



Project Summary

Fundamental Combustion Research Applied to Pollution Formation Volume I. FCR Program Overview and Gas-Phase Chemistry

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This volume (Volume I) is an overview of the entire contract and the summary of the technical effort in gas-phase chemistry.

EPA's first fundamental combustion research (FCR) applied to pollution control program was a subcontract oriented program focused on the simultaneous control of nitrogen oxides (NO_x) and particulate from large, confined, 1-atmosphere, turbulent diffusion flames burning heavy residual oil and pulverized coal. The program had three major objectives:

- To generate the understanding of combustor behavior necessary to aid EPA/AEERL's Combustion Research Branch (CRB) in developing control strategies to minimize NO_x emissions from stationary sources.
- To develop engineering models which would allow effective utilization of a large body of fundamental information in the development of new NO_x control techniques.
- To identify critical information necessary for low NO_x combustor development and to generate it in a time frame which was consistent with the needs of the CRB technology development programs.

The FCR program was divided into three program areas and two support areas. The major program areas were concerned with (1) gas-phase chemistry, (2) the physics and chemistry of

two-phase systems, and (3) transport processes in reacting systems. This organization was designed to address the critical phenomena that occurred to solid or liquid fuels in turbulent diffusion flames in order to describe fuel NO formation from stationary sources. The two support areas were for the development of measurement techniques and the development of analytical tools required during the program and for future investigations. Table 1 lists the major individual projects that made up the program and the organizations primarily responsible for the effort.

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 a separate report of the same title (see Project Report ordering information at back).

Introduction

This volume describes efforts associated with gas-phase chemistry (GPC) and provides a detailed account of the FCR gas-phase effort which was divided into these principal tasks:

1. *Elementary Kinetic Development.*
To develop an elementary gas-phase kinetic mechanism which describes combustion reactions for hydrocarbons—through C_2 structures—and the fate of fuel ni-

Table 1. Fundamental Combustion Research Program

Project	Organization
Gas-Phase Chemistry	
<i>Kinetic Mechanism Development</i>	<i>Energy and Environmental Research</i>
<i>The Modeling of Fuel Nitrogen Chemistry in Combustion: The Influence of Hydrocarbon</i>	<i>Massachusetts Institute of Technology</i>
<i>The Formation and Destruction of Nitrogenous Species During Hydrocarbon/Air Combustion</i>	<i>Exxon Research and Development</i>
<i>High Temperature Reactor Studies</i>	<i>Energy and Environmental Research</i>
Physics and Chemistry of Two-Phase Systems	
<i>The Physical and Chemical Effects Occurring During the Thermal Decomposition of Coal Particles</i>	<i>Energy and Environmental Research</i>
<i>Detailed Measurements of Long Pulverized Coal Flames for the Characterization of Pollutant Formation</i>	<i>International Flame Research Foundation</i>
<i>An Experimental Approach to the Study of Heavy Fuel Oil Spray Combustion in Shear Layers</i>	<i>United Technologies Research Center</i>
<i>The Characterization of Coals During Thermal Decomposition</i>	<i>United Technologies Research Center</i>
<i>Volatility of Fuel Nitrogen</i>	<i>Rockwell International</i>
<i>Pollutant Formation from Combusting Pulverized Coal Clouds</i>	<i>Acurex</i>
<i>Pollutant Formation During the Combustion of Residual Fuel Oils in Backmixed Reactors</i>	<i>Battelle Memorial Laboratory</i>
<i>Mechanisms of Nitric Oxide Reduction on Solid Particles</i>	<i>Institut Francais du Petrole</i>
Transport Phenomenon and Engineering Analysis	
<i>Development of a Coherent Flame Model for Turbulent Chemically-Reacting Flames</i>	<i>California Institute of Technology/TRW</i>
<i>A Computer Program for General Flame Analysis</i>	<i>Energy and Environmental Research</i>
<i>Mathematical Modeling of Microscale Combustion of a Coal Particle</i>	<i>Energy and Environmental Research</i>
Measurements Support	
<i>Chemiluminescent Measurements of Nitric Oxide in Combustion Products</i>	<i>Energy and Environmental Research</i>
<i>Measurements of Fuel Nitrogen Species in Flames</i>	<i>University of Utah</i>
<i>Spray Characterization</i>	<i>Energy and Environmental Research</i>
<i>The Application of Droplet-sizing Interferometry and Holography to the Measurement of Spray Droplet Size</i>	<i>Spectron Development Laboratory</i>

trogen (including HCN, NH₃, NO, and the respective intermediates).

- Data Generation.** To generate a sufficient data base for model verification for the full mechanism (hydrocarbons + full nitrogen). A suitable quantity of data for development of the more complex portions of the gas-phase model do not exist.
- Higher Hydrocarbons.** To develop a methodology for modeling the

combustion of complex hydrocarbon fuels. Such modeling is not currently possible using elementary reactions.

The GPC effort fell into three principal subdivisions. Elementary GPC consisted of the compilation and testing of a comprehensive elementary gas-phase mechanism which describes fuel nitrogen chemistry in hydrocarbon flames. The maximum complexity of the mechanism was limited by the availability of

elementary rate data (specifically, no hydrocarbons larger than C₂ were considered). The gas-phase mechanism was tested by comparing mechanistic predictions against well-characterized data. For the most complex simulations (i.e., utilizing the full hydrocarbon/nitrogen mechanism) an insufficient number of data exist for adequate testing. Thus, a second thrust of the GPC effort was to generate the necessary data. These measurements consisted of species measurements from a jet-stirred combustor and a plug-flow burner.

Assuming an accurate and complete gas-phase mechanism is assembled, only hydrocarbon fuels of C₂ or simpler structure can be simulated. The likelihood that the elementary mechanistic approach can be extended to more complex hydrocarbons is remote. Hence, a third thrust of GPC was to develop a quasi-global method of incorporating some aspects of higher hydrocarbon chemistry into the model.

Elementary Gas-Phase Chemistry

Work on the elementary gas-phase mechanism proceeded in three well-characterized divisions: methodology development, collection of reactions and rates, and testing and modification of the mechanism.

The mechanism development methodology is a system of rules and procedures governing the testing of mechanism components and the combination of the components into more complex mechanisms. The objective of the methodology is to provide an efficient way to assemble and test the mechanism while ensuring internal consistency within the mechanism. Important features include: (1) careful selection of data for simulation such that critical questions are resolved (e.g., shock-tube ignition delays are used to resolve questions on chain initiation and branching portions of a mechanism), and (2) previously proven portions of a mechanism may be modified only after repeating the original proving simulations.

The assembled elementary reactions can be conveniently divided into the subsets H₂/O₂, CO/H₂/O₂, CH₂O, NH₃, and HCN, as shown in Figure 1. An extensive series of tests of the proposed mechanism were conducted comparing predictions against various types of shock-tube and flame data.

The results indicated that the H₂/O₂ and CO/H₂/O₂ subsets yielded excellent

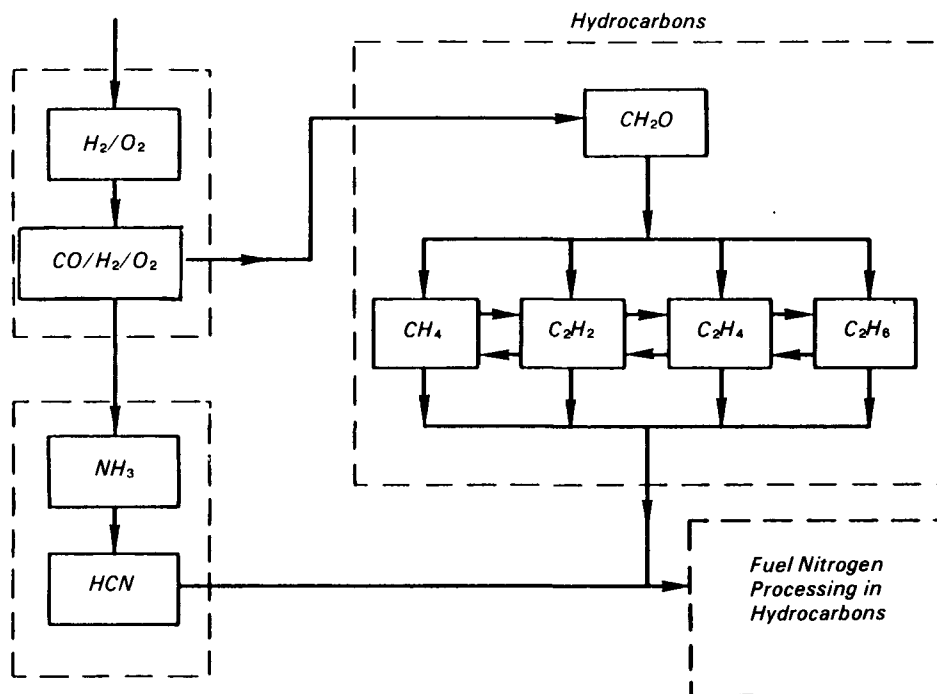


Figure 1. Overview of kinetic mechanisms.

agreement with the verification data in all cases. The comparisons included shock-tube ignition delays and radical growth rates, flat-flame profiles, and flat-flame speeds. General features of methane oxidation were well reproduced; however, radical profiles and the appearance of C_2 species were not predicted as well. The nitrogen chemistry generally predicted the overall reduction of fixed nitrogen into N_2 quite well, but was less successful in predicting the reduced nitrogen speciation. In general, the success of the predictions corresponded to the number and quality of the fundamental data used to derive the rates. Thus, the least studied systems showed the least successful reproductions: HCN chemistry, and hydrocarbon/nitrogen interaction.

Data Generation

An abundant quantity of data suitable for mechanism verification for simple compounds is in the literature. The usable quantity of data decreases as the compounds involved become more complex. Only a very small amount of literature data is available for testing the entire (hydrocarbons + fuel nitrogen) mechanism. Thus, one of the tasks of the elementary gas-phase chemistry program was to generate such a body of useful data.

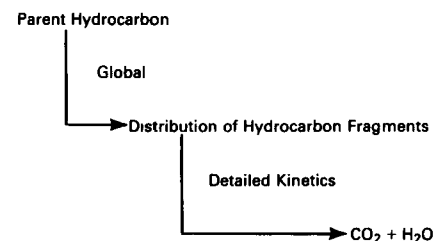
The approach was to obtain data on the fate of doped nitrogen in well characterized hydrocarbon combustion environments. Two experiments were used: the Exxon jet-stirred reactor and the Exxon Multiburner (a flat-flame firing into an isothermal plug-flow reactor). Temperatures ranged from 1800 to 2000 K and equivalence ratios were varied from 0.7 to 1.8. Fuels were methane, ethylene, or propane, and fuel-nitrogen was represented by ammonia or an ammonia/nitric oxide mixture. The measurements included the standard combustion products (O_2 , CO, CO_2 , H_2 , and total hydrocarbons) and nitrogen specification (HCN, NH_3 , NO, and NO_2).

Modeling of Nitrogen Conversion in Higher Hydrocarbon Environments

Modeling of combustion processes by elementary reactions is, of necessity, limited to hydrocarbons of C_2 or simpler structure. Modeling of the combustion of higher hydrocarbons has in the past usually been performed by assuming some kind of global oxidative pyrolysis step. Among the possibilities discussed are:

1. Global oxidation of the hydrocarbon fuel to CO_2 and H_2O following

- an empirically determined rate constant.
 2. Two semi-global steps: in the first, the parent hydrocarbon is oxidized to CO and H_2O ; and the second consists of the oxidation of the CO to CO_2 .
 3. Quasi-global methods combine global steps with elementary kinetics. The usual form has the hydrocarbon oxidized to CO and H_2 by a global step. The CO and H_2 are subsequently oxidized by an elementary kinetic mechanism.
- The novel quasi-global approach proposed in this study follows the general form:



The justification of this technique is that the oxidative pyrolysis of most complex hydrocarbons into an array of fragments of C_2 or simpler structure is a rapid process compared to subsequent reactions (in particular, fuel-nitrogen chemistry). The principal accomplishments in this task are:

1. Demonstration of the feasibility of the approach outlined above. A study of the literature covering the pyrolysis into hydrocarbon fragments justifies the assumptions of the quasi-global mode.
2. Some of the data needed to assign speciation to the hydrocarbon fragments have been obtained.

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The complete report, entitled "Fundamental Combustion Research Applied to Pollution Formation: Volume I. FCR Program Overview and Gas-phase Chemistry," (Order No. PB 86-122 660/AS; Cost: \$28.95, subject to change) will be available only from:

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