NO	NO2	N2	H2	H2O
0.34	13.14	0.0010	4.19	0.0	0.0	72.04	0.0017	10.24

SOOT MEASUREMENT (GRAMS/HR) 4.0

COMBUSTION TEMPERATURE (°F) RESIDENCE TIME (MILLISEC)

1853.12 ( 5.0) 6.3

EFFICIENCIES  
 CARBON HYDROGEN COMBUSTION  
 96.7 0.4

LIGNID FUEL JET STIRRED COMBUSTOR DATA OUTPUT

DATE : OCT 2, 1979  
 RUN NUMBER: 102-A

FRONT FUEL: STALEX WT 308  
 REAR FUEL : JP-10

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 366.0  
 REAR FUEL 47.0

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 94.14.9  
 REAR FUEL 1004.0

CARBON MATERIAL BALANCE  
 94.4

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 4094.0  
 REAR COMBUSTION AIR 4094.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 3137.1

OXYGEN MATERIAL BALANCE  
 94.4

NITROGEN FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT POINT 168.0  
 TOTAL 168.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC  
 FUEL TO OXIDANT RATIO  
 F FUEL H FUEL  
 0.322 0.334

BASED ON MASS FEED RATES  
 FUEL TO OXIDANT RATIO  
 F FUEL H FUEL OVERALL  
 0.151 0.117 0.268

BASED ON FLUE GAS ANALYSIS  
 FUEL TO OXIDANT RATIO  
 EQUIVALENCE RATIO  
 0.257 0.82

WET FLUE GAS ANALYSIS (MOLE PERCENT)

CO	CO2	HC	H2O	NOX	N2	H2	SOOT MEASUREMENT (GRAMS/HR)
0.40	13.64	0.0004	4.30	0.0	71.77	0.0440	7.7

COMBUSTION TEMPERATURE (K)  
 1904.1 ± 1 (5.0)

RESIDENCE TIME (MILLISEC)  
 6.1

EFFICIENCIES  
 CARBON BURNOUT COMBUSTION

94.4 97.8

LIQUID FUEL JET STIPPED COMBUSTOR DATA OUTPUT

DATE : OCT 2, 1979  
 RUN NUMBER: 102-H  
 FRONT FUEL : STATEX HT 30%  
 REAR FUEL : JH-10

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 474.0  
 REAR FUEL 366.0  
 FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 10044.0  
 REAR FUEL 9436.9  
 CARRON MATERIAL BALANCE  
 94.2

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 4098.0  
 REAR COMBUSTION AIR 4098.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 3137.1  
 OXYGEN MATERIAL BALANCE  
 98.4  
 NITROGEN FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC  
 FUEL TO OXIDANT RATIO  
 F FUEL 0.322  
 R FUEL 0.304  
 0.151  
 0.117  
 0.268  
 0.47  
 0.38  
 0.85  
 0.256  
 0.82  
 BASED ON MASS FEED RATES  
 FUEL TO OXIDANT RATIO  
 EQUIVALENCE RATIO  
 F FUEL R FUEL OVERALL  
 0.47 0.38 0.85  
 BASED ON FLUE GAS ANALYSIS  
 FUEL TO OXIDANT RATIO  
 EQUIVALENCE RATIO  
 0.256 0.82

WET FLUE GAS ANALYSIS (MOLE PERCENT)

TOTAL CM-MOLES/HR 418.0  
 CO 0.40  
 CO2 13.68  
 HC 0.0008  
 H2 0.0440  
 H2O 9.81  
 NO 0.0  
 NOX 0.0  
 N2 71.77  
 O2 4.70  
 SOOT MEASUREMENT (GRAMS/HR)  
 6.7

COMBUSTION TEMPERATURE (K)

1998.1 ± ( 5.0)  
 RESIDENCE TIME (MILLISEC)  
 6.1

EFFICIENCIES

CARRON THROUGH COMBUSTION  
 95.3  
 97.9

LIQUID FUEL JET STIRRED COMBUSTOR DATA OUTPUT

DATE : OCT 2, 1979

RUN NUMBER: 103-A

FRONT FUEL: STATEX MT 30X

REAR FUEL: JP-10

FUEL FEED RATES (GRAMS/HR) CARBON MATERIAL BALANCE

FRONT FUEL 630.0 REAR FUEL 252.0 FRONT FUEL 10044.0 REAR FUEL 9436.9 TOTAL 89.3

OXIDANT FLOW RATES (GRAMS/HR) OXYGEN MATERIAL BALANCE

FRONT ATOMIZING AIR 1770.0 REAR ATOMIZING AIR 768.0 FRONT COMBUSTION AIR 4098.0 REAR COMBUSTION AIR 4098.0 OXYGEN 636.0 TOTAL OXIDANT 3137.1

NITROGEN FLOW RATES (GRAMS/HR)

FRONT ATOMIZING 0.0  
REAR ATOMIZING 0.0  
SIGHT PORT 168.0  
TOTAL 168.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC FUEL TO OXIDANT RATIO 0.322 0.404 0.201 0.080 0.281 0.62 0.26 0.89 0.258 0.81

BASED ON MASS FEED RATES  
FUEL TO OXIDANT RATIO OVERALL F FUEL R FUEL OVERALL

BASED ON FLUE GAS ANALYSIS  
FUEL TO OXIDANT RATIO OVERALL

WET FLUE GAS ANALYSIS (MOLE PERCENT)

TOTAL GM-MOLES/HR 417.3 CO 0.53 CO2 13.5% H2O 0.0 NOX 0.0 N2 71.90 H2O 9.78

SOOT MEASUREMENT (GRAMS/HR)

8.3

COMBUSTION TEMPERATURE (K) RESIDENCE TIME (MILLISEC)

1993.1 ± 10.0 6.1

EFFICIENCIES COMBUSTION

CARBON MONOXIDE 95.6

COMBUSTION 97.4

LIQUID FUEL JEC STIRRED COMBUSTOR DATA OUTPUT

DATE : OCT 2, 1979  
 RUN NUMBER: 103-H  
 FRONT FUEL: STATEX HT J08  
 REAR FUEL : JP-10

FUEL FEED RATES (GRAMS/HR)		CARBON MATERIAL BALANCE
FRONT FUEL	252.0	
REAR FUEL		89.3
FUEL HEATING VALUES (CAL/GRAM)		
FRONT FUEL	10044.0	
REAR FUEL	9436.9	

OXIDANT FLOW RATES (GRAMS/HR)		OXYGEN MATERIAL BALANCE		NITROGEN FLOW RATES (GRAMS/HR)
FRONT ATOMIZING AIR	1770.0		97.5	FRONT ATOMIZING
REAR ATOMIZING AIR	768.0			REAR ATOMIZING
FRONT COMBUSTION AIR	4098.0			SIGHT PORT
REAR COMBUSTION AIR	4098.0			TOTAL
OXYGEN	636.0			168.0
TOTAL OXIDANT	3137.1			

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC		BASED ON MASS FEED RATES		
FUEL TO OXIDANT RATIO		EQUIVALENCE RATIO		BASED ON FLUE GAS ANALYSIS
F FUEL	R FUEL	F FUEL	R FUEL	FUEL TO OXIDANT RATIO
0.322	0.304	0.201	0.090	0.257
		0.62	0.26	0.81
		0.281	0.89	

TOTAL GWT-MOLES/HR		WET FLUE GAS ANALYSIS (MOLE PERCENT)			SOOT MEASUREMENT (GRAMS/HR)			
		CO	CO2	HC	NOX	N2	H2	H2O
417.3		0.5	13.54	0.0	6.21	0.0	71.90	0.0362
							9.78	8.2

COMBUSTION TEMPERATURE (K)

1993.1 ± 10.0

6.1

EFFICIENCIES  
 CARBON BURNOUT COMBUSTION

95.7

97.6

LIQUID FUEL JET STIRRED COMBUSTOR DATA OUTPUT

DATE : OCT 4, 1979  
 RUN NUMBER: 110-A

FRONT FUEL: STATEX MT 30%  
 REAR FUEL: JP-10

CARBON MATERIAL BALANCE

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 288.0  
 REAR FUEL 348.0

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 10044.0  
 REAR FUEL 9436.9

98.1

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 4098.0  
 REAR COMBUSTION AIR 4058.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 3137.1

OXIDANT MATERIAL BALANCE 104.4

NITROGEN FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC FUEL TO OXIDANT RATIO  
 F FUEL R FUEL 0.372 0.304

BASED ON MASS FEED RATES  
 FUEL TO OXIDANT RATIO OVERALL F FUEL R FUEL OVERALL 0.111 0.092 0.203 0.34 0.30 0.65

BASED ON FLUE GAS ANALYSIS  
 FUEL TO OXIDANT RATIO OVERALL 0.190 0.61

WET FLUE GAS ANALYSIS (MOLE PERCENT)  
 CO 0.15  
 CO2 10.91  
 HC 0.0002  
 H2 0.0060  
 H2O 7.49  
 NO 0.0  
 NOX 0.0  
 N2 71.70

SOOT MEASUREMENT (GRAMS/HR)  
 6.6

COMBUSTION TEMPERATURE (K) 1773.15 (40.0)  
 RESIDENCE TIME (MILLISEC) 7.0

EFFICIENCIES  
 CARBON BURNOUT 93.7  
 COMBUSTION 98.5

LIQUID FUEL JET STIRRED COMBUSTION DATA OUTPUT

DATE : OCT 4, 1979  
 RUN NUMBER: 110-M  
 FRONT FUEL: STATEX MT 30%  
 REAR FUEL: 1 JP-10

FUEL FEED RATES (GRAMS/HR)	FUEL HEATING VALUE (CAL/GRAM)	CARBON MATERIAL BALANCE
FRONT FUEL	FRONT FUEL	
REAR FUEL	REAR FUEL	
348.0	10045.0	9436.9
288.0		98.1

OXIDANT FLOW RATES (GRAMS/HR)	OXYGEN MATERIAL BALANCE	NITROGEN FLOW RATES (GRAMS/HR)
FRONT ATOMIZING AIR	104.4	FRONT ATOMIZING
REAR ATOMIZING AIR		REAR ATOMIZING
FRONT COMBUSTION AIR		SIGHT PORT
REAR COMBUSTION AIR		TOTAL
OXYGEN		168.0
TOTAL OXIDANT		

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC	BASED ON MASS FEED RATES		BASED ON FUEL GAS ANALYSIS	
FUEL TO OXIDANT RATIO	FUEL TO OXIDANT RATIO	EQUIVALENCE RATIO	FUEL TO OXIDANT RATIO	EQUIVALENCE RATIO
F FUEL	R FUEL	OVERALL	F FUEL	R FUEL
0.372	0.304	0.203	0.34	0.30
			0.34	0.65
			0.190	0.61

WET FUEL GAS ANALYSIS (MOLE PERCENT)

TOTAL GM-MOLS/HR	CO	CO2	HC	O2	NO	NOX	N2	H2O	SOOT MEASUREMENT (GRAMS/HR)
418.5	0.15	10.91	0.0002	9.75	0.0	0.0	71.70	0.0060	6.7

COMBUSTION TEMPERATURE (K) RESIDENCE TIME (MILLIFEC)

1773.12 (40.0) 7.0

EFFICIENCIES COMBUSTION

CARBON BURNOUT 91.6

98.5

LIQUID FUEL JET STIRRED COMBUSTOR DATA OUTPUT

DATE : OCT 4, 1979  
 RUN NUMBER: 111-A

FRONT FUEL STATEX MT 30x  
 REAR FUEL : JP-10

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 344.0  
 REAR FUEL 344.0

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 10664.0  
 REAR FUEL 5436.9

CARBON MATERIAL BALANCE

96.9

OXIDANT FLOW RATES (GRAMS/HR)

FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 4098.0  
 REAR COMBUSTION AIR 4098.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 3137.1

OXYGEN MATERIAL BALANCE

96.7

NITROGEN FLOW RATES (GRAMS/HR)

FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

STOICHIOMETRIC  
 FUEL TO OXIDANT RATIO  
 F FUEL W FUEL 0.322 0.304

FUEL OXIDANT MIXTURE CONDITIONS

BASED ON MASS FEED RATES  
 FUEL TO OXIDANT RATIO 0.233 0.233  
 F FUEL R FUEL OVERALL F FUEL W FUEL OVERALL 0.34 0.40 0.75

BASED ON FLUE GAS ANALYSIS  
 FUEL TO OXIDANT RATIO 0.234  
 EQUIVALENCE RATIO 0.75

WET FLUE GAS ANALYSIS (MOLE PERCENT)

TOTAL GAS-MOLES/HR		WET FLUE GAS ANALYSIS (MOLE PERCENT)		SOOT MEASUREMENT (GRAMS/HR)	
CO	0.19	CO <sub>2</sub>	12.53	HC	0.0002
		O <sub>2</sub>	5.82	NO	0.0
		N <sub>2</sub>	72.51	N <sub>2</sub>	0.0170
		N <sub>2</sub>	0.0	H <sub>2</sub>	0.93
		N <sub>2</sub>	0.0	H <sub>2</sub> O	4.9

COMBUSTION TEMPERATURE (K)

1853.12 (15.0)

RESIDENCE TIME (MILLISEC)

6.6

EFFICIENCIES  
 CARBON NUMBER COMBUSTION

95.3

98.6

(TODD FUEL JET STOPPED COMBUSTOR DATA OUTPUT

DATE : OCT 4, 1979  
 RUN NUMBER: 111-M

FRONT FUEL: STATED MT 30x  
 REAR FUEL: JP-10

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 348.0  
 REAR FUEL 384.9

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 10044.0  
 REAR FUEL 9436.9

CARBON MATERIAL BALANCE  
 96.8

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 4098.0  
 REAR COMBUSTION AIR 4098.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 3137.0

OXYGEN MATERIAL BALANCE  
 96.7

NITROGEN FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC  
 FUEL TO OXIDANT RATIO  
 F FUEL R FUEL  
 0.322 0.304

BASED ON MASS FEED RATES  
 FUEL TO OXIDANT RATIO  
 F FUEL R FUEL OVERALL  
 0.111 0.122 0.233

BASED ON FLUE GAS ANALYSIS  
 FUEL TO OXIDANT RATIO  
 EQUIVALENCE RATIO OVERALL  
 0.34 0.40 0.75  
 0.234 0.75

WET FLUE GAS ANALYSIS (MOLE PERCENT)

TOTAL GM-MOLES/HR  
 413.8

CO 0.19  
 CO2 12.53  
 HC 0.0002  
 O2 5.42  
 NO 0.0  
 NOX 0.0

SOOT MEASUREMENT (GRAMS/HR)  
 H2 0.0170  
 H2O 0.93  
 4.2

COMBUSTION TEMPERATURE (K)

1853.12 ( 15.0)

RESIDENCE TIME (MILLISEC)

6.6

EFFICIENCIES  
 CARBON BURDENT COMBUSTION

96.0

98.7

LIQUID FUEL JET STIRRED COMBUSTION DATA OUTPUT

DATE : OCT 4, 1979  
 RUN NUMBER: 112-A

FRONT FUEL: STATEX MT 30%  
 REAR FUEL: JP-10

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 480.0  
 REAR FUEL 348.0

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 10044.0  
 REAR FUEL 9435.9

CARBON MATERIAL BALANCE

94.6

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 4098.0  
 REAR COMBUSTION AIR 4098.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 3137.1

OXYGEN MATERIAL BALANCE

96.6

NITROGEN FLOW RATES (GRAMS/HR)

FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC FUEL TO OXIDANT RATIO  
 F FUEL R FUEL F FUEL R FUEL OVERALL F FUEL R FUEL OVERALL

BASED ON MASS FEED RATES

BASED ON FLOE GAS ANALYSIS

0.322 0.304 0.111 0.153 0.264 0.34 0.50 0.85 0.258 0.83

FUEL TO OXIDANT RATIO

EQUIVALENCE RATIO

F FUEL R FUEL OVERALL

EQUIVALENCE RATIO

WET FLOE GAS ANALYSIS (MOLE PERCENT)

SOOT MEASUREMENT (GRAMS/HR)

TOTAL GM-MOLES/HR 416.8  
 CO 0.34 CO2 13.62 HC 0.0002 H2 0.0130 H2O 10.22  
 NO 0.0 NOX 0.0 N2 71.98

COMBUSTION TEMPERATURE (K)

RESIDENCE TIME (MILLISEC)

1923.1 (15.0)

6.6

EFFICIENCIES  
 CARBON EFFICIENCY 98.4  
 COMBUSTION 98.4

LIQUID FUEL JET STIRRED COMBUSTOR DATA OUTPUT

DATE 1 OCT 4, 1979  
 RUN NUMBER 112-B

FRONT FUEL: STATEX MT 30X  
 REAR FUEL: JP-10

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 349.0  
 REAR FUEL 480.0

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 10044.0  
 REAR FUEL 9436.9

CARBON MATERIAL BALANCE  
 94.7

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 4098.0  
 REAR COMBUSTION AIR 4098.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 3137.1

OXYGEN MATERIAL BALANCE  
 96.6

NITROGEN FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC  
 FUEL TO OXIDANT RATIO  
 F FUEL 0.372  
 H FUEL 0.304

BASED ON MASS FEED RATES  
 FUEL TO OXIDANT RATIO  
 F FUEL 0.111  
 R FUEL 0.153  
 OVERALL 0.264

BASED ON FLUE GAS ANALYSIS  
 FUEL TO OXIDANT RATIO  
 0.34  
 0.50  
 0.85  
 0.259  
 0.83

WET FLUE GAS ANALYSIS (MOLE PERCENT)

TOTAL GM-MOLES/HR  
 416.8

CO 0.34  
 CO2 13.62  
 HC 0.0002  
 H2 3.82  
 H2O 0.0  
 NO 0.0  
 NOX 0.0

SOOT MEASUREMENT (GRAMS/HR)  
 4.20  
 10.72  
 3.9

COMBUSTION TEMPERATURE (K)  
 1923.1 ± 15.0

RESIDENCE TIME (MILLISEC.)  
 6.4

EFFICIENCIES  
 CARBON BURROUT 95.3  
 COMBUSTION 98.4

LIQUID FUEL JET STIRRED COMBUSTOR DATA OUTPUT

DATE : OCT 4, 1979  
 RUN NUMBER: 113-A

FRONT FUEL: STALEX MT 30%  
 REAR FUEL: JP-10

FUEL FEED RATES (GRAMS/HR)	FUEL HEATING VALUES (CAL/GRAM)	CARBON MATERIAL BALANCE
FRONT FUEL 344.0	FRONT FUEL 10044.0	
REAR FUEL 576.0	REAR FUEL 9436.9	97.3

OXIDANT FLOW RATES (GRAMS/HR)	OXYGEN MATERIAL BALANCE	NITROGEN FLOW RATES (GRAMS/HR)
FRONT ATOMIZING AIR 1770.0	98.0	FRONT ATOMIZING 0.0
REAR ATOMIZING AIR 768.0		REAR ATOMIZING 0.0
FRONT COMBUSTION AIR 4098.0		SIGHT PORT 168.0
REAR COMBUSTION AIR 4098.0		TOTAL 168.0
OXYGEN 636.0		
TOTAL OXIDANT 3137.1		

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC	BASED ON MASS FEED RATES		BASED ON FLUE GAS ANALYSIS	
FUEL TO OXIDANT RATIO	FUEL TO OXIDANT RATIO	EQUIVALENCE RATIO	FUEL TO OXIDANT RATIO	EQUIVALENCE RATIO
F FUEL 0.322	F FUEL 0.111	F FUEL 0.34	0.293	0.94
R FUEL 0.304	R FUEL 0.144	R FUEL 0.60		
	OVERALL 0.295	OVERALL 0.95		

TOTAL GAS-SOLIDS/HR	WET FLUE GAS ANALYSIS (MOLE PERCENT)				SOOT MEASUREMENT (GRAMS/HR)
422.6	CO	CO2	H2	H2O	
	0.24	14.82	0.0002	1.40	0.0
					0.1510
					11.28
					4.6

COMBUSTION TEMPERATURE (K) RESIDENCE TIME (MILLISEC)

1963.1 (10.0) 6.2

EFFICIENCIES CARBON MONUMENT COMBUSTION

95.6 96.1



LIQUID FUEL JET STIRRED COMBUSTOR DATA OUTPUT

DATE : OCT 4, 1979  
 RUN NUMBER: 114-A  
 FRONT FUEL: STATEX HT 30%  
 REAR FUEL: JP-10

CARBON MATERIAL BALANCE

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 348.0 REAR FUEL 672.0  
 FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 10044.0 REAR FUEL 9436.9  
 93.5

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 4098.0  
 REAR COMBUSTION AIR 4098.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 3137.0

OXYGEN MATERIAL BALANCE  
 99.6

NITROGEN FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC FUEL TO OXIDANT RATIO  
 F FUEL 0.322 R FUEL 0.304  
 BASED ON MASS FEED RATES  
 FUEL TO OXIDANT RATIO OVERALL 0.325  
 F FUEL 0.214 R FUEL 0.214  
 EQUIVALENCE RATIO 1.05  
 F FUEL 0.34 R FUEL 0.71  
 BASED ON FLUE GAS ANALYSIS  
 FUEL TO OXIDANT RATIO 0.305  
 EQUIVALENCE RATIO 0.99

WET FLUE GAS ANALYSIS (MOLE PERCENT)

TOTAL GM-MOLES/HR 430.7  
 CO 2.68 CO2 13.91 HC 0.0050 H2 69.66 H2O 12.70  
 NO 0.0 NOX 0.0  
 SOOT MEASUREMENT (GRAMS/HR) 4.7

COMBUSTION TEMPERATURE (K) 1983.1 ± (20.0)  
 RESIDENCE TIME (MILLISEC) 6.2

EFFICIENCIES  
 CARBON RIPRODUC COMBUSTION 95.5  
 51.5

LIPPED FUEL JET STRIPED COMBUSTION DATA OUTPUT

DATE : OCT 22 1979  
 RUN NUMBER 116-A  
 FRONT FUEL : STATEX MT 102  
 REAR FUEL : JP-10

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 348.0  
 REAR FUEL 672.0  
 CARRON MATERIAL BALANCE 93.6

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 10044.0  
 REAR FUEL 9436.9

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 4098.0  
 REAR COMBUSTION AIR 4098.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 3137.1

HYDROGEN FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

OXYGEN MATERIAL BALANCE 99.6

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC FUEL TO OXIDANT RATIO 0.372  
 F FUEL 0.311  
 R FUEL 0.214  
 OVERALL 0.325

BASED ON MASS FEED RATES  
 FUEL TO OXIDANT RATIO 0.34  
 F FUEL 0.71  
 R FUEL 1.05  
 OVERALL 1.05

BASED ON FLUE GAS ANALYSIS  
 FUEL TO OXIDANT RATIO 0.306  
 EQUIVALENCE RATIO 0.99

TOTAL GM-MOLES/HR 470.7

WET FLUE GAS ANALYSIS (MGLE PERCENT)

CO	2.68	CO2	13.91	HC	0.0050	NO	0.0	NOX	0.0
					1.42		0.0		69.66
									0.3140
									17.20

SOOT MEASUREMENT (GRAMS/HR) 5.9

COMBUSTION TEMPERATURE (°F) 1943.15 (20.0)  
 RESIDENCE TIME (MILLISEC) 6.2

EFFICIENCIES  
 CARBON SUBNOBT 94.3  
 COMBUSTION 91.6



LIQUID FUEL STATIONED COMBUSTION DATA OUTPUT

DATE : OCT 4, 1979  
 RUN NUMBER: 115-R  
 FRONT FUEL: STATER MT JUS  
 REAR FUEL : JP-10

FUEL FLOW RATES (GRAMS/HR)  
 FRONT FUEL 10045.0  
 REAR FUEL 1600.0  
 CARRON MATERIAL BALANCE  
 94.2

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 43000  
 REAR FUEL 43000

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 17750  
 REAR ATOMIZING AIR 700  
 FRONT COMBUSTION AIR 40200  
 REAR COMBUSTION AIR 40000  
 TOTAL OXIDANT 100450  
 OXYGEN MATERIAL BALANCE  
 104.0

NITROGEN FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

FUEL OXIDANT MIXTURE CONDITIONS

BASED ON MASS FEED RATES  
 FUEL TO OXIDANT RATIO EQUIVALENCE RATIO  
 F FUEL R FUEL OVERALL F FUEL R FUEL OVERALL  
 0.332 0.332 0.180 0.220 0.400 0.56 0.72 0.362 1.16

WET FLUE GAS ANALYSIS (MOLE PERCENT)

WET FLUE GAS ANALYSIS (MOLE PERCENT)	SOOT MEASUREMENT (GRAMS/HR)
CO 0.11	H2 0.20
CO2 11.55	H2O 12.37
HC 0.0750	N2 66.06
NO 1.16	N2 1.6420
NOX 0.0	12.37
O2 0.0	37.0

COMBUSTION TEMPERATURE (K)  
 1974.1 (10.0)  
 RESIDENCE TIME (MILLISEC)  
 6.2

EFFICIENCIES  
 CARRON EFFICIENT COMBUSTION  
 74.1 74.7

LIQUID FUEL JET STIRRED COMBUSTION DATA OUTPUT

DATE : OCT 4, 1979  
 RUN NUMBER : 116-A  
 FRONT FUEL: STATEX WT. 30X  
 REAR FUEL : JP-10

FUEL FEED RATES (GRAMS/HR)	FUEL HEATING VALUES (CAL/GRAM)	CARBON MATERIAL BALANCE
FRONT FUEL	FRONT FUEL	
REAR FUEL	REAR FUEL	
590.0	10044.0	9436.9
		NOT APPLICABLE

OXIDANT FLOW RATES (GRAMS/HR)	OXYGEN MATERIAL BALANCE	NITROGEN FLOW RATES (GRAMS/HR)
FRONT ATOMIZING AIR	NOT APPLICABLE	FRONT ATOMIZING
REAR ATOMIZING AIR		REAR ATOMIZING
FRONT COMBUSTION AIR		SIGHT PORT
REAR COMBUSTION AIR		TOTAL
OXYGEN		168.0
TOTAL OXIDANT		168.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC	BASED ON MASS FEED RATES		BASED ON FLUE GAS ANALYSIS	
FUEL TO OXIDANT RATIO	FUEL TO OXIDANT RATIO	EQUIVALENCE RATIO	FUEL TO OXIDANT RATIO	EQUIVALENCE RATIO
F FUEL	R FUEL	F FUEL	R FUEL	
0.272	0.254	0.220	0.476	0.480
			0.72	1.22
				NOT APPLICABLE

WET FLUE GAS ANALYSIS (MOLE PERCENT)		SCOT MEASUREMENT (GRAMS/HR)	
CO	CO2	H2	H2O
13.55	4.14	0.0	60.91
			2.9672
			17.04
			34.4

COMBUSTION TEMPERATURE (K)  
 2130.12 (10.0)  
 RESIDENCE TIME (MILLISEC)  
 6.5

EFFICIENCIES  
 CARBON MONOXIDE COMBUSTION  
 80.7  
 61.4

LIQUID FUEL JET STIRRED COMBUSTION DATA OUTPUT

DATE : OCT 4, 1979  
 RUN NUMBER: 116-H  
 FRONT FUEL: STATEX HT 30A  
 REAR FUEL : JP-10

CARBON MATERIAL BALANCE

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 400.0  
 REAR FUEL 500.0

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 10044.0  
 REAR FUEL 9636.9

NOT APPLICABLE

REACTANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 748.0  
 FRONT COMBUSTION AIR 4008.0  
 REAR COMBUSTION AIR 4098.0  
 OXYGEN 636.0  
 TOTAL OXYDANT 3137.1

OXYGEN MATERIAL BALANCE

NOT APPLICABLE

NITROGEN FLOW RATES (GRAMS/HR)

FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

FUEL OXYDANT MIXTURE CONDITIONS

STOICHIOMETRIC  
 FUEL TO OXYDANT RATIO 0.322 0.306  
 F FUEL 0.256 0.220 0.476 0.80 0.72 1.52  
 F FUEL 9.16 0.0 1.34 0.0 0.0 60.91  
 F FUEL 0.584 0.0 0.0 0.0 0.0 2.0672  
 OVERALL F FUEL 0.838 0.220 0.476 0.80 0.72 1.52

BASED ON MASS FEED RATES

BASED ON FLUE GAS ANALYSIS

FUEL TO OXYDANT RATIO

FUEL TO OXYDANT RATIO

EQUIVALENCE RATIO

EQUIVALENCE RATIO

F FUEL 9.16 0.0 1.34 0.0 0.0 60.91

F FUEL 0.584 0.0 0.0 0.0 0.0 2.0672

OVERALL F FUEL 0.838 0.220 0.476 0.80 0.72 1.52

NOT APPLICABLE

SOOT MEASUREMENT (GRAMS/HR)

WET FLUE GAS ANALYSIS (MOLE PERCENT)

TOTAL COMPOUNDS/HR	CO	CO2	HC	O2	NO	NOX	N2	H2	H2O
492.6	13.50	9.16	0.0	1.34	0.0	0.0	60.91	2.0672	17.04
									34.5

COMBUSTION TEMPERATURE (K)

1911.10 (10.0)

RESIDENCE TIME (MILLISEC)

6.5

EFFECTIVENESS

CARBON BURNOUT COMBUSTION

61.4

85.7

LIQUID FUEL JET STIRRED COMBUSTOR DATA OUTPUT

DATE : OCT 9, 1974  
 RUN NUMBER: 123-A  
 FRONT FUEL: STATEX MT 30%  
 REAR FUEL: JP-10

FUEL FLOW RATES (GRAMS/HR)	FUEL HEATING VALUES (CAL/GRAM)	CARBON MATERIAL BALANCE
FRONT FUEL 666.0	FRONT FUEL 10064.0	
REAR FUEL 666.0	REAR FUEL 9436.9	96.9

OXIDANT FLOW RATES (GRAMS/HR)	OXYGEN MATERIAL BALANCE	NITROGEN FLOW RATES (GRAMS/HR)
FRONT ATOMIZING AIR 1770.0	107.4	FRONT ATOMIZING 0.0
REAR ATOMIZING AIR 768.0		REAR ATOMIZING 0.0
FRONT COMBUSTION AIR 7344.0		SIGHT PORT 168.0
REAR COMBUSTION AIR 7344.0		TOTAL 168.0
OXYGEN 600.0		
TOTAL OXIDANT 4613.0		

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC	BASED ON MASS FEED RATES	BASED ON FLUE GAS ANALYSIS
FUEL TO OXIDANT RATIO	FUEL TO OXIDANT RATIO	FUEL TO OXIDANT RATIO
F FUEL 0.332	F FUEL 0.144	F FUEL 0.241
R FUEL 0.122	R FUEL 0.267	R FUEL 0.085
O FUEL 0.394	O FUEL 0.38	O FUEL 0.77
OVERALL 0.267	OVERALL 0.48	OVERALL 0.241

WET FLUE GAS ANALYSIS (MOLE PERCENT)

TOTAL GRAMS/HR	CO	CO2	H2O	NO	NOX	N2	H2	H2O	SOOT MEASUREMENT (GRAMS/HR)
565.0	0.29	13.02	0.0005	5.42	0.0	71.46	0.0130	9.40	7.2

COMBUSTION TEMPERATURE (K) 1963.12 (10.0)  
 RESIDENCE TIME (MILLISEC) 4.0

EFFICIENCIES  
 CARBON THROUGH COMBUSTION 98.4  
 O2 98.4

LIQUID FUEL JET STIRRED COMBUSTION DATA OUTPUT

DATE: OCT 9, 1979  
 RUN NUMBER: 123-H

FRONT FUEL: STAREX MT JOR  
 REAR FUEL: JP-10

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 466.0  
 REAR FUEL 466.0

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 10044.0  
 REAR FUEL 9436.9

CARBON MATERIAL BALANCE

97.1

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 7344.0  
 REAR COMBUSTION AIR 7344.0  
 OXYGEN 400.0  
 TOTAL OXIDANT 4613.8

OXYGEN MATERIAL BALANCE

107.4

NITROGEN FLOW RATES (GRAMS/HR)

FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC  
 FUEL TO OXIDANT RATIO  
 F FUEL R FUEL 0.332

BASED ON MASS FEED RATES  
 FUEL TO OXIDANT RATIO  
 F FUEL R FUEL 0.177

EQUIVALENCE RATIO  
 F FUEL R FUEL 0.144

BASED ON FLUE GAS ANALYSIS  
 FUEL TO OXIDANT RATIO  
 EQUIVALENCE RATIO 0.267

OVERALL 0.267

0.38

0.48

0.85

0.241

0.77

WET FLUE GAS ANALYSIS (MOLE PERCENT)

TOTAL GRAMS/HR	CO	CO2	HC	O2	NO	NOX	N2	H2O	SOOT MEASUREMENT (GRAMS/HR)
445.0	0.29	13.07	0.0005	5.42	0.0	0.0	71.86	0.0130	8.4

COMBUSTION TEMPERATURE (K)

1963.1 (30.0)

RESIDENCE TIME (MILLISEC)

4.0

EFFICIENCIES

CARBON THROUGH COMBUSTION

95.1

98.3

LIQUID FUEL JET STIRRED COMBUSTOR DATA OUTPUT

DATE : OCT 9, 1979  
 RUN NUMBER: 124-A  
 FRONT FUEL: STATEX MT J08  
 REAR FUEL : JP-10

CARBON MATERIAL BALANCE

FRONT FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 348.0  
 REAR FUEL 558.0  
 TOTAL 906.0

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 10044.0  
 REAR FUEL 9436.9

NITROGEN FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT POINT 168.0  
 TOTAL 168.0

OXYGEN MATERIAL BALANCE  
 103.2

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 4212.0  
 REAR COMBUSTION AIR 4212.0  
 OXYGEN 900.0  
 TOTAL OXIDANT 3454.2

FUEL OXIDANT MIXTURE CONDITIONS

BASED ON FLUE GAS ANALYSIS  
 FUEL TO OXIDANT RATIO 0.244  
 EQUIVALENCE RATIO 0.79

STOICHIOMETRIC  
 FUEL TO OXIDANT RATIO 0.322  
 F FUEL 0.304  
 R FUEL 0.101  
 OXYGEN 0.152  
 TOTAL 0.262

SOOT MEASUREMENT (GRAMS/HR)

WET FLUE GAS ANALYSIS (MOLE PERCENT)  
 CO2 14.30  
 CO 0.25  
 HC 0.0005  
 O2 5.43  
 NO 0.0  
 NOX 0.0  
 H2O 10.68

COMBUSTION TEMPERATURE (K)  
 1973.1 ± 10.0  
 RESIDENCE TIME (MILLISEC)  
 6.0

EFFICIENCIES  
 CAPTURE, HURNDY COMBUSTION 98.6  
 95.9

LIQUID FUEL JET STIRRED COMBUSTOR DATA OUTPUT

DATE : OCT 9, 1979  
 RUN NUMBER: 174-H  
 FRONT FUEL: STATEX MT 30X  
 REAR FUEL : JP-10

FUEL FEED RATES (GRAMS/HR)	FUEL HEATING VALUES (CAL/GRAM)	CARBON MATERIAL BALANCE
FRONT FUEL	FRONT FUEL	
REAR FUEL	REAR FUEL	
748.0	10044.0	9436.9
558.0		96.0

OXIDANT FLOW RATES (GRAMS/HR)	OXYGEN MATERIAL BALANCE	NITROGEN FLOW RATES (GRAMS/HR)
FRONT ATOMIZING AIR		FRONT ATOMIZING
REAR ATOMIZING AIR	103.2	REAR ATOMIZING
FRONT COMBUSTION AIR		SIGHT PORT
REAR COMBUSTION AIR		TOTAL
OXYGEN		168.0
TOTAL OXIDANT		168.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC	BASED ON MASS FEED RATES		BASED ON FLUE GAS ANALYSIS	
FUEL TO OXIDANT RATIO	FUEL TO OXIDANT RATIO	EQUIVALENCE RATIO	FUEL TO OXIDANT RATIO	EQUIVALENCE RATIO
F FUEL	P FUEL	O FUEL	R FUEL	O FUEL
0.322	0.304	0.101	0.162	0.262
		0.31	0.53	0.84
		0.31	0.53	0.84

WET FLUE GAS ANALYSIS (MOLE PERCENT)

TOTAL GM-MOL/LS/HR	CO	CO2	HC	NO	NOX	N2	H2O	SOOT MEASUREMENT (GRAMS/HR)
442.0	0.29	14.30	0.0005	5.43	0.0	69.29	0.0140	4.2

COMBUSTION TEMPERATURE (K)

1973.12( 10.0)

RESIDENCE TIME (MILLISEC)

6.0

EFFICIENCIES

CARBON BURNOUT 98.0

COMBUSTION

98.6

LIQUID FUEL JET STIRRED COMBUSTOR DATA OUTPUT

DATE : OCT 9, 1979  
 RUN NUMBER: 125-A  
 FRONT FUEL: STATEX M1 30%  
 REAR FUEL: JP-10

CARBON MATERIAL BALANCE  
 95.6

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL REAR FUEL  
 10046.0 9436.9

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL REAR FUEL  
 3.4.0 366.0

NITROGEN FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

OXYGEN MATERIAL BALANCE  
 100.3

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 2736.0  
 REAR COMBUSTION AIR 2736.0  
 OXYGEN 810.0  
 TOTAL OXIDANT 2676.4

FUEL OXIDANT MIXTURE CONDITIONS

BASED ON FLUE GAS ANALYSIS  
 FUEL TO OXIDANT RATIO EQUIVALENCE RATIO  
 0.322 0.304 0.110 0.137 0.267 0.40 0.45 0.85 0.254 0.81

STOICHIOMETRIC  
 FUEL TO OXIDANT RATIO  
 F FUEL R FUEL  
 0.322 0.304 0.110 0.137 0.267 0.40 0.45 0.85

SOOT MEASUREMENT (GRAMS/HR)

WET FLUE GAS ANALYSIS (MOLE PERCENT)

WET FLUE GAS ANALYSIS (MOLE PERCENT)		EFFICIENCIES	
CO	CO2	HC	NOX
9.29	15.19	0.0005	4.74
0.0	0.0	0.0	68.77
0.0	0.0	0.0	0.0130
0.0	0.0	0.0	10.96
0.0	0.0	0.0	4.0

RESIDENCE TIME (MILLISEC)

COMBUSTION TEMPERATURE (K)

8.0

1973.12( 15.0)

EFFICIENCIES  
 CARBON HIPPOUT COMBUSTION

98.6

96.2

LIQUID FUEL JET STIPPER COMBUSTOR DATA OUTPUT

DATE 1 OCT 9, 1979  
 RUN NUMBER: 125-H

FRONT INLET: STAREX HT 30%  
 REAR FUEL: JP-10

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 366.0  
 REAR FUEL 94.5

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 4436.9  
 REAR FUEL 4436.9

CARBON MATERIAL BALANCE

95.5

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 2736.0  
 REAR COMBUSTION AIR 2736.0  
 OXYGEN 410.0  
 TOTAL OXIDANT 2576.4

OXYGEN MATERIAL BALANCE

100.3

NITROGEN FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC  
 FUEL TO OXIDANT RATIO  
 F FUEL R FUEL

0.322 0.304

BASED ON MASS FEED RATES  
 FUEL TO OXIDANT RATIO  
 F FUEL R FUEL OVERALL

0.130 0.137 0.267 0.40 0.45 0.85

BASED ON FLUE GAS ANALYSIS  
 FUEL TO OXIDANT RATIO  
 F FUEL R FUEL OVERALL

0.254 0.81

WET FLUE GAS ANALYSIS (MOLE PERCENT)

TOTAL GM-MOLES/HR	CO	CO2	HC	O2	NO	NOX	N2	H2O
327.4	0.29	15.19	0.0005	4.78	0.0	0.0	68.77	0.0130

SOOT MEASUREMENT (GRAMS/HR)

3.6

COMBUSTION TEMPERATURE (K)

1973.12 (15.6)

RESIDENCE TIME (MILLISEC)

8.0

EFFICIENCIES  
 CARBON THROUGH COMBUSTION

96.5

98.6



LIQUID FUEL JET STIRRED COMBUSTION DATA OUTPUT

DATE : OCT 9, 1979  
 RUN NUMBER: 176-R

FURNIT FUEL: STATED WT 30R  
 HEAR FUEL : JP-10

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 344.0 REAR FUEL 240.0 CARBON MATERIAL BALANCE 97.7

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 10044.0 HEAR FUEL 9436.9

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 1878.0  
 REAR COMBUSTION AIR 1878.0  
 OXYGEN 690.0  
 TOTAL OXIDANT 2156.6

OXYGEN MATERIAL BALANCE 101.1

NITROGEN FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC  
 FUEL TO OXIDANT RATIO  
 F FUEL R FUEL 0.322 0.304  
 BASED ON MASS FEED RATES  
 FUEL TO OXIDANT RATIO 0.161 0.111 0.273 0.50 0.37 0.47  
 EQUIVALENCE RATIO 0.550 0.37 0.47  
 F FUEL R FUEL OVERALL

BASED ON FLUE GAS ANALYSIS  
 FUEL TO OXIDANT RATIO 0.263 0.84  
 EQUIVALENCE RATIO

TOTAL GM-MOLES/HR 241.5

WET FLUE GAS ANALYSIS (MOLE PERCENT)

CO	CO2	HC	NO	NOX	N2	H2	H2O
0.50	15.87	0.0005	6.52	0.0	68.20	0.0620	10.85

SOOT MEASUREMENT (GRAMS/HR) 4.2

COMBUSTION TEMPERATURE (K)  
 1973.1 ± 20.0  
 RESIDENCE TIME (MILLISEC) 9.9

EFFICIENCIES  
 CARBON BURNOUT 96.0  
 COMBUSTION 97.7



LIQUID FUEL JET STAGED COMBUSTION DATA OUTPUT

DATE : OCT 23, 1974  
 RUN NUMBER: 150-B  
 FRONT FUEL: STATEX MT 304  
 REAR FUEL: JP-10

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 480.0  
 REAR FUEL 480.0  
 FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 10044.0  
 REAR FUEL 9436.9  
 CARBON MATERIAL BALANCE 104.1

EXHAUST FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 740.0  
 FRONT COMBUSTION AIR 4095.0  
 REAR COMBUSTION AIR 4094.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 3137.1  
 NITROGEN FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC  
 FUEL TO OXIDANT RATIO  
 F FUEL R FUEL OVERALL  
 0.372 0.304 0.311 0.153 0.264 0.34 0.50 0.85  
 BASED ON MASS FEED RATES  
 FUEL TO OXIDANT RATIO EQUIVALENCE RATIO  
 F FUEL H FUEL OVERALL  
 0.264 0.264 0.264 0.85  
 BASED ON FLUE GAS ANALYSIS  
 FUEL TO OXIDANT RATIO EQUIVALENCE RATIO  
 0.85

TOTAL COMPOUNDS/HR  
 CO 1.34  
 CO2 14.73  
 H2O 6.4  
 H2 0.0  
 HC 0.0  
 NO 0.0  
 NOX 0.0  
 H2 70.68  
 H2O 9.92  
 SOOT MEASUREMENT (GRAMS/HR)  
 0.0

COMBUSTION TEMPERATURE (K)  
 1920.12 (20.0)  
 RESIDENCE TIME (MILLISEC)  
 6.5

EFFICIENCIES  
 CARBON IMPINGEMENT COMBUSTION 98.0

LIGUID FUEL JET STIRRED COMBUSTION DATA OUTPUT

DATE : OCT 21, 1979  
 RUN NUMBER: 151-A

FRONT FUEL: STAYEX MT 30%--100 PPM MN  
 REAR FUEL : JP-10

FUEL FEED RATES (GRAMS/HR)			
FRONT FUEL	348.0	480.0	
REAR FUEL			
FUEL HEATING VALUES (CAL/GRAM)			
FRONT FUEL	10044.0	9436.9	
REAR FUEL			
CARBON MATERIAL BALANCE			97.3

OXIDANT FLOW RATES (GRAMS/HR)		OXYGEN MATERIAL BALANCE		NITROGEN FLOW RATES (GRAMS/HR)	
FRONT ATOMIZING AIR	1770.0	49.1		FRONT ATOMIZING	0.0
REAR ATOMIZING AIR	758.0			REAR ATOMIZING	0.0
FRONT COMBUSTION AIR	4098.0			SLIGHT PORT	168.0
REAR COMBUSTION AIR	4098.0			TOTAL	168.0
OXYGEN	536.0				
TOTAL OXIDANT	3137.1				

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC FUEL TO OXIDANT RATIO	BASED ON MASS FEED RATES		BASED ON FLUE GAS ANALYSIS	
	F FUEL	R FUEL	F FUEL	R FUEL
0.372	0.304	0.111	0.153	0.264
		0.34	0.50	0.85
				0.259
				0.83

TOTAL GM-MOLES/HR	WET FLUE GAS ANALYSIS (MOLE PERCENT)				SOOT MEASUREMENT (GRAMS/HR)
	CO	CO2	HC	H2O	
419.7	0.65	13.73	0.0	4.10	0.0
				NOX	N2
				0.0	71.69
					0.0940
					10.07
					5.0

COMBUSTION TEMPERATURE (K)  
 1963.1 ± (40.0)

EFFICIENCIES  
 CARBON BURNOUT 95.2  
 COMBUSTION 97.6  
 RESIDENCE TIME (MILLISEC) 6.5

LIQUID FUEL JET STIRRED COMBUSTION DATA OUTPUT

DATE : OCT 23, 1974  
 RUN NUMBER: 351-R

FRONT FUEL: STATEX HT JOK--100 PPM MN  
 REAR FUEL : JP-10

FUEL FEED RATES (GRAMS/HR) CARBON MATERIAL BALANCE  
 FRONT FUEL 348.0 REAR FUEL 440.0 FRONT FUEL 10044.0 REAR FUEL 9436.9 TOTAL 97.4

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 4098.0  
 REAR COMBUSTION AIR 4098.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 3137.1

OXYGEN MATERIAL BALANCE

99.1

NITROGEN FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC BASED ON MASS FEED RATES  
 FUEL TO OXIDANT RATIO FUEL TO OXIDANT RATIO EQUIVALENCE RATIO FUEL TO OXIDANT RATIO EQUIVALENCE RATIO  
 F FUEL R FUEL OVERALL F FUEL R FUEL OVERALL F FUEL R FUEL OVERALL

0.322	0.304	0.111	0.153	0.264	0.34	0.50	0.85	0.259	0.83
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WET FLUE GAS ANALYSIS (MOLE PERCENT)

TOTAL GM-MOLES/HR		CO	CO2	HC	O2	NO	NOX	N2	H2	H2O	SOOT MEASUREMENT (GRAMS/HR)
419.7	9.45	13.79	0.0	4.10	0.0	0.0	0.0	71.49	0.0940	10.07	5.5

COMBUSTION TEMPERATURE (K) RESIDENCE TIME (MILLISEC)

1903.12 (40.0) 6.5

EFFICIENCIES COMBUSTION

CARBON BURNOUT 94.8

97.6

LIQUID FUEL JET STIRRED COMBUSTOR DATA OUTPUT

DATE : OCT 25, 1979  
 RUN NUMBER: 1A0-A  
 FRONT FUEL: STATEX MT J08  
 REAR FUEL: JP-10

CARRON MATERIAL BALANCE

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 348.0 REAR FUEL 480.0  
 FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 10044.0 REAR FUEL 9436.9

95.9

OXYGEN MATERIAL BALANCE  
 99.9

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 4098.0  
 REAR COMBUSTION AIR 4098.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 3137.1

NITROGEN FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC RATIO  
 FUEL TO OXIDANT RATIO 0.322  
 F FUEL 0.304  
 R FUEL 0.111  
 H FUEL 0.153  
 O FUEL 0.264  
 N FUEL 0.34  
 C FUEL 0.50  
 S FUEL 0.85

BASED ON MASS FEED RATES  
 EQUIVALENCE RATIO  
 F FUEL 0.264  
 H FUEL 0.50  
 R FUEL 0.85

BASED ON FLUE GAS ANALYSIS  
 FUEL TO OXIDANT RATIO 0.253  
 EQUIVALENCE RATIO 0.81

WET FLUE GAS ANALYSIS (MOLE PERCENT)

TOTAL GAS-MOLES/HR 420.2

CO	3.36	CO <sub>2</sub>	13.66	HC	0.0075	NO	4.47	NOX	0.00	N <sub>2</sub>	71.39	H <sub>2</sub>	0.0766	H <sub>2</sub> O	10.07
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SOOT MEASUREMENT (GRAMS/HR) 5.9

COMBUSTION TEMPERATURE (K)

1963.12 (10.0)

RESIDENCE TIME (MILLISEC)

6.3

EFFICIENCIES  
 CARBON FURNOUT COMBUSTION

94.3 98.0

LIQUID FUEL JET STIRRED COMBUSTOR DATA OUTPUT

DATE : OCT 25, 1979  
 RUN NUMBER: 160-8

FRONT FUEL: STATEX MT 303  
 REAR FUEL: JF-10

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 489.0  
 REAR FUEL 344.0

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 9436.9  
 REAR FUEL 10044.0

CARBON MATERIAL BALANCE

95.6

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 4098.0  
 REAR COMBUSTION AIR 4098.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 3137.1

OXYGEN MATERIAL BALANCE

99.9

NITROGEN FLOW RATES (GRAMS/HR)

FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

FUEL/OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC  
 FUEL TO OXIDANT RATIO

F FUEL 0.304  
 R FUEL 0.111

FRONT OXIDANT RATIO 0.264  
 REAR OXIDANT RATIO 0.153

OVERALL FUEL R FUEL 0.34  
 OVERALL FUEL R FUEL 0.264

BASED ON MASS FEED RATES  
 EQUIVALENCE RATIO

F FUEL 0.50  
 R FUEL 0.85

FRONT OXIDANT RATIO 0.253  
 REAR OXIDANT RATIO 0.81

BASED ON FLUE GAS ANALYSIS  
 FUEL TO OXIDANT RATIO 0.0766  
 EQUIVALENCE RATIO 10.07

WET FLUE GAS ANALYSIS (MOLE PERCENT)

TOTAL MM-MOLES/HR 420.2

CO	0.34	CO <sub>2</sub>	13.64	HC	0.0035	H <sub>2</sub>	0.0	NOX	0.0

SOOT MEASUREMENT (GRAMS/HR)

H<sub>2</sub> 0.0766  
 H<sub>2</sub>O 10.07  
 TOTAL 3.9

COMBUSTION TEMPERATURE (K)

1963.1 ± (10.0)

RESIDENCE TIME (MILLISEC)

6.3

EFFICIENCIES  
 CARBON BURBOUT 96.3  
 COMBUSTION 94.2

LIQUID FUEL JET STIRRED COMBUSTOR DATA OUTPUT

DATE : OCT 25, 1979  
 RUN NUMBER: 161-A  
 FRONT FUEL: STATEX MT 308--1000 PPM MN  
 REAR FUEL : JP-10

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 348.0  
 REAR FUEL 480.0

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 10044.0  
 REAR FUEL 9436.9

CARBON MATERIAL BALANCE  
 97.0

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 1768.0  
 FRONT COMBUSTION AIR 4098.0  
 REAR COMBUSTION AIR 4098.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 3137.1

OXYGEN MATERIAL BALANCE  
 98.1

NITROGEN FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT POINT 168.0  
 TOTAL 168.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC		BASED ON MASS FEED RATES		BASED ON FLUE GAS ANALYSIS	
FUEL TO OXIDANT RATIO		FUEL TO OXIDANT RATIO		FUEL TO OXIDANT RATIO	
F FUEL	R FUEL	F FUEL	R FUEL	F FUEL	R FUEL
0.322	0.304	0.111	0.153	0.34	0.50
		0.264	0.264	0.85	0.85
				0.261	0.84

WET FLUE GAS ANALYSIS (MOLE PERCENT)

TOTAL GM-MOLES/HR		COMBUSTION TEMPERATURE (K)		RESIDENCE TIME (MILLISEC)	
CO	CO2	HC	OP	NO	NOX
0.37	13.42	0.0030	4.02	0.0	0.0
				71.61	0.3067
					9.87
					6.1

EFFICIENCIES

CARBON INPUT	COMBUSTION
96.2	97.2

LIQUID FUEL JET STIRRED COMBUSTION DATA OUTPUT

DATE : OCT 25, 1979  
 RUN NUMBER: 16J-H  
 FRONT FUEL: STATEX MT J02--1000 PPM MN  
 REAR FUEL : JP-10

FUEL FEED RATES (GRAMS/HR)			
FRONT FUEL	348.0	FUEL HEATING VALUES (CAL/GRAM)	
REAR FUEL	480.0	FRONT FUEL	10044.0
		REAR FUEL	9436.9
			96.8

OXIDANT FLOW RATES (GRAMS/HR)			
FRONT ATOMIZING AIR	1770.0	NITROGEN FLOW RATES (GRAMS/HR)	
REAR ATOMIZING AIR	768.0	FRONT ATOMIZING	0.0
FRONT COMBUSTION AIR	4098.0	REAR ATOMIZING	0.0
REAR COMBUSTION AIR	4098.0	SIGHT PORT	168.0
OXYGEN	636.0	TOTAL	168.0
TOTAL OXIDANT	3137.1		

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC				
FUEL TO OXIDANT RATIO		BASED ON MASS FEED RATES		BASED ON FLUE GAS ANALYSIS
F FUEL	0.372	FUEL TO OXIDANT RATIO	0.264	FUEL TO OXIDANT RATIO
R FUEL	0.304	OVERALL	0.34	OVERALL
		F FUEL	0.50	F FUEL
		R FUEL	0.85	R FUEL
		OVERALL	0.34	OVERALL
				0.260
				0.84

TOTAL GM-MOLES/HR		WET FLUE GAS ANALYSIS (MOLE PERCENT)				SOOT MEASUREMENT (GRAMS/HR)
419.0		CO	CO2	HC	H2	H2O
		0.37	13.82	0.0030	4.02	0.0
						0.0
						11.61
						0.3067
						9.47
						6.5

COMBUSTION TEMPERATURE (K)  
 1963.1 ± 10.0

RESIDENCE TIME (MILLISEC)

6.3

EFFICIENCIES  
 CARBON BURNOUT

95.7

COMBUSTION

97.3

LIQUID FUEL JET STIRRED COMBUSTOR DATA OUTPUT

DATE : OCT 26, 1979  
 RUN NUMBER: 170-A

FRONT FUEL: STAREX MT 30%  
 REAR FUEL: JP-10

CARBON MATERIAL BALANCE  
 93.8

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 10044.0  
 REAR FUEL 9436.9

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 368.0  
 REAR FUEL 680.0

NITROGEN FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

OXYGEN MATERIAL BALANCE  
 98.6

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 4098.0  
 REAR COMBUSTION AIR 4098.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 3137.1

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC  
 FUEL TO OXIDANT RATIO 0.322 0.304  
 F FUEL 0.111 0.153  
 R FUEL 0.264 0.251  
 OVERALL F FUEL 0.34 0.51  
 OVERALL R FUEL 0.85 0.81

BASED ON MASS FEED RATES  
 FUEL TO OXIDANT RATIO 0.251  
 EQUIVALENCE RATIO 0.81

BASED ON FLUE GAS ANALYSIS  
 FUEL TO OXIDANT RATIO 0.251  
 EQUIVALENCE RATIO 0.81

500) MEASUREMENT (GRAMS/HR)

WET FLUE GAS ANALYSIS (MOLE PERCENT)

CO	CO2	HC	O2	N2	H2O	NOX	N2	H2
0.229	13.48	0.0010	4.37	0.0	71.66	0.0132	10.17	6.1

COMBUSTION TEMPERATURE (K) RESIDENCE TIME (MILLISEC)

1963.1 ± 10.0 6.3

EFFICIENCIES  
 CARBON BURNOUT COMBUSTION  
 96.1 94.5

LIQUID FUEL JET STERRED COMBUSTION DATA OUTPUT

DATE : OCT 26, 1974  
 RUN NUMBER: 170-H

FRONT FUEL: STATEX HT 30X  
 REAR FUEL : JP-10

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 480.0  
 REAR FUEL 480.0

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 10045.0  
 REAR FUEL 9435.9

CARBON MATERIAL BALANCE  
 94.3

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 4098.0  
 REAR COMBUSTION AIR 4098.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 3137.1

OXYGEN MATERIAL BALANCE  
 98.6

NITROGEN FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC  
 FUEL TO OXIDANT RATIO  
 F FUEL R FUEL 0.304  
 0.322 0.304

BASED ON MASS FEED RATES  
 FUEL TO OXIDANT RATIO  
 F FUEL R FUEL OVERALL 0.111 0.153 0.264 0.34 0.50 0.85

BASED ON FLUE GAS ANALYSIS  
 FUEL TO OXIDANT RATIO  
 0.251 0.81

TOTAL GM-MILES/HR 418.7

WET FLUE GAS ANALYSIS (MOLT. PERCENT)

CO	CO2	HC	NO	NOX	N2	H2O
0.29	13.48	0.0030	4.37	0.0	71.66	0.0132
						10.17

SOOT MEASUREMENT (GRAMS/HR) 7.8

COMBUSTION TEMPERATURE (K)  
 1963.12( 10.6)

RESIDENCE TIME (MILLISEC)  
 6.3

EFFICIENCIES  
 CARBON MONOXIDE COMBUSTION  
 92.5 98.2

LIQUID FUEL JET STIRRED COMBUSTOR DATA OUTPUT

DATE : OCT 26, 1979  
 RUN NUMBER: 170-A

FRONT FUEL: STATEX HT 30A--1000 PPM FF  
 REAR FUEL : JP-10

CARBON MATERIAL BALANCE

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 344.0  
 REAR FUEL 480.0

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 10044.0  
 REAR FUEL 9436.9

CARBON MATERIAL BALANCE  
 94.0

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 4098.0  
 REAR COMBUSTION AIR 4098.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 3137.1

OXYGEN MATERIAL BALANCE  
 98.4

NITROGEN FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

FUEL OXIDANT MIXTURE COMPOSITIONS

STOICHIOMETRIC  
 FUEL TO OXIDANT RATIO 0.322  
 F FUEL 0.111  
 R FUEL 0.153  
 OXYGEN 0.304

BASED ON MASS FEED RATES  
 FUEL TO OXIDANT RATIO 0.264  
 F FUEL 0.34  
 R FUEL 0.50  
 OXYGEN 0.85

BASED ON FLUX GAS ANALYSIS  
 FUEL TO OXIDANT RATIO 0.252  
 EQUIVALENCE RATIO 0.81

WET FLUE GAS ANALYSIS (MOLE PERCENT)

CO	CO2	HC	O2	NO	NOX	N2	H2O
0.17	13.63	0.0025	4.24	6.0	0.0	71.72	0.0397

TOTAL GM-MOLES/HR 418.3

SOOT MEASUREMENT (GRAMS/HR) 4.4

COMBUSTION TEMPERATURE (K) RESIDENCE TIME (MILLISEC)

1953.1 (16.0) 6.3

EFFICIENCIES  
 CARBON INPUT COMBUSTION

95.8 98.9

LIQUID FUEL JET STIRRED COMBUSTION DATA OUTPUT

DATE : OCT 26, 1979  
 RUN NUMBER: 171-1  
 FRONT FUEL: STAFF MT JCR--1000 PPM FF  
 REAR FUEL: J9-10

CARBON MATERIAL BALANCE  
 94.5

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL REAR FUEL  
 10044.0 9476.9

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL REAR FUEL  
 348.0 480.0

NITROGEN FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT POINT 168.0  
 TOTAL 168.0

OXYGEN MATERIAL BALANCE  
 94.4

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 4098.0  
 REAR COMBUSTION AIR 4098.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 3137.1

FUEL OXIDANT MIXTURE CONDITIONS

BASED ON FUEL GAS ANALYSIS  
 FUEL TO OXIDANT RATIO EQUIVALENCE RATIO  
 0.372 0.304  
 F FUEL R FUEL H FUEL OVERALL  
 0.111 0.151 0.264 0.34 0.50 0.95  
 0.753 0.81

STOICHIOMETRIC  
 FUEL TO OXIDANT RATIO EQUIVALENCE RATIO  
 F FUEL R FUEL H FUEL OVERALL  
 0.111 0.151 0.264 0.34 0.50 0.95

SOOT MEASUREMENT (GRAMS/HR)

WET FLUX GAS ANALYSIS (MOLE PERCENT)  
 CO CO2 HC H2 HD HDX H2 H2O  
 0.17 13.63 0.0025 4.28 0.0 0.0 71.72 0.0397 10.16  
 418.3 8.6

COMBUSTION TEMPERATURE (K) RESIDENCE TIME (MILLISEC)

6.3

EFFICIENCIES  
 CARBON BURNOUT COMBUSTION  
 91.7 98.4

1963.1 (10.0)

LIQUID FUEL JET STIRRED COMBUSTION DATA OUTPUT

DATE : NOV 15, 1979  
 RUN NUMBER : 182-A  
 FRONT FUEL : STATEX M.T. JOR  
 REAR FUEL : JP-10

CARBON MATERIAL BALANCE

FUEL FEED RATES (GRAMS/HR)			
FRONT FUEL	348.0	480.1	96.0
REAR FUEL			
FUEL HEATING VALUES (CAL/GRAM)			
FRONT FUEL	10044.0	9436.9	
REAR FUEL			
OXYGEN MATERIAL BALANCE			
	96.8		
NITROGEN FLOW RATES (GRAMS/HR)			
FRONT ATOMIZING AIR	1770.0		0.0
REAR ATOMIZING AIR	768.0		0.0
FRONT COMBUSTION AIR	4048.0		168.0
REAR COMBUSTION AIR	4098.0		
OXYGEN	636.0		
TOTAL OXIDANT	3137.1		168.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC								
FUEL TO OXIDANT RATIO								
F FUEL	0.322	0.100	0.131	0.153	0.264	0.34	0.50	0.85
R FUEL								
OVERALL								
FUEL TO OXIDANT RATIO								
F FUEL								
R FUEL								
OVERALL								
BASED ON FLUE GAS ANALYSIS								
FUEL TO OXIDANT RATIO								
OVERALL								
EQUIVALENCE RATIO								
F FUEL								
R FUEL								
OVERALL								
BASED ON FLUE GAS ANALYSIS								
FUEL TO OXIDANT RATIO								
OVERALL								
EQUIVALENCE RATIO								
F FUEL								
R FUEL								
OVERALL								

SOOT MEASUREMENT (GRAMS/HR)

FRONT FUEL	4.75	13.7	6.0	3.73	0.6	0.0	71.95	6.0120	10.22	7.7
REAR FUEL										
OVERALL										

COMBUSTION TEMPERATURE (K)

1445.8 155.6  
 EFFICIENCIES  
 CARBON FUEL  
 COMBUSTION 98.1

RESIDENCE TIME (MILLISEC)

6.2

LIQUID FUEL RT STEPPER COMMISSION DATA OUTPUT

DATE : NOV 15, 1979  
 RUN NUMBER: 142-4  
 FRONT FUEL STATUS: MT 302  
 REAR FUEL : 0-10

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 440.0  
 REAR FUEL 240.0

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 10064.0  
 REAR FUEL 9436.9

CARBON MATERIAL BALANCE  
 96.3

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 2680.0  
 FRONT COMBUSTION AIR 4060.0  
 REAR COMBUSTION AIR 4098.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 3137.0

HYDROGEN FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 144.0  
 TOTAL 168.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC  
 FUEL TO OXIDANT RATIO  
 F FUEL R FUEL

BASED ON MASS FEED RATES  
 FUEL TO OXIDANT RATIO  
 F FUEL R FUEL

BASED ON FLUE GAS ANALYSIS  
 FUEL TO OXIDANT RATIO  
 F FUEL R FUEL

EFFICIENCIES  
 CARBON BURNED COMBUSTION

WET FLUE GAS ANALYSIS (MOLE PERCENT)  
 CO 0.32  
 CO2 13.77  
 H2O 617.0

WET FLUE GAS ANALYSIS (MOLE PERCENT)  
 CO 0.34  
 CO2 13.73  
 H2O 617.0

WET FLUE GAS ANALYSIS (MOLE PERCENT)  
 CO 0.34  
 CO2 13.73  
 H2O 617.0

COMBUSTION TEMPERATURE (K)  
 1923.12 (10.0)

RESIDENCE TIME (MILLISEC)  
 6.2

EFFICIENCIES  
 CARBON BURNED COMBUSTION  
 98.1

LIQUID FUEL JET STIRRED COMBUSTION DATA OUTPUT

DATE : NOV 15, 1979  
 RUN NUMBER: 183-A

FRONT FUEL: STAFFX M1 30X--1000 PPM PH  
 REAR FUEL : JP-10

FUEL FEED RATES (GRAMS/HR)		CARBON MATERIAL BALANCE
FRONT FUEL	348.0	
REAR FUEL	480.0	
		93.7
FUEL HEATING VALUES (CAL/GRAM)		
FRONT FUEL	10044.0	
REAR FUEL	9436.0	

OXIDANT FLOW RATES (GRAMS/HR)		OXYGEN MATERIAL BALANCE		NITROGEN FLOW RATES (GRAMS/HR)
FRONT ATOMIZING AIR	1770.0	98.7		FRONT ATOMIZING
REAR ATOMIZING AIR	768.0			0.0
FRONT COMBUSTION AIR	4098.0			REAR ATOMIZING
REAR COMBUSTION AIR	4098.0			168.0
OXYGEN	536.0			TOTAL
TOTAL OXIDANT	3137.0			168.0

STOICHIOMETRIC		FUEL OXIDANT MIXTURE CONDITIONS		BASED ON FLUE GAS ANALYSIS	
FUEL TO OXIDANT RATIO		FUEL TO OXIDANT RATIO		FUEL TO OXIDANT RATIO	
F FUEL	0.322	F FUEL	0.34	F FUEL	0.85
R FUEL	0.111	R FUEL	0.26	R FUEL	0.251
		OVERALL	0.50	OVERALL	0.81

WET FLUE GAS ANALYSIS (MOLE PERCENT)		SOOT MEASUREMENT (GRAMS/HR)	
CO	0.27	CO	0.0
CO2	13.34	NOX	0.0
H2O	0.0	H2	0.0792
		H2O	10.11
			9.8

COMBUSTION TEMPERATURE (K) : 1500.0  
 RESIDENCE TIME (MILLISEC) : 6.3

EFFICIENCIES  
 CARBON MONOXIDE COMBUSTION : 97.8

LUBRICANT FUEL JET STEPPED COMBUSTION DATA OUTPUT

DATE : NOV 15, 1979

RUN NUMBER: 188

FRONT FUEL: STATEX M1 J0%--1000 PPM PA

REAR FUEL: JP-10

FUEL FEED RATES (GRAMS/HR)  
FRONT FUEL

348.0

FUEL HEATING VALUES (CAL/GRAM)  
FRONT FUEL

10044.0

CARBON MATERIAL BALANCE

93.4

OXIDANT FLOW RATES (GRAMS/HR)  
FRONT ATOMIZING AIR 1770.0  
REAR ATOMIZING AIR 759.0  
FRONT COMBUSTION AIR 4098.0  
REAR COMBUSTION AIR 4098.0  
OXYGEN 636.0  
TOTAL OXIDANT 3137.1

OXYGEN MATERIAL BALANCE

98.7

NITROGEN FLOW RATES (GRAMS/HR)

FRONT ATOMIZING 0.0  
REAR ATOMIZING 0.0  
SIGHT PORT 168.0  
TOTAL 168.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC  
FUEL TO OXIDANT RATIO  
F FUEL R FUEL

0.322 0.304

BASED ON MASS FEED RATES  
FUEL TO OXIDANT RATIO  
F FUEL R FUEL OVERALL

0.111 0.153 0.264 0.34 0.50 0.85

BASED ON FLUE GAS ANALYSIS  
FUEL TO OXIDANT RATIO  
EQUIVALENCE RATIO

0.250 0.80

TOTAL GM-MOLES/HR

418.9

WET FLUE GAS ANALYSIS (MOLE PERCENT)

CO 0.24 CO2 13.35 HC 0.0

NO 0.0 NOX 0.0

N2 71.62 H2O 10.11

H2 7.5

SOOT MEASUREMENT (GRAMS/HR)

COMBUSTION TEMPERATURE (K)

1953.1 ± (10.0)

RESIDENCE TIME (MILLISEC)

6.3

EFFICIENCIES  
CARBON BURNOUT COMBUSTION

92.9

98.0

LIQUID FUEL JET STIRRED COMBUSTOR DATA OUTPUT

DATE : NOV 15, 1979  
 RUN NUMBER: 191-A

FRONT FUEL: STATEX MT 308  
 REAR FUEL : NO REAR FUEL

CARBON MATERIAL BALANCE

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 10046.0 9436.9  
 REAR FUEL 0.0 0.0

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 0.0  
 REAR FUEL 0.0

NITROGEN FLOW RATES (GRAMS/HR)

FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

OXYGEN MATERIAL BALANCE

96.2

Oxidant Flow Rates (GRAMS/HR)

FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 4098.0  
 REAR COMBUSTION AIR 4094.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 3137.1

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC FUEL TO OXIDANT RATIO

F FUEL 0.322 0.304 0.302 0.294 0.0 0.94 0.0 0.94

BASED ON MASS FEED RATES

F FUEL 0.307 0.0 0.302 0.294 0.0 0.94 0.0 0.94

FUEL TO OXIDANT RATIO

F FUEL 0.322 0.304 0.302 0.294 0.0 0.94 0.0 0.94

BASED ON FLUE GAS ANALYSIS

F FUEL 0.322 0.304 0.302 0.294 0.0 0.94 0.0 0.94

WET FLUE GAS ANALYSIS (MOLE PERCENT)

CO2	15.40	0.0	2.29	0.0	0.0	0.0	0.0
CO	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H2O	72.28	0.0	72.28	0.0	0.0	0.0	0.0
N2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
SOOT MEASUREMENT (GRAMS/HR)	21.4	0.0	0.0	0.0	0.0	0.0	0.0

COMBUSTION TEMPERATURE (K)

1963.1 (10.0)

RESIDENCE TIME (MILLISEC)

6.0

EFFICIENCIES

CARBON BURNOUT 92.5

COMBUSTION 96.7

LIQUID FUEL JET STIRRED COMBUSTOR DATA OUTPUT

DATE : NOV 15, 1979

RUN NUMBER: 131-H

FRONT FUEL: STALEX 4T 30\*

REAR FUEL: NO REAR FUEL

FUEL FEED RATES (GRAMS/HR)  
FRONT FUEL 7.48.0  
REAR FUEL 0.0

FUEL HEATING VALUES (CAL/GRAM)  
FRONT FUEL 10064.0  
REAR FUEL 9436.9

CARBON MATERIAL BALANCE

93.9

OXYDANT FLOW RATES (GRAMS/HR)  
FRONT ATOMIZING AIR 1775.0  
REAR ATOMIZING AIR 768.0  
FRONT COMBUSTION AIR 4098.0  
REAR COMBUSTION AIR 4098.0  
OXYGEN 636.0  
TOTAL OXYDANT 3137.1

OXYGEN MATERIAL BALANCE

96.7

NITROGEN FLOW RATES (GRAMS/HR)

FRONT ATOMIZING 0.0  
REAR ATOMIZING 0.0  
SIGT PORT 168.0  
TOTAL 168.0

STOICHIOMETRIC  
FUEL TO OXYDANT RATIO  
F FUEL 0.322  
R FUEL 0.304

BASED ON MASS FEED RATES  
FUEL TO OXYDANT RATIO  
F FUEL 0.302  
R FUEL 0.280

BASED ON FLUE GAS ANALYSIS  
FUEL TO OXYDANT RATIO  
0.295

FUEL OXYDANT MIXTURE CONDITIONS

F FUEL 0.94  
R FUEL 0.94  
OVERALL 0.94

WET FLUE GAS ANALYSIS (MOLE PERCENT)

TOTAL GM-MOLES/HR	CO	CO2	HC	UP	NO	NOX	N2	H2O	SOOT MEASUREMENT (GRAMS/HR)
412.1	0.51	15.44	0.0	2.29	0.0	0.0	72.28	0.0248	19.6

COMBUSTION TEMPERATURE (K)

1983.1 ± 10.0

RESIDENCE TIME (MILLISEC)

6.0

EFFICIENCIES

CARBON BURNOUT 93.1

COMBUSTION 96.4

LIGUID FUEL JET STEPPED COMBUSTION DATA OUTPUT

DATE : NOV 5, 1979  
 RUN NUMBER: 200-A

FRONT FUEL: STALIX MT J07  
 REAR FUEL: JP-10

CARBON MATERIAL BALANCE

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 348.0 480.0  
 REAR FUEL 480.0

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 10044.0 9436.9  
 REAR FUEL 9436.9

107.7

NITROGEN FLOW RATES (GRAMS/HR)

FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

OXYGEN MATERIAL BALANCE

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 764.0  
 FRONT COMBUSTION AIR 4094.0  
 REAR COMBUSTION AIR 4094.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 3137.0

103.7

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC BASED ON MASS FEED RATES  
 FUEL TO OXIDANT RATIO FUEL TO OXIDANT RATIO FUEL TO OXIDANT RATIO  
 F FUEL R FUEL OVERALL F FUEL R FUEL OVERALL F FUEL R FUEL OVERALL

0.372 0.304 0.111 0.157 0.264 0.34 0.50 0.45 0.261 0.84

BASED ON FLUE GAS ANALYSIS  
 FUEL TO OXIDANT RATIO FUEL TO OXIDANT RATIO FUEL TO OXIDANT RATIO

SOOT MEASUREMENT (GRAMS/HR)

WET FLUE GAS ANALYSIS (MOLE PERCENT)  
 CO CO2 HC NO NOX H2O  
 0.20 14.86 0.0 4.29 0.0 70.79 0.0742 9.09 6.6

COMBUSTION TEMPERATURE (K)

2000.12 (5.0)

RESIDENCE TIME (MICROSEC)

7.1

EFFICIENCIES

CARBON EFFICIENT COMBUSTION

93.6 94.1

LIQUID FUEL JET STIRRED COMBUSTION DATA OUTPUT

DATE : NOV 5, 1979  
 RUN NUMBER: 200-H  
 FRONT FUEL: STATEX M) 30X  
 REAR FUEL: JP-10

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 740.0  
 REAR FUEL 480.0  
 FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 10044.0  
 REAR FUEL 9436.9  
 CARBON MATERIAL BALANCE  
 102.7

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 4098.0  
 REAR COMBUSTION AIR 4098.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 3137.1

OXIDATION MATERIAL BALANCE  
 103.7

NITROGEN FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC  
 FUEL TO OXIDANT RATIO  
 F FUEL R FUEL  
 0.322 0.304  
 0.111 0.153  
 0.264 0.264  
 0.36 0.50  
 0.85 0.84

BASED ON MASS FEED RATES  
 FUEL TO OXIDANT RATIO  
 F FUEL R FUEL OVERALL  
 0.261 0.261

BASED ON FLUE GAS ANALYSIS  
 FUEL TO OXIDANT RATIO  
 EQUIVALENCE RATIO  
 OVERALL  
 0.261 0.84

TOTAL G4-MOLEF5/HR  
 423.8

WET FLUE GAS ANALYSIS (MOLE PERCENT)

CO	CO2	HC	O2	NO	NOX	N2	H2O
0.24	14.56	0.0	4.29	0.0	0.0	70.79	9.99
						0.0782	6.3

SOOT MEASUREMENT (GRAMS/HR)

COMBUSTION TEMPERATURE (K)  
 2004.1 ( 5.0)  
 RESIDENCE TIME (MILLISEC)  
 6.1

EFFICIENCIES  
 CARBON BURNOUT 94.0  
 COMBUSTION 98.1

LIQUID FUEL JET STIRRED COMBUSTION DATA SHEET

DATE 1 NOV 5, 1979  
 RUN NUMBER: 291-A

FRONT FUEL: STERLING R 204  
 REAR FUEL: JP-10

CARBON MATERIAL BALANCE

100.8

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL REAR FUEL

10049.0 9436.9

FUEL FLOW RATES (GRAMS/HR)  
 FRONT FUEL REAR FUEL

342.0 476.0

OXIDANT FLOW RATES (GRAMS/HR)

FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 4098.0  
 REAR COMBUSTION AIR 4098.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 3137.1

OXYGEN MATERIAL BALANCE

102.0

NITROGEN FLOW RATES (GRAMS/HR)

FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC BASED ON MASS FEED RATES

F FUEL	R FUEL	F FUEL OVERALL	R FUEL OVERALL	F FUEL R FUEL OVERALL	EQUIVALENCE RATIO	FUEL TO OXIDANT RATIO
0.316	0.304	0.109	0.151	0.250	0.55	0.50
					0.86	0.86

BASED ON FLUE GAS ANALYSIS  
 FUEL TO OXIDANT RATIO EQUIVALENCE RATIO

0.257 0.83

WET FLUE GAS ANALYSIS (MOLE PERCENT)

TOTAL GM-MOLES/HR	CO	CO2	HC	O2	H2O	NOX	N2	H2	SOOT MEASUREMENT (GRAMS/HR)
473.1	0.34	14.04	0.20	4.24	0.0	0.0	70.91	0.1368	2.0
								10.24	

COMBUSTION TEMPERATURE (°C)

2043.12 ( 5.0)

RESIDENCE TIME (MILLISEC)

6.0

EFFICIENCIES

CARBON EFFICIENCY COMBUSTION

77.1

98.2

LIQUID FUEL JET STIRRED COMBUSTION DATA OUTPUT

DATE : NOV 5, 1974  
 RUN NUMBER: 210-A  
 FRONT FUEL: STATEX MT 508  
 REAR FUEL: JP-10

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL 360.0  
 REAR FUEL 480.0

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL 10044.0  
 REAR FUEL 9436.9  
 CARBON MATERIAL BALANCE 101.3

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 4099.0  
 REAR COMBUSTION AIR 4099.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 1137.1

NITROGEN FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGMA POINT 168.0  
 TOTAL 168.0

OXYGEN MATERIAL BALANCE  
 100.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC FUEL TO OXIDANT RATIO  
 F FUEL 0.376  
 R FUEL 0.304  
 OXYGEN 0.115  
 TOTAL OXIDANT 0.153  
 BASED ON MASS FEED RATES  
 FUEL TO OXIDANT RATIO  
 F FUEL 0.268  
 R FUEL 0.153  
 OXYGEN 0.034  
 TOTAL OXIDANT 0.268  
 BASED ON FLUE GAS ANALYSIS  
 FUEL TO OXIDANT RATIO 0.34  
 EQUIVALENCE RATIO 0.50  
 OVERALL FUEL R FUEL 0.85  
 EQUIVALENCE RATIO 0.86

WET FLUE GAS ANALYSIS (PERCENT)

CO	CO2	HC	NO	NOX	H2	H2O
0.29	14.86	5.0	0.0	0.0	0.1954	9.10
					SOOT MEASUREMENT (GRAMS/HR)	
					0.0	

COMBUSTION TEMPERATURE (K)  
 2063.1 ± 10.0

RESIDENCE TIME (MILLISEC)  
 5.9

EFFICIENCIES  
 CARBON BURN 96.5  
 COMBUSTION 97.4



LIQUID FUEL JET STIRRED COMBUSTOR DATA OUTPUT

DATE : JAN 7, 1979  
 RUN NUMBER: 220-A

FRONT FUEL: STATEX MT 30%  
 REAR FUEL: JP-10

CARBON MATERIAL BALANCE

FUEL HEATING VALUES (CAL/GRAM)  
 FRONT FUEL REAR FUEL

96.4

FUEL FEED RATES (GRAMS/HR)  
 FRONT FUEL REAR FUEL

1004.0 9536.9

OXIDANT FLOW RATES (GRAMS/HR)

OXYGEN MATERIAL BALANCE

NITROGEN FLOW RATES (GRAMS/HR)

FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 768.0  
 FRONT COMBUSTION AIR 4122.0  
 REAR COMBUSTION AIR 4122.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 3148.3

FRONT ATOMIZING 0.0  
 REAR ATOMIZING 0.0  
 SIGHT PORT 168.0  
 TOTAL 168.0

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC FUEL TO OXIDANT RATIO  
 F FUEL R FUEL OVERALL F FUEL R FUEL OVERALL

BASED ON MASS FEED RATES  
 FUEL TO OXIDANT RATIO EQUIVALENCE RATIO

BASED ON FLUE GAS ANALYSIS  
 FUEL TO OXIDANT RATIO EQUIVALENCE RATIO

0.372 0.304 0.111 0.152 0.263 0.34 0.50 0.85 0.253 0.81

WET FLUE GAS ANALYSIS (MOLE PERCENT)

SOOT MEASUREMENT (GRAMS/HR)

TOTAL GM-MOLES/HR	CO	CO2	HC	O2	NO	NOX	N2	H2	H2O
422.3	0.19	13.77	0.0260	4.56	0.0	0.0	71.36	0.0078	10.07

COMBUSTION TEMPERATURE (K)

RESIDENCE TIME (MILLISEC)

1953.12( 10.0)

6.3

EFFICIENCIES  
 CARBON BURNOUT COMBUSTION

91.5 94.3

LIQUID FUEL JET STIRRED COMBUSTOR DATA OUTPUT

DATE : Jan 7, 1979  
 TIME CORRECTED 220-11  
 FRONT FUEL : 5.1646 G/HR  
 REAR FUEL : 0.2510

CARBON MATERIAL BALANCE  
 96.9

FUEL TO AIR RATIO VALUES (G/GM AIR)  
 FRONT FUEL 10044.0  
 REAR FUEL 9436.9

FUEL FLOW RATES (GRAMS/HR)  
 FRONT FUEL 348.0  
 REAR FUEL 480.0

NITROGEN FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING 9.0  
 REAR ATOMIZING 0.0  
 SIGHT POINT 164.0  
 TOTAL 164.0

OXYGEN MATERIAL BALANCE  
 100.8

OXIDANT FLOW RATES (GRAMS/HR)  
 FRONT ATOMIZING AIR 1770.0  
 REAR ATOMIZING AIR 758.1  
 FRONT COMBUSTION AIR 4122.0  
 REAR COMBUSTION AIR 4122.0  
 OXYGEN 636.0  
 TOTAL OXIDANT 11488.1

FUEL OXIDANT Mixture CONDITIONS

STOICHIOMETRIC FUEL TO OXIDANT RATIO 0.322 0.304  
 F FUEL R FUEL  
 0.111 0.152 0.263 0.36 0.50 0.85  
 BASED ON MASS FEED RATES EQUIVALENCE RATIO  
 FUEL TO OXIDANT RATIO OVERALL  
 0.253 0.81  
 HASED ON FIVE GAS ANALYSIS EQUIVALENCE RATIO

WET FLUE GAS ANALYSIS (MOLE PERCENT)

	CO	CO2	H2	O2	NO	NOX	N2	H2O
TOTAL GM-MOLE/HR	0.14	13.79	0.0266	4.56	0.0	0.0	71.36	10.07
477.3								9.1

COMBUSTION TEMPERATURE (K) 1953.15 (10.0)  
 RESIDENCE TIME (MILLISEC) 6.3

EFFICIENCIES COMBUSTION  
 CARBON BURNOUT 91.3  
 98.2

LIGUID FUEL JET STIRRED COMBUSTOR DATA OUTPUT

DATE : JAN 7, 1979  
 RUN NUMBER: 221-A

FRONT FUEL: STATEX MT 303--1000 PPM 7R  
 REAR FUEL: JP-10

FUEL FEED RATES (GRAMS/HR)		CARBON MATERIAL BALANCE
FRONT FUEL		
REAR FUEL		
348.0	480.0	95.0
FUEL HEATING VALUES (CAL/GRAM)		
FRONT FUEL		
REAR FUEL		
10044.0	9436.9	

OXIDANT FLOW RATES (GRAMS/HR)		OXYGEN MATERIAL BALANCE		NITROGEN FLOW RATES (GRAMS/HR)
FRONT ATOMIZING AIR	1770.0		101.7	FRONT ATOMIZING
REAR ATOMIZING AIR	768.0			REAR ATOMIZING
FRONT COMBUSTION AIR	4122.0			SIGHT PORT
REAR COMBUSTION AIR	4122.0			TOTAL
OXYGEN	636.0			168.0
TOTAL OXIDANT	3143.3			

FUEL OXIDANT MIXTURE CONDITIONS

STOICHIOMETRIC		BASED ON MASS FEED RATES		BASED ON FUEL GAS ANALYSIS
FUEL TO OXIDANT RATIO		FUEL TO OXIDANT RATIO		FUEL TO OXIDANT RATIO
F FUEL	0.322	F FUEL	0.36	F FUEL
H FUEL	0.304	H FUEL	0.50	H FUEL
		OVERALL	0.263	OVERALL
			0.152	
			0.246	
			0.679	

WET FUEL GAS ANALYSIS (MOLE PERCENT)

TOTAL GAS-MOLES/HR	CO	CO2	H2	H2O	N2	WET FUEL GAS ANALYSIS (MOLE PERCENT)
423.1	0.19	13.50	0.0136	5.01	0.0	0.0
						0.0052
						10.00
						9.4

COMBUSTION TEMPERATURE (K)

6.3

1964.12 (10.0)

EFFICIENCIES

CARRIAGE HEATOUT COMBUSTION

98.1

91.0



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