



## Project Summary

# Fundamental Combustion Research Applied to Pollution Formation: Volume II. Physics and Chemistry of Two-Phase Systems

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As a part of EPA's Fundamental Combustion Research (FCR) Program, eight studies were conducted by various investigators to better understand the physics and chemistry of two-phase combustion with respect to pollution formation. Reports from these studies are grouped into three sections, bound separately, which comprise Volume II of the FCR report series. Volume IIa describes mechanisms of fuel nitrogen processing in large-scale utility flames burning pulverized coal and heavy fuel oils, in three parts: (1) The High Temperature Decomposition and Combustion of Pulverized Coal (EERC); (2) Detailed Measurement of Long Pulverized Coal Flames for the Characterization of Pollutant Formation (International Flame Research Foundation); and (3) Heavy Oil Combustion in Shear Layers (United Technologies Research Center). Volume IIb gives information on the influence of various combustion parameters (i.e., fuel type, stoichiometry, residence time, temperature and mixing) on the fate of volatile fuel nitrogen, in four parts: (1) Method for Characterization of Coal During Thermal Decomposition (United Technologies Research Center); (2) The Volatility of Fuel Nitrogen Species (Rockwell); (3) Stirred Reactor Study of Pollutant Formation from Combusting

Pulverized Coal Clouds (Acurex) and (4) Pollutant Formation from Combustion of Fuel Oils in a Well-Mixed Combustor (Battelle). Volume IIc gives information on the kinetic rates and mechanisms of nitrogen oxide (NO) reduction on solid particles, in three parts: (1) Trials on NO and NH<sub>3</sub>, Alumina, Quartz, Graphite, and Soot; (2) Comparative Study of Coal and Char; and (3) Trials on Fly Ashes and Study of Reactions Involving Hydrogen Cyanide (Institut Francais du Petrole).

*This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in three separate volumes of the same title (see Project Report ordering information at back).*

### Introduction

The EPA has conducted a wide range of research projects under its Fundamental Combustion Research Applied to Pollution Formation (FCR) program. The principal goal of the FCR program was to generate the understanding of combustion behavior necessary to help develop control strategies to minimize nitrogen oxide (NO<sub>x</sub>) emissions from stationary sources. Because of the increased use of coal and residual fuel oils, the dominant stationary

source of  $\text{NO}_x$  for the foreseeable future is the conversion of nitrogen in the fuel. This observation implies a need to understand the various phenomena associated with burning fuels containing high levels of nitrogen.

The FCR program involved program planning, management, and synthesis of the overall program, and subcontracting to various organizations separate projects included within program elements. Subcontracts accounted for 70% of the program and were used to ensure that FCR had the benefit of the best scientific talent available. Every effort was made to use subcontractors who had the necessary experience and, in many cases, equipment to produce quality results in a short time frame.

A wide variety of combustion phenomena can have a direct impact on the  $\text{NO}_x$  emission rate from pulverized coal and residual oil fired boilers. The FCR program structure, described in Figure 1, was established to allow for investigation into phenomena believed to be critical to meeting the program goals. Three major program areas were augmented by two program support areas. The major program area, Transport Process in Reacting Systems allowed for studies into the ballistics and fluid mechanics of bringing fuel and air into contact with each other and into the transport of the reacting mixture under boiler conditions. The major program area, Physics and Chemistry of Two-Phase Systems, is devoted to understanding the decomposition and processing of solid and liquid fuels as a function of the reactive environment and local thermal conditions. The Gas Phase Chemistry major program area was provided to better understand the gas phase reactions leading to  $\text{NO}$  formation, particularly reactions involving nitrogenous species from fuel devolatilization. The two program support areas, Analytical Tool Development and Measurement Systems were provided to assist in performing experiments and analyzing data. This program structure is designed to permit studies into a wide variety of areas influencing  $\text{NO}_x$  formation and control. It also permits focusing individual studies leading to two major program outputs:

- A description of the chemical limits on  $\text{NO}$  production in order to ascertain the lower bounds of both fuel and thermal  $\text{NO}$  production under a series of process constraints which were not limited in any way by fuel/ air contacting.

- A description of fuel  $\text{NO}$  formation in turbulent diffusion flames for gas, liquid, and pulverized coal systems.

Documentation of research performed under the FCR program is contained in four basic volumes and a special report. Each volume (or volume series reports on the work accomplished in a major program area or program support area. Volume I (EPA-600/7-85-048) covers work in the Gas-Phase Chemistry program area. Volume II addresses Physics and Chemistry of Two-Phase Systems, Volume III is devoted to the FCR effort in Measurement Systems, and Volume IV is concerned with Analytical Tool Development and Transport Processes. In addition, a special report (EPA-600/7-85-048) has been issued to document the proceedings of a workshop held by FCR contractors.

Most of the FCR effort was devoted to the Physics and Chemistry of Two-Phase Systems program area which consisted of eight individual research projects. Accordingly, Volume II has been subdivided into three separately bound components denoted as Volumes IIa, IIb, and IIc.

### Physics and Chemistry of Two-Phase Systems

The critical processes which must be addressed to understand the interplay between two-phase combustion and pollution formation are listed in Figure 2. The processes are displayed in relative position against a photograph of an actual turbulent pulverized-coal diffusion flame. The ability to address these processes represents the benchmark of the accomplishments of the FCR program in this major program area. The processes, and, therefore, the important areas of research, are:

**Ignition.** The ignition of flames influences not only stability, which is an extremely important operating parameter, but also premixing which can strongly impact fuel nitrogen conversion.

**Physical Processes During Devolatilization.** The mechanism by which volatiles are released from the coal matrix can dramatically influence a wide variety of phenomena including temperature response, ignition, the environment in which volatile nitrogen will react, and soot formation. Very little is known about how pulverized coal or fuel oil actually decomposes in flames.

**Nitrogen Devolatilized.** Bench-scale tests indicate that the conversion of volatile nitrogen is the largest contributor to total fuel nitrogen conversion to  $\text{NO}$ . Also, the volatility of fuel nitrogen is strongly tied to the fuel type and the time/temperature history of the particular application; therefore, it is imperative that the volatility of fuel nitrogen be understood if the conditions for minimum fuel nitrogen conversion are to be generalized.

**Species Evolved and Fraction of Mass Devolatilized.** The amount of hydrocarbon species evolved from the fuel is expected to impact the local stoichiometry, soot formation and the local temperature; also, the impact of fuel type and time/temperature history is not well understood. Of particular interest is the form the nitrogenous compound and the light and heavy hydrocarbon yield.

**Temperature Response.** The temperature response of the fuel particles and droplets influences almost all aspects of the pollution formation sequence. Little is known about what factors influence the particle temperature and how that parameter, in turn, affects other parameters.

**Soot Formation.** Soot formation is important because it is a primary pollutant itself, it can act as a smoke limit to how rich the primary stage can be taken, and it can act as a source of carbonaceous material on which fuel nitrogen species can be reduced to molecular nitrogen. The mechanisms of soot formation from pulverized coal and fuel oil combustion have as yet not been explored. Little is even known about the amounts of soot formed in such flames.

**Char  $\text{NO}$  Reduction.**  $\text{NO}$  can react with heterogeneous particulate to be reduced to molecular nitrogen. The degree to which this occurs from flame-formed particulate, and under what conditions, is not known.

**Char Nitrogen Conversion to  $\text{NO}_x$ .** The traditional staging low- $\text{NO}_x$  concept addresses only the volatile nitrogen species. The conversion of the nitrogen that remains in the char to  $\text{NO}$  thus represents the ultimate limit that can be achieved using staged combustion. The conversion of the remaining char nitrogen needs to be explored if this limit is to be lowered. Further, questions remain concerning how the first-stage processes

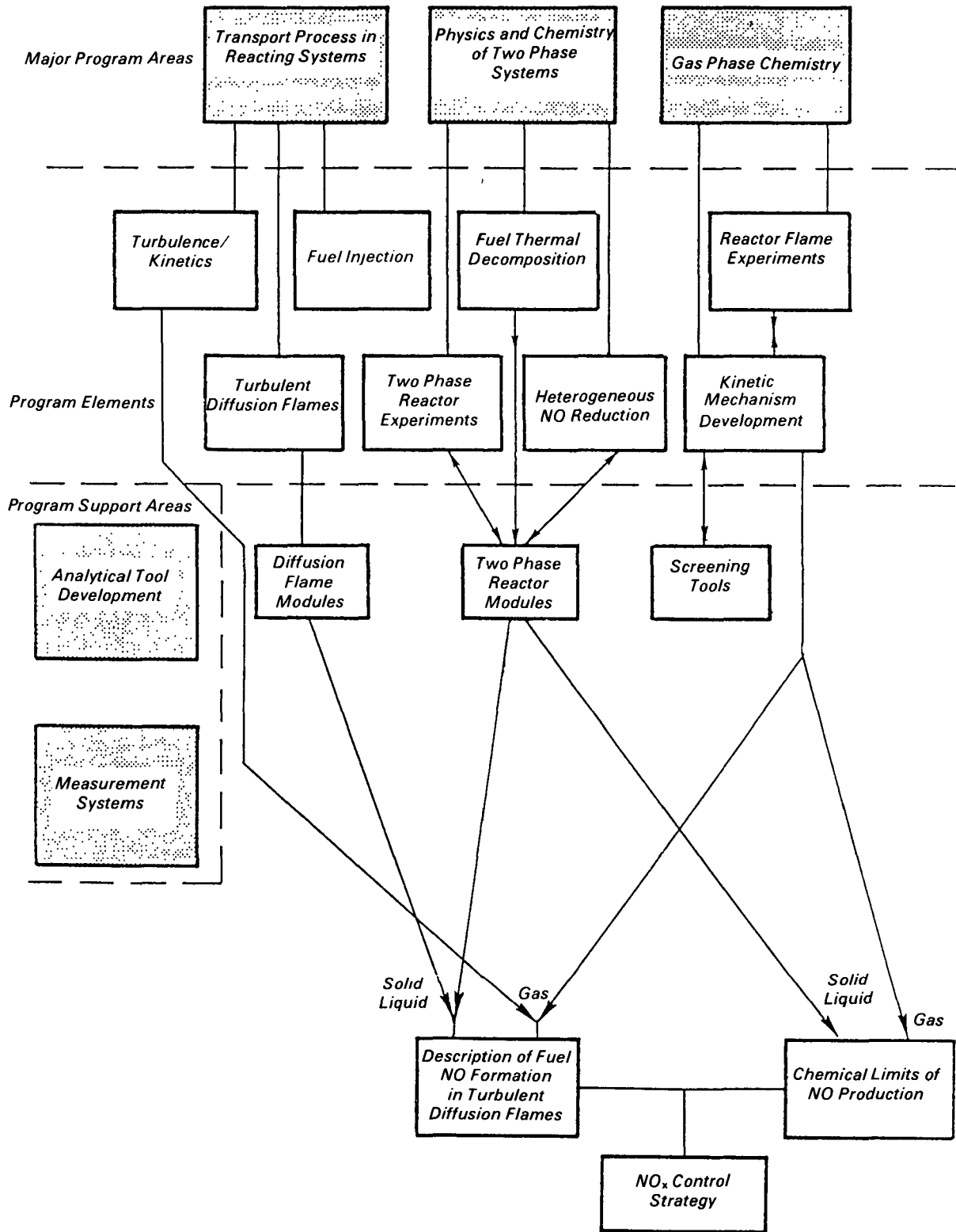


Figure 1. FCR-I program structure.

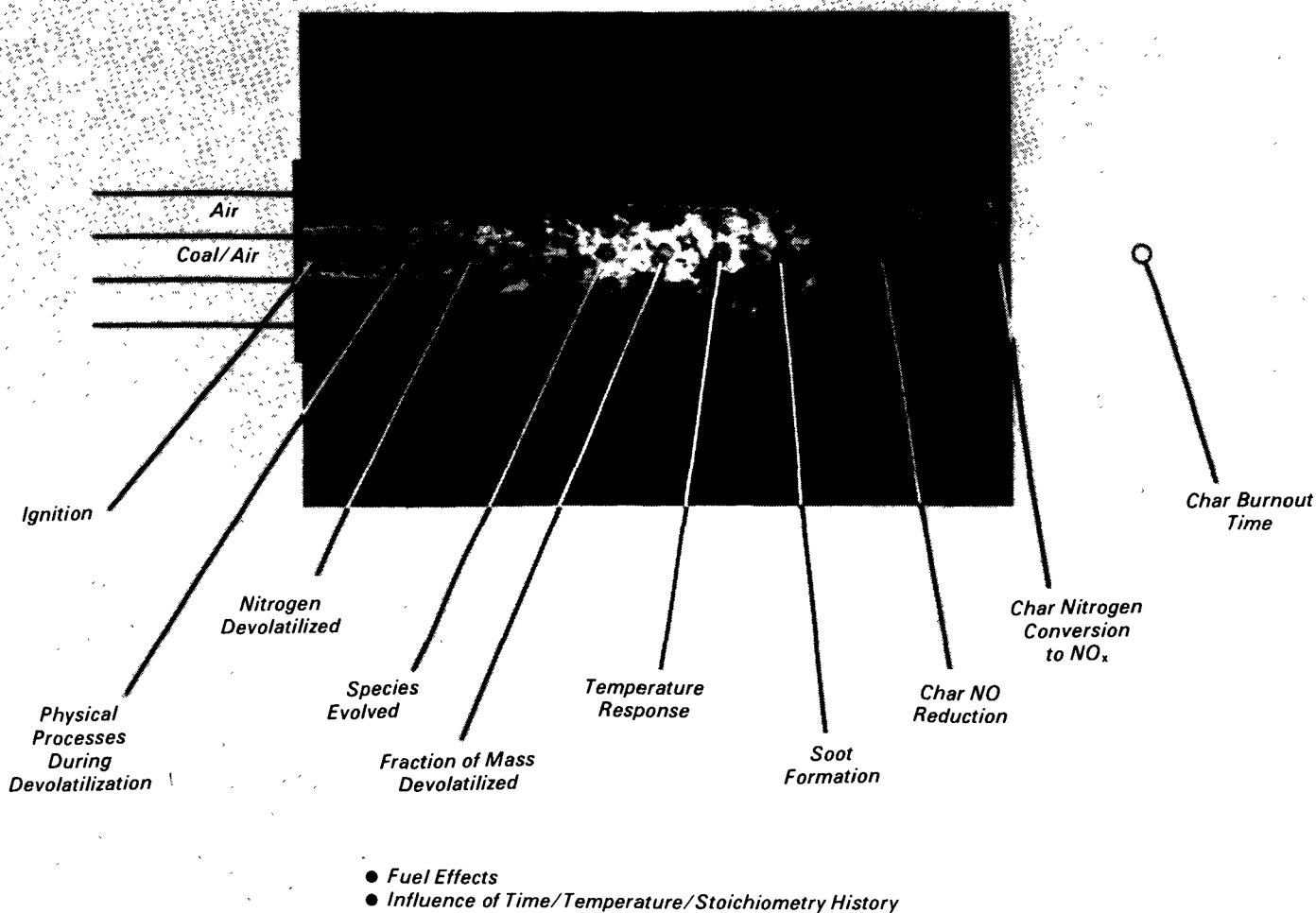


Figure 2. Critical processes influencing the fate of fuel nitrogen in pulverized coal flames.

influences the subsequent character and reactivity of the char. This can be an important aspect of whether the char will burn out within the combustor volume.

A program plan was developed to both determine what questions were necessary for the development of multimedia control technologies for stationary sources and to address those questions. It was not possible to address every issue, but a focused program evolved which was directed toward the important issues of relevance to the Combustion Research Branch (CRB) of EPA in order for the results to be applied. This major program element (i.e., the physics and chemistry of two-phase combustion) consisted of eight well-defined priority target areas, and

the ensuing research effort was guided toward the specific problem of the area.

The target areas and the individual projects which made up these areas are:

*Flame Combustion Processes* (Volume IIa)

The High Temperature Decomposition and Combustion of Pulverized Coal - EER

Detailed Measurement of Long Pulverized-Coal Flames for the Characterization of Pollutant Formation - International Flame Research Foundation

Heavy Oil Combustion in Shear Layers - United Technologies Research Center

*Devolatilization and Volatile Reactions* (Volume IIb)

Method for Characterization of Coal During Thermal Decomposition - United Technologies Research Center

The Volatility of Fuel Nitrogen Species - Rockwell

Stirred Reactor Study of Pollutant Formation from Combusting Pulverized Coal Clouds - Acurex

Pollutant Formation from Combustion of Fuel Oils in a Well-Mixed Combustor - Battelle

*Heterogeneous NO Reduction* (Volume IIc)

Mechanisms of Nitric Oxide Reduction on Solid Particles - Institut Francais du Petrole

The first program area (Volume IIa) consists of programs to define the physical and chemical processes

occurring in large scale utility flames burning pulverized coal or heavy fuel oils. The major emphasis is on understanding the mechanisms of fuel nitrogen processing in flames of this type, developing a data base for model development, and exploring scale effects. The second area (Volume IIb) considers only the devolatilization and early combustion processes. The programs in this area were designed to yield information on the influence of combustion parameters such as fuel type, stoichiometry, residence time, temperature, and degree of mixing on the fate of volatile fuel nitrogen. The final area (Volume IIc) provides information on the kinetic rates and mechanisms of heterogeneous NO reduction for typical combustion-generated particulate, which are necessary to assess the relative importance of heterogeneous reduction processes.

### **Volume IIa - Flame Combustion Processes**

This volume consists of final documentation on three individual efforts dealing with flame combustion processes.

#### **High Temperature Decomposition and Combustion of Pulverized Coal (EER)**

Despite the fact that coal has been burned for decades and has been the subject of study for nearly as long, little is actually known about the physical processes occurring to the individual coal particles and their close environment. The purpose of this study was to fill this data gap by directly observing the microscale phenomena that occur around individual coal particles as they burn in an environment simulating large-scale, turbulent diffusion flames.

The experimental facility employed was a downfired flat-flame burner with a centerline port for injection of pulverized coal particles. The methane/air fired flat-flame burner produced a background of hot reaction products. As the pulverized coal particles entered this environment, they were ignited and produced a long flame which was remarkably similar to many practical boiler flames.

A variety of optical and intrusive measurement techniques were employed to examine the microscale phenomena associated with the burning coal particles. Both holography and high speed shadowgraph photography were used to visualize the burning particles.

Two color optical pyrometry was used to measure the particle temperature, and sodium D line reversal was used to measure gas temperature. Extractive sampling was employed to determine the local gas chemical composition and to examine the morphology of the particulate.

Figure 3 presents a mosaic of flame observations and indicates spatial variation of surface morphology and the local environment of the burning coal particles. Photographs from re-constructed holograms (on the righthand side of Figure 3) indicate that the devolatilizing coal particles can produce a cloud of soot particles which are seen to collapse into long fibrous shapes. These results were the first experiments to indicate the formation of either the soot cloud or the long structures. The experimental program includes trial series examining coal type, initial particle size, particle injection velocity and background gas temperature and stoichiometry.

#### **Detailed Measurements of Long-Pulverized Coal Flames for the Characterization of Pollutant Formation (IFRF)**

This study utilized state-of-the-art measuring techniques to characterize in detail a number of long pulverized coal flames under well-defined input and boundary conditions. These experiments were relatively large scale, having been conducted in a 1.9 x 1.9 m cross section furnace fired at the 2 MW<sub>t</sub> level.

Measurements in these flames included the determination of local gas and solids compositions and concentrations, temperatures, and radiative and aerodynamic characteristics. The measurements were of sufficient detail for use in validation of predictive procedures both for global combustion processes and for specific phenomena relating to coal particle combustion.

The flames for all six trials were produced with a very simple double concentric, parallel-flow burner system. This burner system generates long flames which are far-field dominated and where the heat release is protracted. Such flame shapes exhibit the real characteristics of certain classes of furnaces flames such as cement kilns and possibly tangentially fired boilers. Further, the far-field domination significantly simplifies the problem of mathematically simulating the process. Thus, the experimental results reported

represent an initial data base for developing a verified model of pulverized coal combustion in a practical furnace environment.

The six long coal flames investigated represent variations due to air and fuel input velocities and temperatures. These variations have a direct impact on the flame mixing characteristics and on the coal particle heating rate. Complete flow field mapping data are presented in both graphic and tabular form. Despite many difficulties encountered in measuring in such flames, particularly for sampling in regions of high temperature and solids concentrations, the consistency between the various measurements is generally good. Indications are that globally the combustion is controlled by mixing and that the influence of fuel kinetics is basically the same in all cases. In particular, NH<sub>3</sub> concentrations are always very low, while HCN was found to form very rapidly and in large amounts. More detailed evaluation of these data is still required for a quantitative interpretation of fuel nitrogen conversion to HCN and to NO.

#### **Heavy Oil Spray Combustion in Shear Layers (UTRC)**

This program consisted of two phases: (1) design and fabrication of an apparatus, and (2) preliminary combustion experiments. A unique shear layer mixing and composition apparatus was developed which simulates high shear, diffusive combustion with heavy oil droplet injection as found in the near-field combustion zone of boilers and furnaces. The apparatus, shown in Figure 4, provides:

- (1) Two-dimensional mixing and combustion of uniform streams of air and rich combustion products fed from either side of a splitter plate.
- (2) Uniform injection of a monodisperse heavy oil spray into the shear layer by means of a linear array of fuel injectors beneath the combustor wall.
- (3) Control of droplet path, residence time, and extent of vaporization.
- (4) Control of hot and cold stream inlet properties.
- (5) Three-dimensional probing of the flow field.

The design phase of the program consisted of two tasks: aerodynamic and thermodynamic design, and mechanical design. A wind tunnel, hot gas generator, combustion chamber, droplet injection system, and phase-sensitive sampling probe were designed initially. The design

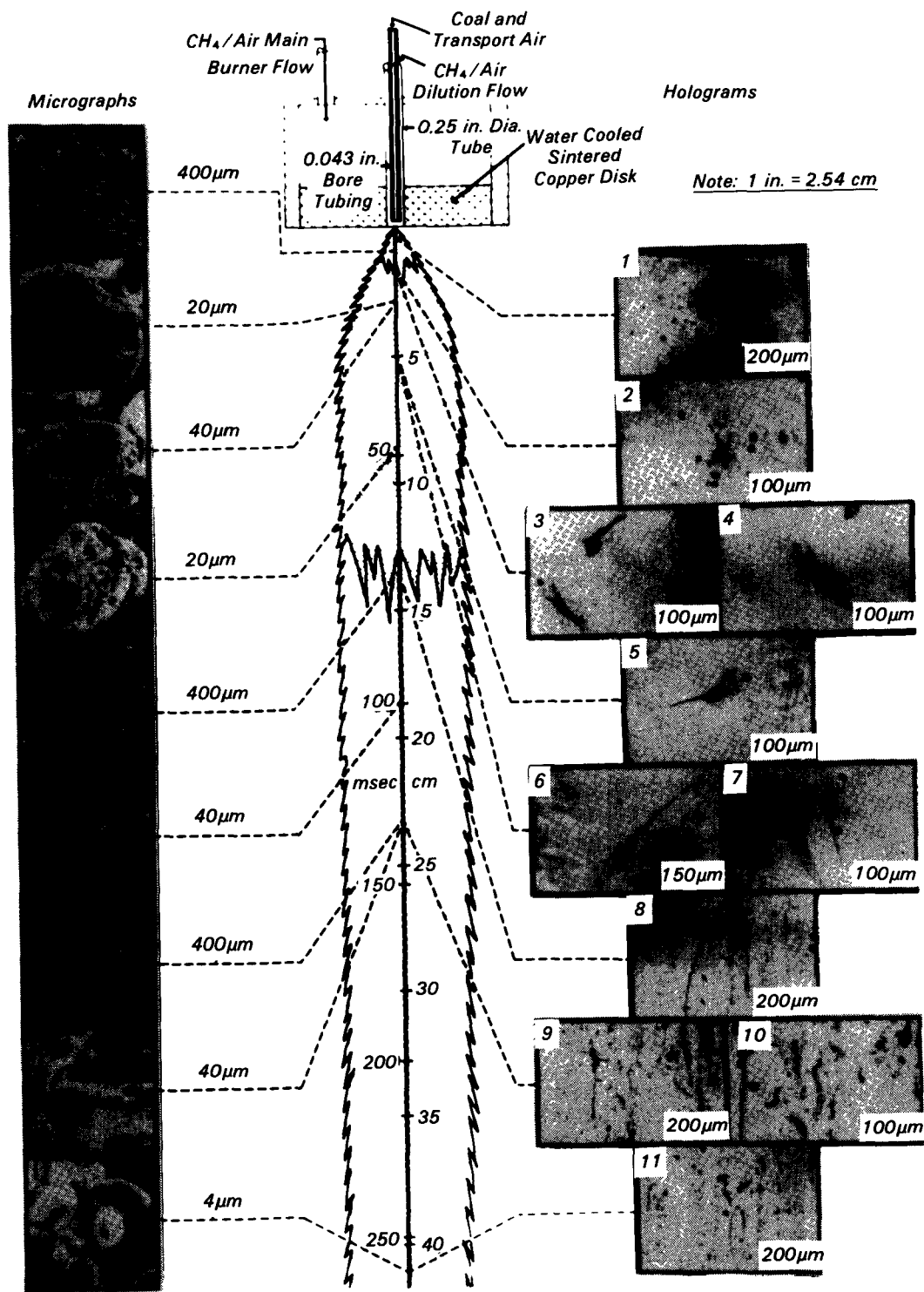


Figure 3. Coal flame visualization.

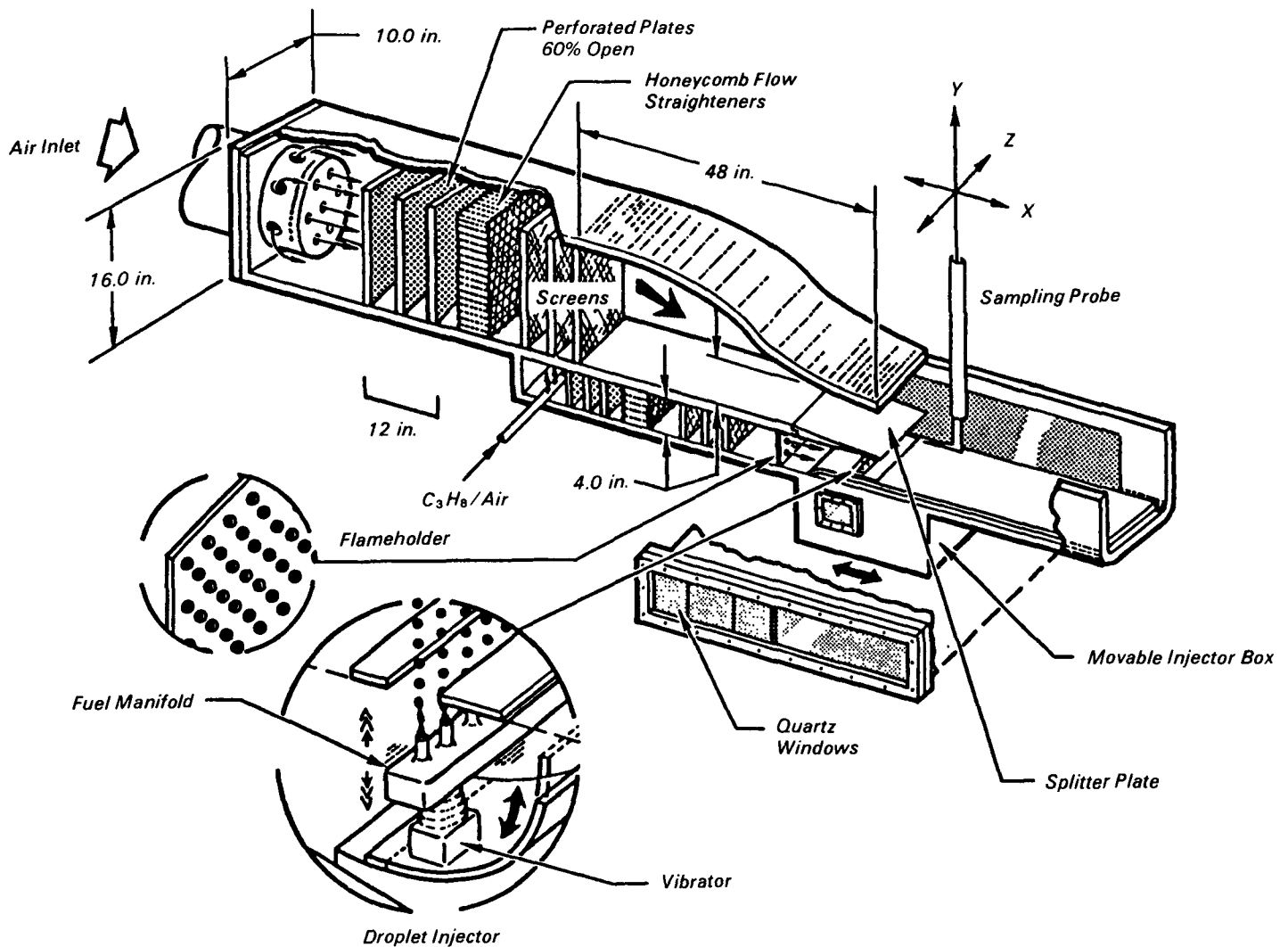


Figure 4. Heavy oil spray combustor.

of the apparatus was influenced most strongly by the diverse requirements of the fuel injection system. The injector was designed so that the angle of droplet penetration into the shear layer could be varied over a wide range. Droplet trajectories were computed for vaporizing No. 6 oil droplets injected from the floor of the combustor into a hot, rich environment provided by a hot gas generator. Hot gas generator dimensions and injector locations were selected to accommodate the required droplet trajectories, provide complete vaporization if desired, and provide sufficient hot soak time for substantial conversion of volatile fuel nitrogen compounds to molecular nitrogen. The design of a low turbulence wind tunnel, combustion

chamber, and phase sensitive probe completed this task.

Due to program time constraints, only initial system verification tests were performed during this effort. The testing which was performed consisted of (1) verification of uniform properties of the hot and cold streams at the splitter plate trailing edge, (2) demonstration of high injection velocities and uniform droplet size and penetration with No. 2, 5, and 6 oils in vibrating multicapillary injectors, (3) determination of stable flow regimes as a function of primary and secondary stream velocities, (4) flame stability and flashback studies, (5) high speed cinematography of the shear layer with injection of No. 2 and 6 fuel oil, and (6) preliminary flame probing.

### Volume 11b - Devolatilization and Volatile Reactions

This volume consists of final documentation of four efforts dealing with devolatilization and reaction of volatile components. As such, the studies concentrate on the early flame zone processing of high nitrogen fuels.

### Method for Characterization of Coal During Thermal Decomposition (UTRC)

This study is a continuation of an earlier effort to develop a model of the coal devolatilization process. Basically, the model assumes that a coal particle can be represented as a series of functional chemical groups which are

split into tar-forming and non-tar-forming fractions. The functional groups include carboxyl, hydroxyl, two ether, non-volatile, aliphatic, aromatic hydrogen, and carbon as shown in Figure 5.

The evolution of each component into a gas phase (carboxyl into CO<sub>2</sub>, aromatic hydrogen into H<sub>2</sub>, etc.) is represented by a first order function of the form  $Y(i) = Y^{\circ}(i)\exp(-K_i t)$ . There are two ether components since CO is typically evolved in two distinct steps. Values for the initial coal composition representation are derived from quantitative infrared measurements, ultimate analysis, and pyrolysis data for the particular fuel.

When coal particles thermally decompose, a substantial portion of the initial mass is evolved as a tar. Infrared analysis of these tars shows that their spectra are very similar to those of the parent coal, except that the tar has enhanced aliphatic content. The evolution of the tar is represented by a first-order diminishing of the tar forming fraction according to  $X = X^{\circ}\exp(-K_x t)$ .

The kinetic rate constants  $K_c$  and  $K_x$  are represented by Arrhenius expressions derived from experimental data. The thrust of the current program was to expand the model to include nitrogen evolution and to examine, theoretically and experimentally, a series of coals being used in other EPA NO<sub>x</sub> control development programs. The experimental studies included vacuum and 1-atmosphere thermal decomposition studies. The vacuum experiments were performed in a heated grid facility which allowed the coal sample to be heated at a controlled rate to a specific final temperature. Fourier transform infrared analysis was used to monitor the volatile yield and speciation as a function of time. The 1-atmosphere experiments were performed in an isothermal furnace and allowed for particle heating rates one to two orders of magnitude greater than in the heated grid trials. These latter tests included examinations of the various coals as well as studies of the high temperature thermal decomposition of the tars.

The various results obtained in this study provide insight into the thermal decomposition process but also indicate the need for significant modification to the basic hypotheses of the model. Specifically, it was observed that the volatile product distribution and evolution rates are sensitive functions of physical parameters such as thermal drive, final temperature, and initial particle size.

Thus, variations in product distributions are not simply the result of variations in the functional group mix of the parent coal. An initial attempt to modify the model is presented as part of this report. The basic result, however, is that additional theoretical and experimental studies are required to produce a generally acceptable model of coal decomposition.

### The Volatility of Fuel Nitrogen Species (Rocketdyne/Rockwell)

This FCR program task is a continuation of an earlier EPA sponsored program where a two-stage inert pyrolysis reactor was developed to study the evolution of fuel nitrogen species. That earlier study showed that reactive volatile nitrogen evolved from the fuel in the first-stage pyrolysis process is converted to HCN in the second stage when the second stage is held at about 1400 K. This two-stage reactor technique, therefore, permits a simple measurement of the reactive nitrogen yield from fuel thermal decomposition.

The thrust of this task was to examine samples of various fuels being used in other CRB-sponsored NO<sub>x</sub> control development programs. A total of 19 fuels (including residual oils, coal derived liquids and coals) were subjected to the two stage pyrolysis process, and the HCN yield was compared to NO production from controlled combustion tests. For the seven coals tested, an encouraging correlation was developed relating the HCN yield from pyrolysis to the percent conversion of fuel bound nitrogen to NO<sub>x</sub> in the combustion tests. This correlation, shown in Figure 6, generates several concerns about its generality and fundamental basis, but the results do indicate a possible approach for relating NO<sub>x</sub> production potential to the chemical characteristics of the fuel.

### Pollutant Formation from Pulverized Coal Clouds and Fuel Oils

The third and the fourth tasks were to develop coal- and oil-fired well-stirred reactors to simulate the early processing of fuels in commercial boilers. The coal-fired reactor development program report is entitled, Stirred Reactor Study of Pollutant Formation from Combusting Pulverized Coal Clouds (Acurex). The oil-fired reactor development program report is entitled, Pollutant Formation from

Combustion of Fuel Oils in a Well-Mixed Combustor (Battelle).

The major portion of both tasks was devoted to developing and characterizing the facilities. In each case, cold flow models were first constructed to evaluate the basic design concepts and to demonstrate the ability to produce a high degree of stirring in the two-phase environment. Next, reacting versions of the facilities were constructed, and extensive characterization experimentation performed. These tests revealed problems with each facility which casts uncertainty on the interpretation of experimental data. For the coal-fired reactor, the gas phase appeared to be well stirred, but the solid phase had much more of a plug flow character. Further, a strong hysteresis effect was associated with the fuel injectors. For the oil-fired facility, a significant fraction of the fuel spray impacted the furnace walls, thereby distorting the early fuel reaction process. Limited combustion testing was performed in both programs, but the above noted experimental difficulties cast doubt on data interpretation.

### Volume IIc - Heterogeneous NO Reduction

This report documents a study performed at the Institut Francais du Petrol into the heterogeneous reaction of NO (and other nitrogenous species) on solid-phase material typically found in industrial flames. This extensive systematic study was performed in a packed-bed reactor maintained at controlled temperatures. Metered quantities of gaseous reactants flowed through the bed, and the outlet composition was monitored as a function of time and reactor conditions.

The program involved systematically varying the complexity of the bed material, beginning with alumina, and building to soot and coal char. The inlet composition of the reacting gases was also systematically varied, beginning with CO/argon mixtures. Hydrogen and the hydrocarbons were added. As regard nitrogenous species, the study includes NO, N<sub>2</sub>, NH<sub>3</sub>, and HCN as input reactant gases. The experimental approach included experiments with each mixture (gas- and solid-phase) of sufficient detail to extract global, intrinsic reaction rates and overall reaction order.

This experimental program, though massive in scope, should be considered an initial screening exercise to identify what heterogeneous reaction paths are of potential importance to defining the N



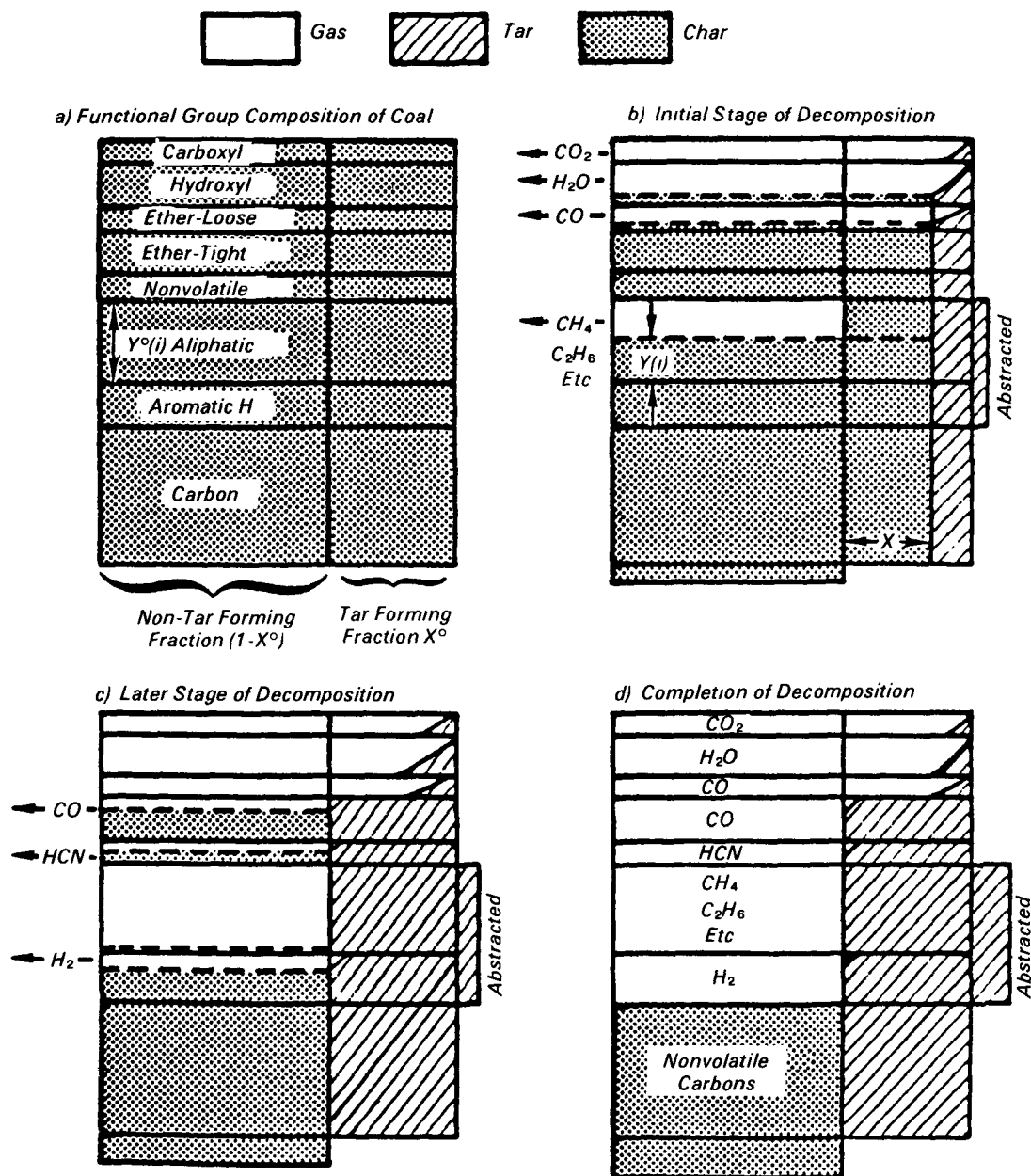


Figure 5. Basic coal devolatilization model.

emission level from pulverized-coal-fired experiments. Of particular significance is the sequence of reactions involving HCN and  $\text{NH}_3$  on soot. As noted in the earlier discussion the study of coal thermal decomposition (Volume IIa), the early devolatilization process is often accompanied by the formation of a cloud of soot particles. This environment (see Figure 3) closely resembles a packed-bed reactor and represents a

field of solid material through which the coal volatiles must pass. The intrinsic rate data developed indicate that heterogeneous reactions of HCN and  $\text{NH}_3$  with soot may lead to formation of molecular nitrogen.

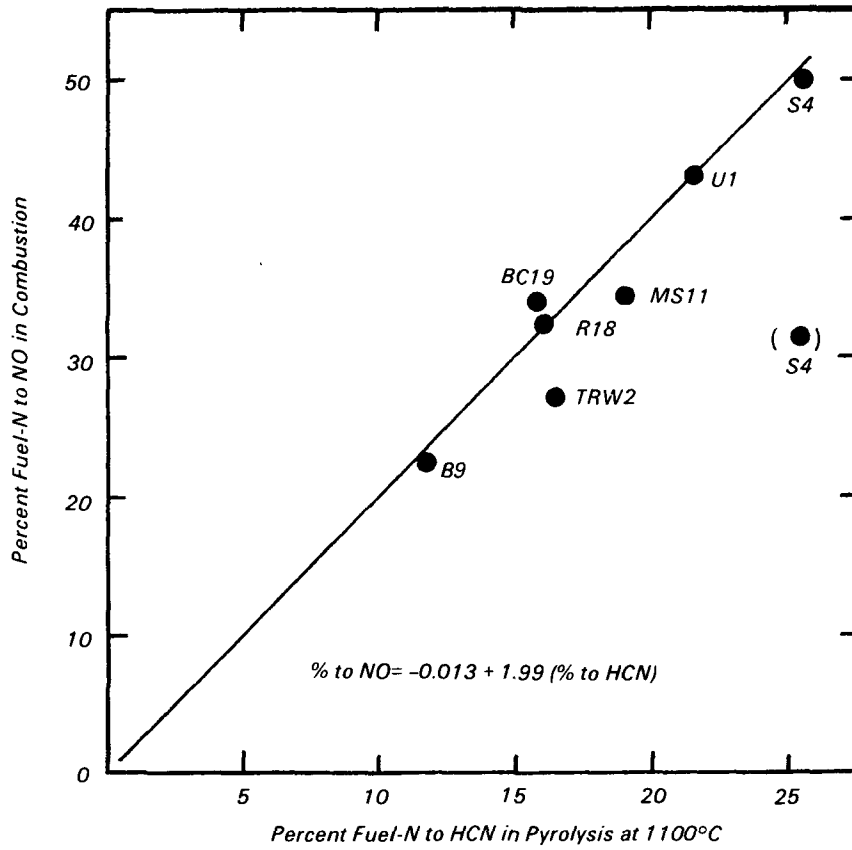


Figure 6. Percent NO in combustion vs. percent HCN in pyrolysis at 1100°C.