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PREFACE

These proceedings document more than 50 presentations and discussions presented at the Third Symposium on Stationary Source Combustion held March 5-8, 1979 at the Sheraton Palace Hotel, San Francisco, California. Sponsored by the Combustion Research Branch of the EPA's Industrial Environmental Research Laboratory - Research Triangle Park, the symposium papers emphasized recent results in the area of combustion modification for NO_x control. In addition, selected papers were also solicited on alternative methods for NO_x control, on environmental assessment, and on the impact of NO_x control on other pollutants.

Dr. Joshua S. Bowen, Chief, Combustion Research Branch, was Symposium Chairman; Robert E. Hall, Combustion Research Branch, was Symposium Vice-Chairman and Project Officer. The welcoming address was delivered by Clyde B. Eller, Director, Enforcement Division, U.S. EPA, Region IX and the opening Address was delivered by Dr. Norbert A. Jaworski, Deputy Director of IERL-RTP.

The symposium consisted of seven sessions:

Session I:	Small Industrial, Commercial and Residential Systems Robert E. Hall, Session Chairman
Session II:	Utilities and Large Industrial Boilers David G. Lachapelle, Session Chairman
Session III:	Advanced Processes G. Blair Martin, Session Chairman
Session IV:	Special Topics Joshua S. Bowen, Session Chairman
Session V:	Stationary Engines and Industrial Process Combustion Systems John H. Wasser, Session Chairman
Session VI:	Fundamental Combustion Research W. Steven Lanier, Session Chairman
Session VII:	Environmental Assessment Wade H. Ponder, Session Chairman

VOLUME IV

Table of Contents

Session VI: Fundamental Combustion Research

Session VII: Environmental Assessment

SESSION VI

FUNDAMENTAL COMBUSTION RESEARCH

W. STEVEN LANIER
SESSION CHAIRMAN

NO_x ABATEMENT IN FOSSIL FUEL COMBUSTION.

Chemical Kinetic Considerations

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ABSTRACT

Homogeneous, gas-phase chemical reactions are of major significance in determining NO_x emission levels from the combustion of condensed phase fossil fuels. The approach under the E.P.A. Fundamental Combustion Research Program to development of an NO_x abatement strategy through optimization of the gas-phase reaction chemistry of nitrogenous species is summarized, and selected applications are presented.

SECTION 1

INTRODUCTION

The Fundamental Combustion Research (FCR) Program of the Environmental Protection Agency is aimed at the establishment of strategies for reducing NO_x production through combustion process modification. Complete characterization of the factors affecting NO_x production must, by nature of the combustion process itself, include consideration of such diverse processes as homogeneous gas phase reactions, heterogeneous gas-solid reactions, heat transfer, and aerodynamics. We report here on current progress under the FCR program in the elucidation of the homogeneous gas-phase chemical kinetic mechanism of NO_x formation in fossil-fuel combustion.

The strategy adopted in the FCR program is discussed in this manuscript. Illustrations of selected results will be presented and updated at the "Third Symposium on Stationary Source Combustion".

With the depletion of natural gas and petroleum reserves (which are lacking or low in nitrogen content - and, hence, relatively low in the emission of NO_x formed from the nitrogen bound in the fuel), and the increasing substitution of coal, coal-derived liquids, residual fuel-oils, and shale oils (which are high in nitrogen content), NO_x emissions, which are already unacceptably high in several urban areas, are bound to increase unless an abatement strategy is developed and implemented. Insofar as the mechanism by which fuel-bound nitrogen is converted to NO_x is complex, and insofar as early attempts[1,2] to reduce NO_x emissions by empirical adjustment of combustion parameters (e.g., temperature, fuel/air ratio, degree of mixedness, etc.) utilizing conventional combustors have achieved only a fraction of their full potential, a more fundamental elucidation of the NO_x formation mechanism has become essential in order to achieve the desired engineering goal of modifying the combustion process in such a way as to favor the conversion of fuel-bound nitrogen to the desired (combustion) end product, N_2, rather than to the undesired product, NO.

As such, the organization of the FCR program has defined the following approach to achieving this end:

a) Identification of chemical reaction sets with an emphasis on fuel nitrogen conversion,

b) Validation of these reaction sets by modeling a wide range of pertinent experimental results, and concommitant computational screening to identify the minimum reaction subsets adequate for prediction of NO_x emission levels,

c) Through these processes, identification of critical gaps in the existing data base necessary for prediction of NO_x levels,

and d) Application of the fuel-N reaction set to the computation of NO_x emission levels from systems of practical interest, and utilization of predictive capabilities for development of NO_x abatement strategies.

In order to clarify the results, initial chemical kinetic studies have concentrated on aerodynamically clean systems in which interpretation of results are not complicated by mixing effects. A parallel effort under the FCR program is the characterization of the aerodynamics and development of methodologies for coupling the kinetics with the flow field in real, aerodynamically complex combustors.

SECTION 2

THE IMPORTANCE OF GAS-PHASE KINETICS

Essential to the development of a combustion modification strategy which minimizes NO_x emissions is a thorough understanding of the gas phase chemistry by which fuel-bound nitrogen is converted to NO_x. This is easily understood by reference to Figure 1 which schematically denotes several of the chemical processes involved in the combustion of coal or residual fuel oil. Indeed, it is well understood that for any condensed phase fuel, combustion may proceed through parallel homogeneous and heterogeneous processes wherein the fuel is initially heated and undergoes devolatilization followed by rapid homogeneous gas phase oxidation of the volatile species and, if a devolatilized residue remains, slower heterogeneous burnout of the char. This is apparently the case for the combustion of pulverized coal and residual fuel oils. Distillate oils, however, may well burn entirely in the gas phase as a diffusion flame surrounding a shrinking, evaporating droplet. Certain fuels, of course, are gaseous from the outset.

Of primary interest here, however, is the chemistry of volatile fuel-nitrogen conversion. Traditional gaseous fuels (natural gas) contain little or no bound nitrogen - although it is projected that the products of coal gasification which undergo a high temperature desulfurization may well contain significant quantities of ammonia. In addition, light distillate oils which for coal and shale-derived fuels may have nitrogen contents in excess of 1% by weight burn entirely in the volatile phase.

For fuels which leave a devolatilized residue, the relative significance of gas phase (versus heterogeneous) processes on NO_x formation is less obvious. The distribution of nitrogeneous species between volatiles and char has recently been studied[3,4,6,7] for pulverized coal combustion for temperatures ranging from 1250 to 1750°K. The results (for a Montana Lignite) shown in Figure 2 clearly demonstrate that at higher temperatures under fuel lean conditions, as much as 80% of the NO_x formed may originate in the volatile phase. This reflects the fact that at high enough temperatures, nearly all of the nitrogen in coal can be driven into the gas phase[3]. One may, however, make an observation, based upon Figure 2 which renders an understanding of the gas phase chemistry all the more vital - namely, that even under conditions (1750°K) where 70% or more of the fuel nitrogen is volatilized during the course of the experiment[5], for equivalence ratios above about 1.5, over 50% of the NO_x originates from the char! These results reflect the long established facts that increases in fuel nitrogen concentration[8] and equivalence ratio[8,9,10] in the gas phase all tend to lower the conversion efficiency to NO_x. The strategy for controlling NO_x emission is to drive as much fuel nitrogen as possible into the gas phase in a primary fuel rich zone where the reaction kinetics can be "engineered" to minimize conversion to NO_x, as opposed to the alternative of allowing the nitrogen to remain in the char where subsequently it will be partially converted to NO_x in the fuel lean secondary combustion zone[11]. Clearly, optimizing this reaction engineering (minimizing NO_x emissions) is best achieved through a true understanding of the gas phase reaction mechanism.

Unfortunately, similar, detailed data pertinent to residual fuel oils (petroleum, shale, or coal derived) are currently lacking. Current EPA sponsored studies should shortly yield phenomenological data on the influence of combustion conditions on the pathways (including volatile/char fractionation) followed by fuel-bound nitrogen for these systems of interest. One might speculate, however, at this time that these fuels may well behave similarly to pulverized coal, and that, in any event, an NO_x abatement strategy is likely to rest heavily, if not entirely, upon control of the reactive chemistry of the volatile, nitrogeneous species.

SECTION III

ESTABLISHMENT OF A KINETIC MECHANISM FOR NO_x FORMATION AND DESTRUCTION FROM FUEL-BOUND NITROGEN.

As indicated above, development of an NO_x control strategy rests heavily upon optimizing the conversion of volatile fuel-nitrogen species to N_2. Insofar as the residence times in typical combustors are far too short to achieve chemical equilibrium in the burnt gases, it is necessary to consider the time dependent flow of nitrogenous species through the many sequential and competing reaction pathways leading to NO_x and N_2 formation, in order to develop a methodology for maximizing or minimizing certain product yields - i.e., both the elementary reaction pathways and reaction rates must be considered.

Although at this time, many details of the NO_x formation and destruction mechanism are not fully understood, a considerable literature[8,12] has appeared in recent years, in which the predominant nitrogenous species appearing as intermediates or products of fuel-nitrogen conversion have been identified, and from which a rough reaction mechanism[13,14,15] may be deduced.

Having identified an adequate species set, a "complete" reaction mechanism has been constructed[15] by permitting all species to inter-react via elementary reactions. Rate constants were selected from a search of the experimental literature, where available, or from tabulated estimates (made, generally, by the method of Johnston[16]). The fuel-nitrogen reaction set is shown in Table 1. Conspicuously absent are several reactions, for example, $NH(NH_2) + NO \rightarrow N_2 + OH(H_2O)$, often invoked in NO mechanisms. Although of questionable "elementary" nature, for completeness, they have been included in modelling efforts.

Current efforts under the FCR program are directed to extending the kinetic mechanisms to higher hydrocarbons. Unfortunately, there is a dearth of elementary mechanistic and rate data for hydrocarbons representative of petroleum, coal, or shale derived fuels. Global modelling[27] of hydrocarbon combustion (by either finite or infinite rate formation of CO and H_2), has proven to be useful for purposes of estimation of heat release rates, but may seriously mis-predict intermediate free radical levels[28] which are crucial to the proper computation of NO_x emissions, particularly under fuel rich conditions. Current semi-global developments[29] are more promising in that they include some higher intermediates between the initial hydrocarbon and CO. The approach under development is the extension of the semi-global method based upon the observation[30] that several relatively small hydrocarbon species appear as (pyrolysis) intermediates in the combustion of higher hydrocarbons. The initial species set under consideration includes C_2H_2 (a major intermediate of aromatic systems), C_2H_4, CH_4, and CO/H_2. The combustion mechanisms of C_2H_2 and C_2H_4 have been recently studied[31] and are under continuing investigation.

SECTION 4

VERIFICATION OF THE REACTION MECHANISM

SELECTION OF FUEL SYSTEMS

It is intuitively clear that the chemistry of NO_x formation is intimately coupled to the chemistry of the combustion of the parent fuel. This is readily understood through the simple observation that NO_x levels are strongly influenced by the concentration/time history of active free radicals (H,O,OH) which are, themselves, strongly determined by the combustion details of the fuel. Clearly, establishment of an adequate fuel-nitrogen reaction mechanism requires modelling of experiments utilizing the simplest fuels whose combustion mechanisms are already well understood.

In this regard, the two best characterized fuel systems are H_2/O_2 and $CO/H_2/O_2$. However, insofar as additional mechanistic complexities pertinent to NO_x formation levels arise in the presence of hydrocarbon fuels (namely, reactions between nitrogenous species and hydrocarbon fragments), it has been necessary, also, to consider the simplest hydrocarbon, methane, as a model fuel, with the H_2 and CO reaction mechanisms logically appearing as subsets of the methane reactions set. Insofar as, at the time of initiation of these studies, no adequately validated methane reaction set was available, it has proven necessary, in parallel with considerations of fuel-nitrogen reactions, to develop and verify a methane mechanism.

The methane/fuel-nitrogen reaction set used in these studies has been developed at Energy and Environmental Research (EER) as a continuation of Engleman's[17] recent EPA compilation of CH_4 reaction data. The method employed by Engleman and continued under the FCR program has been to assemble a species set, consider all possible reactions among species of the set, and, having made a best judged assignment of rate coefficients, to computationally screen out all reactions and species whose influence on computed results is insignificant. By this method the screened set appearing in Table 2[18] was constructed. This is the set successfully used by EER in their NO_x modelling results summarized below, and, contained in this set are reaction subsets which, used with unaltered rates constants, have proven successful in modelling NO_x levels in H_2 and in CO/H_2 systems.

It is recognized, in the light of recent experimental and computational results[19,20,21] that methane combustion produces C_2 and higher hydrocarbon species not included in this set. The successes achieved with the EER set in modelling NO_x levels, temperatures, and residual oxygen levels suggest that exclusion of higher hydrocarbons from the methane set is justifiable for the systems modelled. The conditions under which the higher hydrocarbons need to be included are being investigated.

In any case, the success achieved in modelling stirred reactor experiments for three reasonably if not perfectly characterized fuels lends credance to the adequacy of the fuel-nitrogen reaction set included in Table 2, and suggests its applicability for modelling NO_x formation levels when included in a reaction scheme for higher hydrocarbon fuels. A continuing activity under the FCR program is to compare the screened set of reactions for the methane/fuel nitrogen mixtures shown in Table 2 with more complete sets that become available. For example, the inclusion of the additional reactions in Table 1 into the EER set is found to yield only negligibly small differences in computed NO_x levels.

The testing of the reaction set has been constrained by the availability of data on fuel nitrogen conversion taken under sufficiently well defined conditions to provide a critical assessment of the proposed mechanism and rate constants. Part of the FCR program is aimed at providing data on well-stirred and plug flow reactors which can be used for model validation.

MODELLING RESULTS OF THE FCR PROGRAM

The reaction set of Table 2 has been used at EER to model a variety of experimental results on CH_4, CO, and H_2 systems. These include stirred reactor experiments, flat flame experiments, and shock tube experiments. Selected examples of modelling results are presented here, a comprehensive review being available elsewhere[22]. It is to be stressed that all modelling results utilize the identical reaction set (or subset) with no adjustment of rate parameters. Numerical integration of the coupled rate equations is achieved utilizing a computer code developed at EER according to the method of Tyson[23].

Initial validation of the reaction set was accomplished through modelling of the experiments of Bartok[24] and Engleman[25] for NO formation in a Longwell jet-stirred reactor. These data included CH_4/air mixtures with and without the addition of fuel-nitrogen in the form of NO or NH_3 to the inlet stream, and CO/H_2/air and H_2/air mixtures without added fuel nitrogen. Nitric oxide emission levels and reactor temperature were the primary variables used to verify the kinetic model. Residual oxygen levels were also used as a check when the data were available. Results of similar calculations using a preliminary reaction set have been presented previously[26]. Modelling results using the reaction set of Table 2 are shown in Figure 3 for the production of thermal NO and in Figure 4 for conversion of fuel-nitrogen (1300 ppm NH_3 in the inlet mixture) to NO in an atmospheric pressure stirred reactor experiment with a 2 msec mean residence time, a specified heat loss of 36.1 cal/gm, and an inlet temperature of 464°K. Additional calculations have established the relative contributions of each reaction pathway to production or destruction of species in the reaction set. The sensitivity of computed results to changes in the values of individual rate constants have also been established computationally.

A generalized computer code for the calculation of diffusion flame behavior has been developed at EER. One natural limit-case of this code is the flat flame. This option has been utilized at EER to model several flat flame experiments as shown in Table 3. Modelling of a methane/air flat flame is shown in Figures 5 - 7.

SECTION 5

APPLICATIONS TO MODELLING REAL COMBUSTION SYSTEMS

Parametric or phenomenological studies of fuel-nitrogen conversion (See Figure 2, for example) have suggested staged combustion[7] as a method of reducing NO_x emissions from volatilized fuel nitrogen species. For coal, the rational is to operate the first stage at high temperatures (where fuel-nitrogen volatilization is maximized), fuel-rich (where volatile fuel-nitrogen conversion to NO_x is minimized) and to operate the second stage at low temperature (where the fixation of atmospheric N_2 via the Zeldovich mechanism to form "thermal" NO_x is minimized), fuel-lean (to complete fuel burnout). As a result of the lean second stage conditions, however, any form of bound nitrogen (other than N_2) such as cyanides or amines which exit the first stage will be partially converted to NO. Thus, minimization of NO_x emissions actually entails minimization of total bound nitrogen emission from the first stage. (In the absence of staging, this would, in any case, be desirable as HCN and NH_3 would be considered undesirable emission products). The degrees of freedom available to the combustion engineer are many, including the temperature, air/fuel ratio, and residence time in the fuel-rich stages and the rates of air addition to and heat removal from the partially burned primary combustion products.

The utility of a validated mechanism such as that of Table 2 is to provide a method for systematically evaluating the effect of different process variables. An example is given in Figure 8 in which the decay of total bound nitrogen in a plug flow section is shown for ammonia-doped methane/air combustion as a function of flame temperature. Such quantitative data are of great pertinence to design considerations - such as first-stage residence time or size - if NO_x emissions are to be kept below appropriate emission standards.

The results of Figure 8 are also valuable as a baseline case about which an optimization strategy for minimizing NO_x emissions is being developed.

Existing modelling capabilities are being applied to determine an optimum mode for coupling the rich primary zone with the lean secondary zone. As indicated earlier[26], several methods of adding secondary dilution air may be considered, varying from "instantaneous" mixing of all the secondary air with the primary products at the entrance to the secondary region, to gradual mixing of the secondary air over the full residence time in the secondary stage, or even, conversely, gradual mixing of the primary products into the secondary dilution air. Chemical kinetic computations predict widely differing NO_x emission levels for different staging configurations and suggest that the decay of bound-nitrogen species can be accelerated by the addition of secondary air in a series of stages. The model can be used to determine the maximum NO_x control achievable by aerodynamic staging.

Kinetic calculations utilizing the simplified methane reaction set (Table 2) have also shown the important role played by hydrocarbon fragments in determining NO_x emissions from a fuel-rich primary zone. It is demonstrable in methane/air systems under conditions of staged combustion hydrocarbon persistence enhances NO_x emissions, largely through HCN forming reactions between hydrocarbon fragments and nitrogen-bearing molecules, as well as through hydrocarbon competition for the active free radicals which destroy HCN. The implication is, therefore, that NO_x minimization is aided through first stage design which maximized hydrocarbon depletion. In this regard, it is of great importance to extend quantitative kinetic modelling capabilities to higher hydrocarbon systems.

SECTION VI

CONCLUSIONS

Gas-phase chemical kinetic modelling under the EPA FCR program has achieved several milestones necessary for the development of a practical strategy for minimization of NO_x emissions from fossil-fuel combustion. Program goals and their current status may be summarized as follows:

1. Development of pertinent reaction sets for fuel-nitrogen reactions and for methane combustion. The fuel-nitrogen set is reasonably complete, although the influence of C_2 and higher

hydrocarbon-species on bound-nitrogen levels in methane combustion remains to be assessed.

2. Validation of these reaction sets through modelling of stirred reactor experiments. In this regard, the reaction set of Table 2 adequately predicts existing stirred reactor data with some fall-off in accuracy under fuel-lean and fuel-rich extremes. Extension of these experiments under the FCR program is expected to provide more extensive data, including HCN and NH_3 concentrations, allowing for more stringent reaction set validation.

3. Extension of modelling capabilities to more complex experimental configurations, including several flame types. The computer code has been developed and is available for critical testing of reaction models against well-characterized data.

4. Application of the methane reaction set (Table 2) to identification of the chemical processes of primary importance for NO_x formation and destruction in a stirred reactor. Assessment of the roll of higher hydrocarbons remains under consideration.

5. Extension of computational capabilities to include fuel-nitrogen conversion in hydrocarbon fuels more representative of fuels of practical interest. A potential semi-global method has been identified, the applicability of which is under current examination.

6. Development of staging methodologies for minimization of NO_x emissions. Consideration of bound-nitrogen decay rates computed in plug-flow utilizing the simplified methane reaction set of Table 2 suggest several concepts pertinent to optimum staging. For example, hydrocarbon persistence is shown to retard HCN decay. Extension of modelling capabilities to more complex fuels is necessary in order to generalize kinetic considerations pertinent to optimization of a staging configuration.

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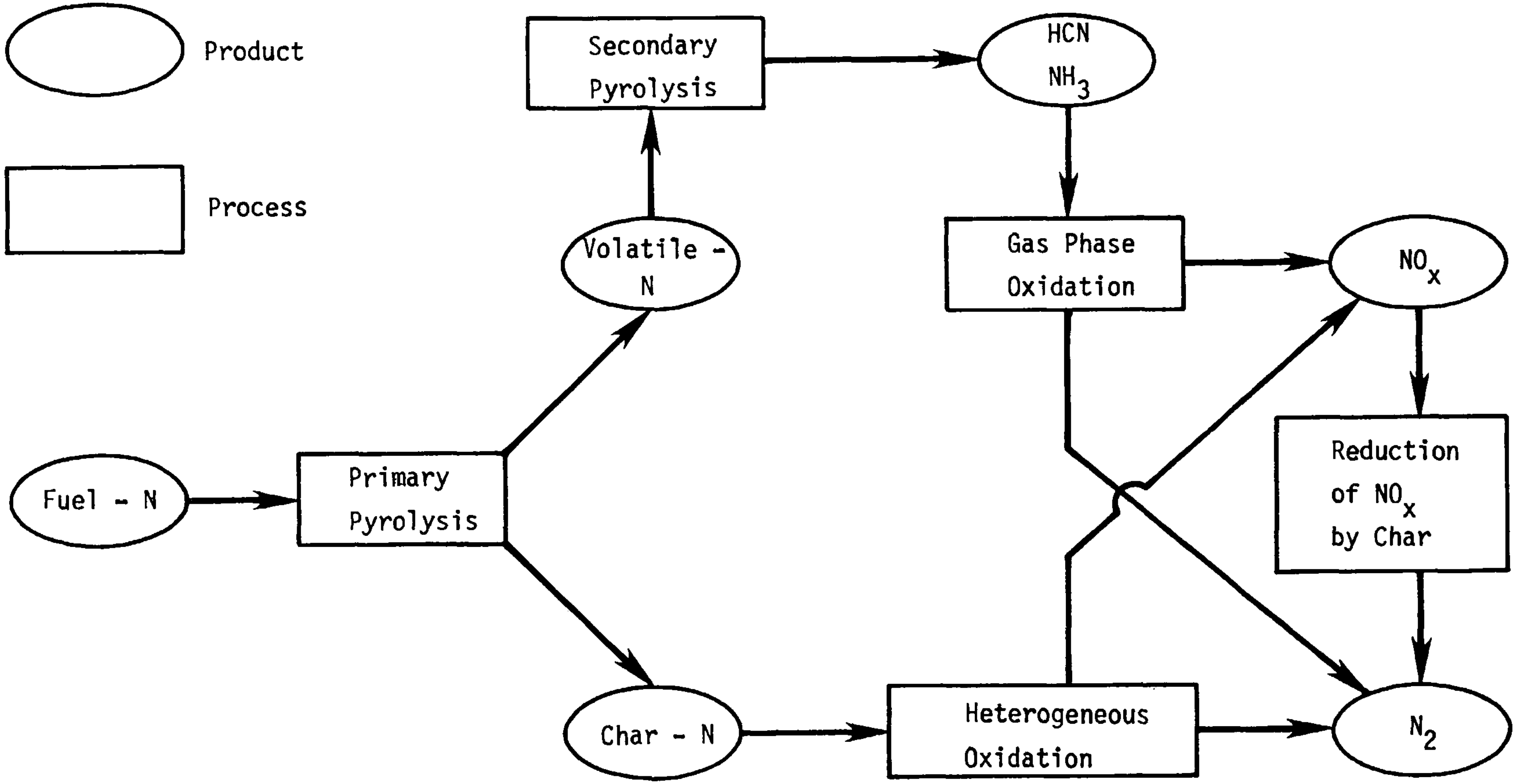

Figure 1. Schematic of Processes Occuring During the Formation of Nitric Oxide From Coal Nitrogen. An Oxidative Pyrolysis Route is not Shown.

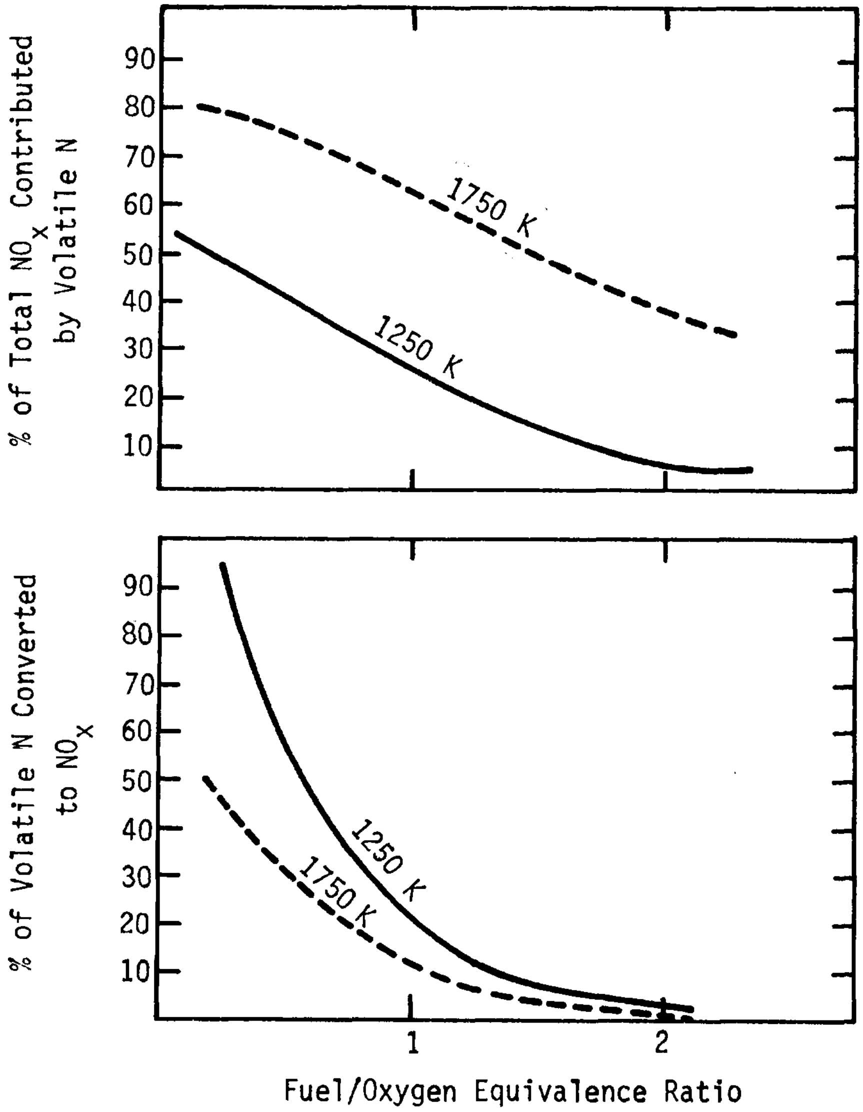

Figure 2. Fate of Volatile Nigrogen During Oxidation: Total Nitric Oxide Contributed by Volatiles (Top); Conversion Efficiency of Volatiles to Nitric Oxide (Botto

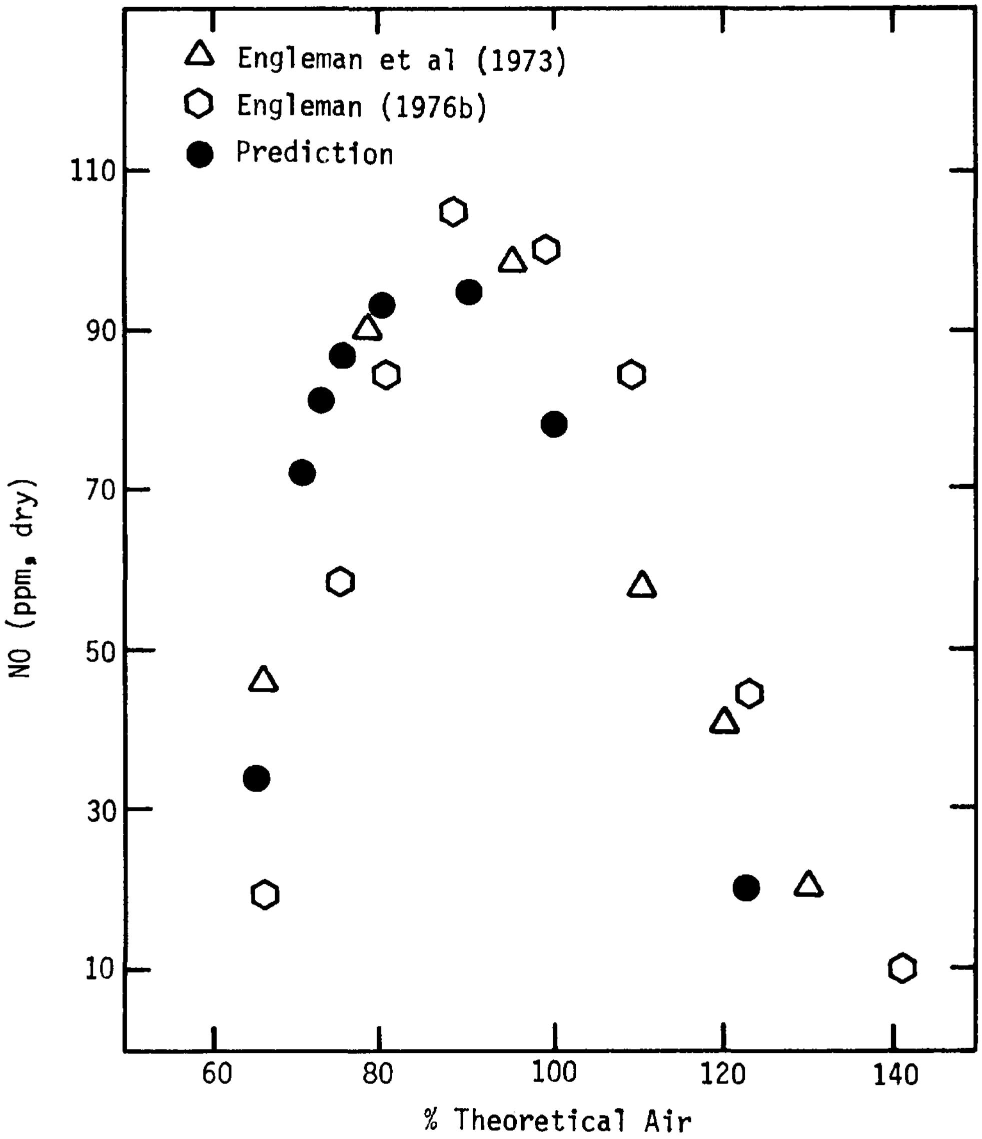

Figure 3. NO Formation for CH_4-air in a Well-stirred Reactor: Predicted and Measured.

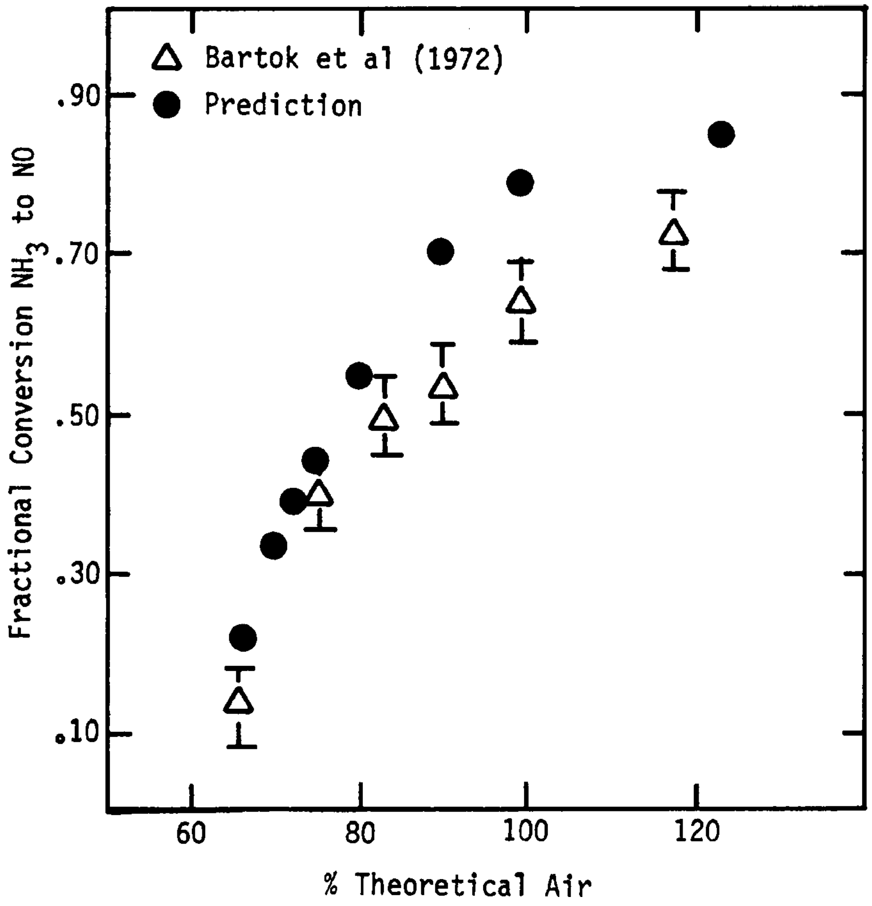

Figure 4. NH_3 Conversion for CH_4-air in a Well-stirred Reactor: Predicted and Measured.

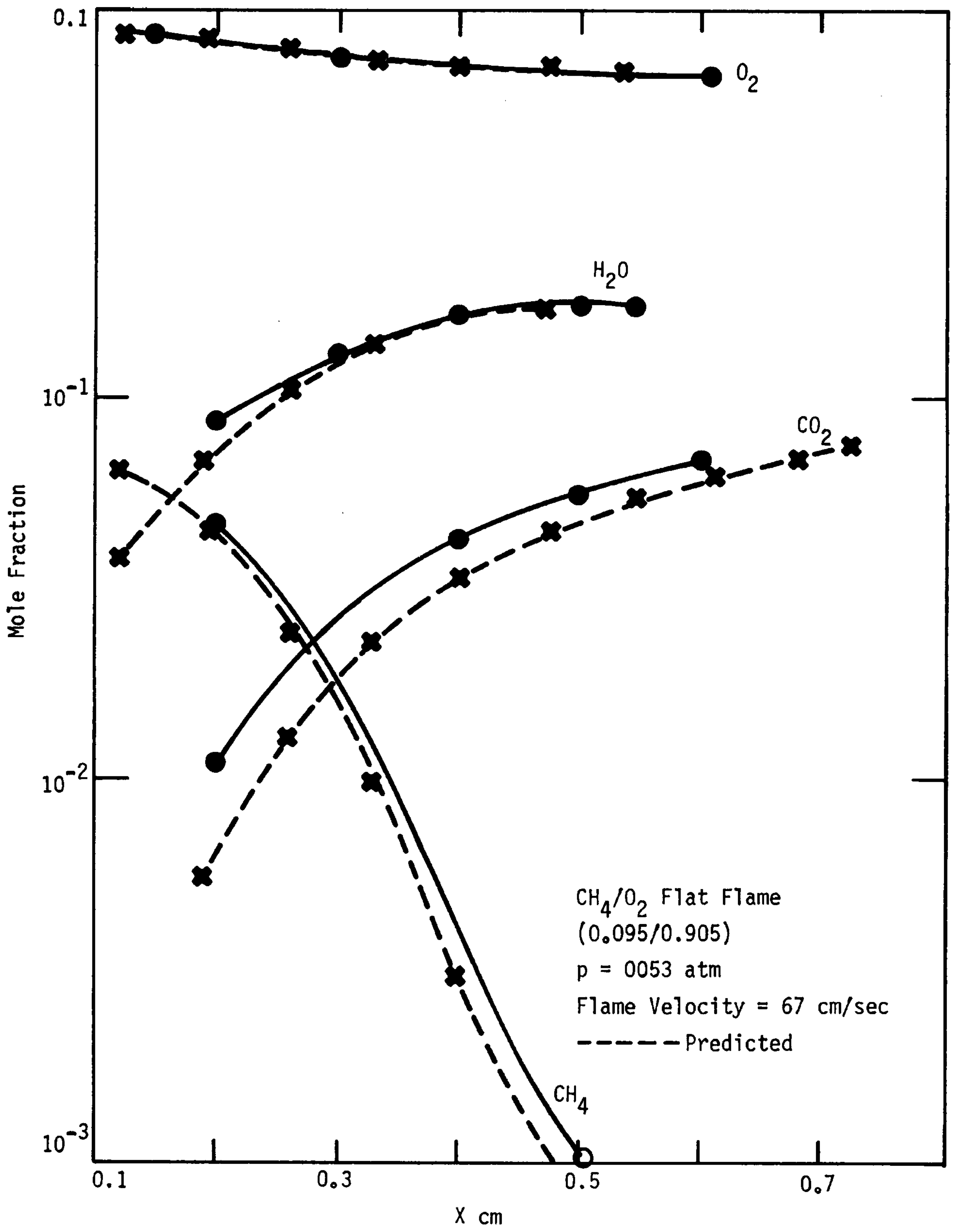
0.1
10^{-1}
10^{-2}
10^{-3}
Mole Fraction
0.1
0.3
0.5
0.7
X cm
O_2
H_2O
CO_2
CH_4
CH_4/O_2 Flat Flame
(0.095/0.905)
p = 0053 atm
Flame Velocity = 67 cm/sec
- - - - - Predicted

Figure 5.

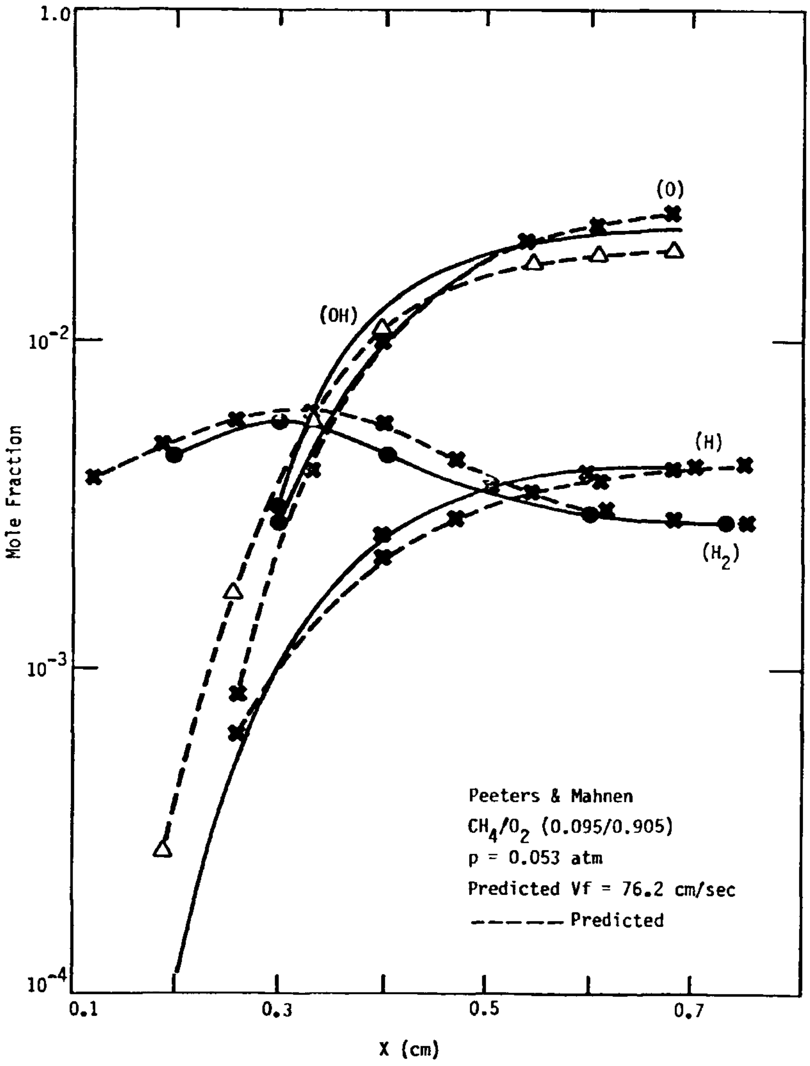

Figure 6.

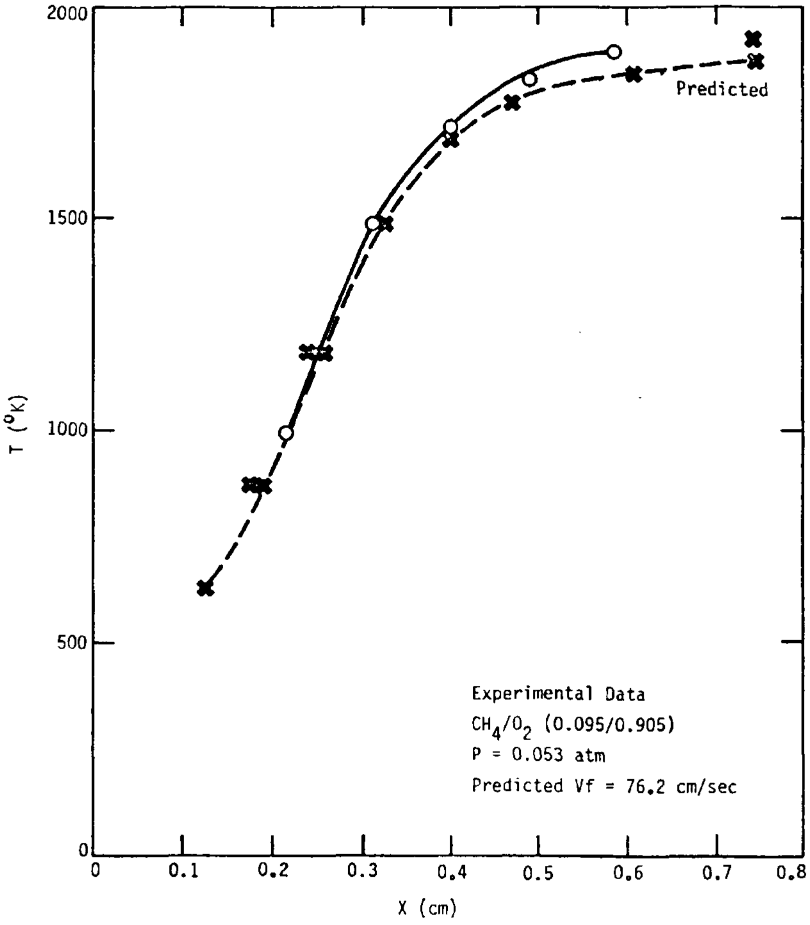

Figure 7.

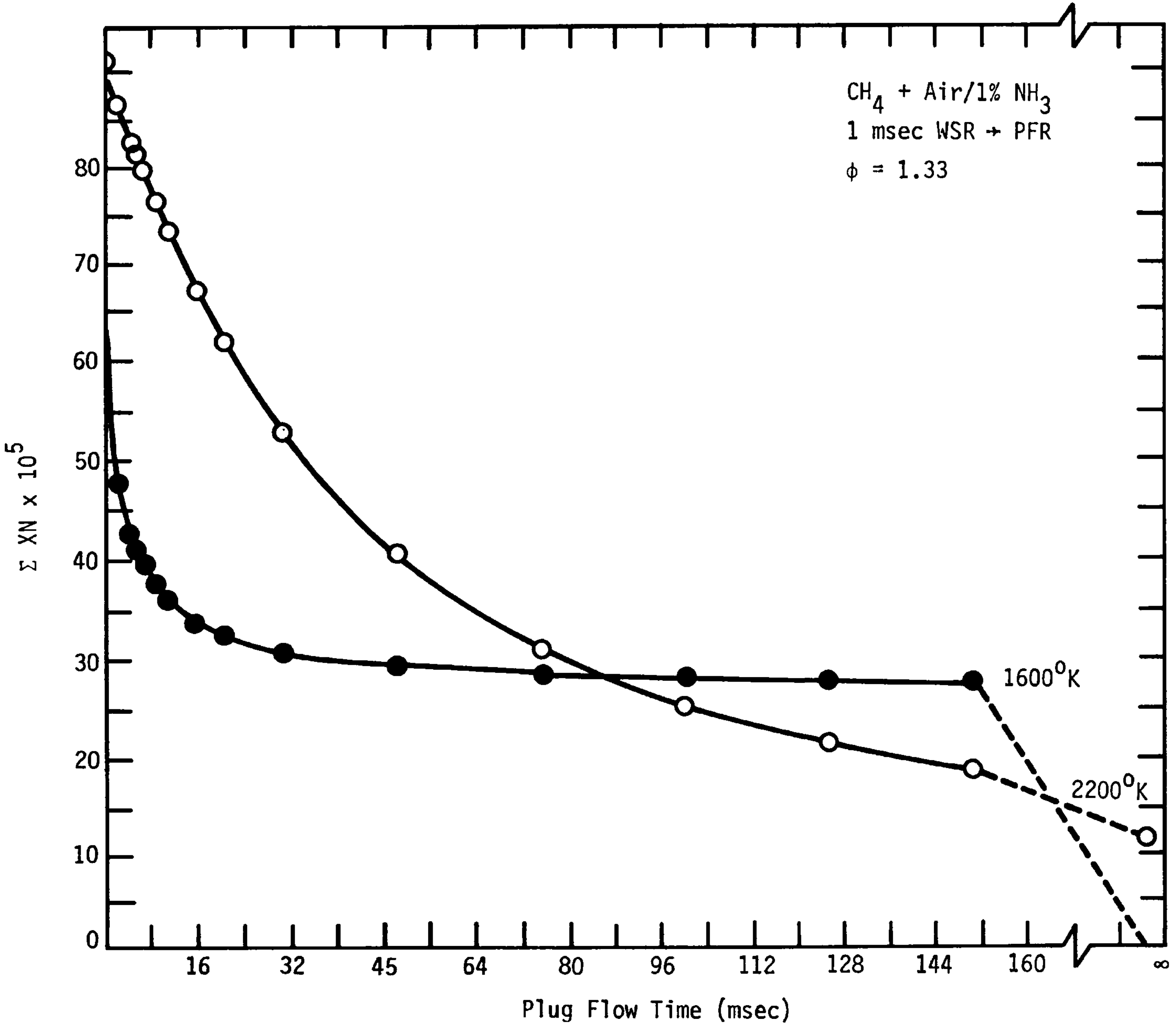
CH$_4$ + Air/1% NH$_3$
1 msec WSR → PFR
ϕ = 1.33
1600°K
2200°K
Σ XN x 10^5
0
10
20
30
40
50
60
70
80
16
32
45
64
80
96
112
128
144
160
∞
Plug Flow Time (msec)

Figure 8.

Table 1. Fuel-Nitrogen Mechanism

$$k_f = AT^N \exp\{-E/RT\}$$

Reaction	$A(\frac{cm^3}{mole\ sec})$	N	E(cal/mole)	References
1. $NO + OH = N + HO_2$	2.1×10^{11}	0.5	76,800	1, *
2. $N + N + M = N_2 + M$	3.02×10^{14}	0	-990	2
3. $NH + NH = N + NH_2$	3.6×10^{11}	0.55	1900	1,4,5,*,†
4. $N + NH_3 = NH + NH_2$	2.1×10^{11}	0.5	23,160	1,*
5. $N + NO_2 = NO + NO$	3.6×10^{12}	0	0	3
6. $N + N_2O = N_2 + NO$	5.0×10^{8}	0	10,000	3,6,*
7. $N + H + M = NH + M$	2.5×10^{17}	-0.5	0	3
8. $NH + H = N + H_2$	6.3×10^{11}	0.5	8000	3,7,*,☐
	1.0×10^{12}	0.68	1800	1,4,8,9,*,☐
9. $NH + O = NO + H$	6.3×10^{11}	0.5	0	3,7,*,☐
	5.0×10^{11}	0.5	5000	1,9,*,☐
10. $NH + O = N + OH$	3.16×10^{11}	0.5	8000	3,7,*,☐
	1.0×10^{12}	0.5	100	1,8,*,☐
11. $NH + OH = N + H_2O$	5.0×10^{11}	0.5	2000	3,10,*,☐
	1.6×10^{12}	0.56	1500	1,4,8,*,☐
12. $N + HO_2 = NH + O_2$	$\geq 1.0 \times 10^{11}$	0	0	3,11
13. $NH + N = N_2 + H$	6.3×10^{11}	0.5	0	3,7,*
14. $NH + NO_2 = HNO + NO$	2.0×10^{11}	0.5	5000	3,10,*
15. $NH + O + M = HNO + M$	1.0×10^{16}	-0.5	0	3,10,*
16. $NH_2 + H = NH + H_2$	1.4×10^{11}	0.67	4300	1,9,12,*
17. $NH_2 + O = NH + OH$	9.2×10^{11}	0.5	0	1,9,12,*

Table 1. Fuel-Nitrogen Mechanism (con't)

Reaction	A($\frac{cm^3}{mole\ sec}$)	N	E(cal/mole)	References
18. $NH_2 + O = HNO + H$	2.1×10^{12}	0	0	13
	$>5 \times 10^{12}$	0	0	14
19. $NH_2 + OH = NH + H_2O$	3.0×10^{10}	0.68	1300	1,9,12,*
20. $NH_2 + NH_2 = NH + NH_3$	1.7×10^{11}	0.63	3600	1,12,*
21. $NH_2 + O_2 = NH + HO_2$	1.0×10^{13}	0	50,500	15,*
22. $NH_3 + H = NH_2 + H_2$	1.9×10^{11}	0.67	3400	1,9,12,*
23. $NH_3 + O = NH_2 + OH$	1.5×10^{12}	0	6000	2,1
24. $NH_3 + OH = NH_2 + H_2O$	4.0×10^{10}	0.68	1100	1,9,12,*
25. $NH_3 + O_2 = NH_2 + HO_2$	5.0×10^{11}	0.5	56,000	15,*
26. $N + NO = N_2 + O$	3.1×10^{13}	0	334	2
27. $N_2O + M = N_2 + O + M$	1.42×10^{14}	0	51,280	16
28. $N_2O + OH = N_2 + HO_2$	3.16×10^{13}	0	15,000	3,*
29. $N_2O + NO = N_2 + NO_2$	2.0×10^{14}	0	50,000	3
30. $NO + M = N + O + M$	1.41×10^{21}	-1.5	153,000	2
31. $NO + H = N + OH$	2.22×10^{14}	0	50,500	17
32. $NO + O = N + O_2$	1.72×10^{9}	1	38,640	18
33. $NO_2 + H = NO + OH$	3.16×10^{14}	0	1500	3,2
34. $NO_2 + O = NO + O_2$	1.0×10^{13}	0	1000	3,2
35. $NO + HO_2 = HNO + O_2$	7.2×10^{10}	0.5	10,800	1,*
36. $NO + HO_2 = NO_2 + OH$	1.0×10^{13}	0	3000	3
37. $HNO + NH = NO + NH_2$	2.0×10^{11}	0.5	2000	1,9,*
38. $NH_3 + NO = HNO + NH_2$	5.0×10^{14}	0	50,000	17,*
39. $NO + H + M = HNO + M$	5.37×10^{15}	0	-600	2

Table 1. Fuel Nitrogen Mechanism (con't)

Reaction	$A(\frac{cm^3}{mole\ sec})$	N	E(cal/mole)	References
40. $HNO + O = NO_2 + H$	5.0×10^{10}	0.5	3000	3,10,*
41. $NO_2 + N = N_2O + O$	5.0×10^{12}	0	0	3,19
42. $N_2O + H = NH + NO$	1.0×10^{11}	0.5	30,000	3,10,*
43. $N_2O + H = N_2 + OH$	7.94×10^{13}	0	15,000	3,2
44. $N_2O + O = NO + NO$	6.23×10^{13}	0	25,400	16
45. $N_2O + O = N_2 + O_2$	6.23×10^{13}	0	25,400	16
46. $N_2O + NH = HNO + N_2$	1.0×10^{11}	0.5	3000	3,10,*
47. $HNO + H = H_2 + NO$	1.0×10^{13}	0	2500	3,20
48. $HNO + H = NH + OH$	2.0×10^{11}	0.5	23000	3,10,*
49. $HNO + O = NH + O_2$	1.0×10^{11}	0.5	7000	3,10,*
50. $HNO + O = NO + OH$	5.0×10^{11}	0.5	0	3,10,*
51. $HNO + OH = NO + H_2O$	7.08×10^{13}	0	2630	18.2
52. $HNO + N = NH + NO$	1.0×10^{11}	0.5	2000	3,10,*
53. $HNO + N = N_2O + H$	5.0×10^{10}	0.5	3000	3,10,*
54. $NH + H + M = NH_2 + M$	2.0×10^{16}	-0.5	0	1,9,*
55. $NH_3 + M = NH_2 + H + M$	5.75×10^{15}	0	77,000	17
56. $NO_2 + M = NO + O + M$	1.1×10^{16}	0	65,571	17,2
57. $HCN + OH = CN + H_2O$	2.0×10^{11}	0.6	5000	3,10,*
58. $CN + H_2 = HCN + H$	6.0×10^{12}	0	5300	21
59. $CN + OH = NCO + H$	5.6×10^{13}	0	0	22
60. $CN + O_2 = NCO + O$	3.2×10^{13}	0	1000	21
61. $HCN + O = NCO + H$	5.2×10^{12}	0	8100	23
62. $CN + O = CO + N$	6.3×10^{13}	0	2400	24
63. $NCO + H = NH + CO$	5.0×10^{11}	0.5	6875	15,*,□
	2.0×10^{13}	0	0	25,*,□

Table 1. Fuel Nitrogen Mechanism (con't)

Reaction	$A(\frac{cm^3}{mole/sec})$	N	E(cal/mole)	References
64. $NCO + O = NO + CO$	5.0×10^{11}	0.5	6875	15,*,□
	2.0×10^{13}	0	0	25,*,□
65. $CN + CO_2 = NCO + CO$	3.7×10^{12}	0	0	26
66. $CN + OH = HCN + O$	3.16×10^{12}	0	3000	3,7,*
67. $CN + HNO = HCN + NO$	4.0×10^{11}	0.5	0	3,10,*
68. $CN + H + M = HCN + M$	3.16×10^{16}	-0.5	0	3,10,*
69. $CN + NH = HCN + N$	1.0×10^{11}	0.5	2000	3,10,*
70. $CN + NH_2 = HCN + NH$	5.0×10^{10}	0.7	2000	10,*
71. $CN + NH_3 = HCN + NH_2$	7.0×10^{10}	0.7	2000	10,*
72. $CO + OH = CO_2 + H$	1.51×10^{7}	1.3	-765	3.27
73. $CO + O_2 = CO_2 + O$	3.16×10^{12}	0	50,000	3.28
74. $CO_2 + M = CO + O + M$	1.0×10^{15}	0	100,000	3.29
75. $CO + HNO = CO_2 + NH$	1.0×10^{11}	0.5	7000	3,10,*
76. $CO_2 + N = CO + NO$	2.0×10^{11}	0.5	30,000	3,10,*
77. $CO + NO_2 = CO_2 + NO$	2.0×10^{12}	0	30,000	3,30
78. $CO + N_2O = CO_2 + N_2$	1.0×10^{11}	0	20,000	3,31
79. $CO + HO_2 = CO_2 + OH$	1.0×10^{11}	0	10,000	3,32
80. $H_2 + OH = H_2O + H$	2.19×10^{13}	0	5150	18,2
81. $H_2O + O = OH + OH$	6.76×10^{13}	0	18,350	18,2
82. $H_2 + O = H + OH$	1.82×10^{10}	1	8900	18.2
83. $O_2 + H = O + OH$	2.19×10^{14}	0	16,800	18.2
84. $H + O + M = OH + M$	8.00×10^{15}	0	0	20
85. $O_2 + M = O + O + M$	3.55×10^{18}	-1	118,000	33
86. $H_2 + M = H + H + M$	2.45×10^{14}	0	96,000	18.2
87. $H_2O + M = H + OH + M$	1.29×10^{15}	0	105,000	18.2

Table 1. Fuel Nitrogen Mechanism (con't)

Reaction	$A(\frac{cm^3}{mole\ sec})$	N	E(cal/mole)	Reference
88. $H + O_2 + M = HO_2 + M$	1.59×10^{15}	0	-1000	2
89. $HO_2 + OH = H_2O + O_2$	5.0×10^{13}	0	1000	3,32
90. $OH + O + M = HO_2 + M$	5.0×10^{16}	0	0	1,34
91. $HO_2 + O = O_2 + OH$	5.0×10^{13}	0	1000	3,32
92. $HO_2 + H = H_2 + O_2$	2.5×10^{13}	0	700	3,32
93. $HO_2 + H = OH + OH$	2.5×10^{14}	0	900	3,32
94. $HO_2 + H = H_2O + O$	1.0×10^{13}	0	1000	3,32

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* Calculated or estimated rate. Non-experimental

+ No data. The calculated value for $NH + NH \rightarrow N_2 + H_2$

☐ Currently, neither value is preferred.

Table 2a.

EER Reaction Set

$K_f = AT^N \exp(-E/RT)$ (cm^3; mole; sec units)

REACTION	A	N	E(kcal/mole)	COMMENTS*
$CH_4 = CH_3 + H$	1.0×10^{17}	0	88.4	Oppenheim et al (1975); (.71)
$CH_3O = CH_2O + H$	4×10^{40}	-7.5	22.6	Benson (1975); estimate
$\#CH_2O = CHO + H$	3.15×10^{17}	0	87.	Engleman (1976); evaluation
$CHO = CO + H$	2.50×10^{20}	-1.5	16.8	Benson (1975); estimate
$CO_2 = CO + O$	1.0×10^{15}	0	100.	Engleman (1976)
$H + NO = HNO$	2.0×10^{16}	0	0	Clyne and Thrush (1962); exp't.
$\#H + O = OH$	1.0×10^{18}	-1.	0	Benson et al (1975); estimate
$H + O_2 = HO_2$	3.0×10^{15}	0	-1.0	Baulch et al (1969); (2.); evaluation
$OH + O = HO_2$	1.6×10^{20}	-1.5	0	Benson et al (1975); estimate
$\#H_2 = H + H$	2.08×10^{15}	.07	103.83	Mallard and Owen (1974)
$H_2O = OH + H$	2.30×10^{24}	-2.	122.6	Benson et al (1975); (3.); estimate
$NO + O = NO_2$	1.38×10^{21}	-1.82	0	Michael et al (1976); exp't.
$\#N_2 = N + N$	4.0×10^{21}	-1.6	225.	Baulch et al (1973); evaluation
$N_2O = N_2 + O$	4×10^{14}	0	51.4	Axworthy (1977)
$\#O + O = O_2$	1×10^{18}	-1.0	0	Benson et al (1975); estimate
$CH_4 + CH_2 = CH_3 + CH_3$	1.26×10^{12}	.70	20.	Engleman (1976)
$CH_4 + CN = HCN + CH_3$	3.16×10^{11}	.70	5.	Engleman (1976)
$CH_4 + H = CH_3 + H_2$	5.0×10^{10}	1.	10.	Walker (1968); exp't.

Table 2b. $K_f = AT^N \exp(-E/RT)$ (cm^3; mole; sec units)

REACTION	A	N	E(kcal/mole)	COMMENTS*
$CH_4 + OH = CH_3 + H_2O$	3.0×10^{13}	0	5.0	Wilson (1972); evaluation
$CH_4 + O = CH_3 + OH$	1.9×10^{14}	0	11.7	Brabbs and Brokaw (1975); exp't
# $CH_3 + CN = HCN + CH_2$	1.0×10^{11}	.70	3.	Engleman (1976)
# $CH_3 + CH_2O = CH_4 + CHO$	$2. \times 10^{11}$	0	6.5	Benson et al (1975); estimate
$CH_3 + OH = CH_2 + H_2O$	2.0×10^{11}	.70	2.	Engleman (1976); (3.); estimate
$CH_3 + OH = CH_3O + H$	6.31×10^{11}	0	0	Engleman (1976)
$CH_3 + HNO = CH_4 + NO$	5.0×10^{11}	.50	0	Engleman (1976); estimate
# $CH_3 + HO_2 = CH_4 + O_2$	1.0×10^{11}	.50	6.0	Engleman (1976); estimate
$CH_3 + O = CH_2O + H$	2.6×10^{14}	0	2.0	Peeters and Vinckier (1975); exp't
# $CH_3 + O_2 = CH_2 + HO_2$	3.16×10^{12}	0	69.5	Engleman (1976)
# $CH_3 + O_2 = CH_2O + OH$	$9. \times 10^{11}$	0	12.	Tsuboi and Wagner (1974); exp't
$CH_3 + O_2 = CH_3O + O$	3.5×10^{13}	0	28.8	Brabbs and Brokaw (1975); exp't
# $CH_2 + CN = CH + HCN$	3.16×10^{12}	0	5.	Engleman (1976)
# $CH_2 + CH_2O = CH_3 + CHO$	2.0×10^{11}	0	6.5	Benson et al (1975); estimate
$CH_2 + H = CH + H_2$	3.16×10^{11}	.70	5.	Engleman (1976)
$CH_2 + OH = CH + H_2O$	5.0×10^{11}	.50	6.	Engleman (1976); estimate
$CH_2 + OH = CH_3 + O$	5×10^{11}	.50	6.	Engleman (1976)
$CH_2 + OH = CH_2O + H$	$1. \times 10^{13}$	0	5.	Engleman (1976)

Table 2c. $K_f = AT^N \exp(-E/RT)$ (cm^3; mole; sec units)

REACTION	A	N	E(kcal/mole)	COMMENTS*
$CH_2 + H_2 = CH_3 + H$	3.0×10^{12}	0.	7.0	Benson et al (1975); estimate
$CH_2 + N_2 = HCN + NH$	1.0×10^{14}	0	60.	Benson et al (1975); ($E_A = 70 \pm 20$); estimat.
$CH_2 + NO = CH_2O + N$	1.6×10^{12}	0	7.	Engleman (1976)
$CH_2 + O = CHO + H$	5×10^{11}	.50	4.	Engleman (1976); estimate
$CH_2 + O_2 = CH_2O + O$	5×10^{11}	.50	7.	Engleman (1976); estimate
#$CH + CH_4 = CH_2 + CH_3$	1.0×10^{12}	0	17.1	Estimate; Tunder et al (1967) method
$CH + CO_2 = CHO + CO$	$1. \times 10^{10}$	.50	6.	Engleman (1976)
$CH + OH = CHO + H$	5×10^{11}	.50	10.	Engleman (1976)
#$CH + HO_2 = CH_2 + O_2$	$1. \times 10^{10}$	.50	15.	Engleman (1976)
$CH + O = CO + H$	5×10^{11}	.50	0	Engleman (1976)
$CH + O_2 = CHO + O$	$5. \times 10^{11}$	.50	6.	Engleman (1976)
#$CH_3O + H = CH_2O + H_2$	1×10^{14}	0	0	Engleman (1976)
#$CH_3O + OH = CH_2O + H_2O$	3.16×10^{13}	0	0	Engleman (1976)
#$CH_3O + N = CH_2O + NH$	$1. \times 10^{14}$	0	0	Engleman (1976)
#$CH_3O + NO = HNO + CH_2O$	5.0×10^{11}	.50	4.23	Estimate; Tunder et al (1967) method
#$CH_3O + O = CH_2O + OH$	$1. \times 10^{14}$	0	0	Engleman (1976)
#$CH_3O + O_2 = CH_2O + HO_2$	$1. \times 10^{12}$	0	6.	Engleman (1976)
$CH_2O + H = CHO + H_2$	1.26×10^{10}	1.	3.2	Engleman (1976)

Table 2d. $K_f = AT^N \exp(-E/RT)$ (cm^3, mole; sec units)

REACTION	A	N	E(kcal/mole)	COMMENTS*
$CH_2O + OH = CHO + H_2O$	3.16×10^{10}	1.	0	Engleman (1976)
$CH_2O + O = CHO + OH$	2.0×10^{11}	1.	4.4	Engleman (1976)
#$CHO + CHO = CH_2O + CO$	1.6×10^{11}	.50	0	Engleman (1976)
#$CHO + CH_2 = CH_3 + CO$	3.16×10^{10}	.70	1.	Engleman (1976)
#$CHO + CH_3 = CH_4 + CO$	3.16×10^{11}	.70	0	Engleman (1976)
#$CHO + H = CO + H_2$	3.0×10^{10}	1.	0	Engleman (1976)
#$CHO + HNO = CH_2O + NO$	3.16×10^{11}	.50	0	Engleman (1976)
#$CHO + CH = CO + H_2O$	3.0×10^{10}	1.	0	Engleman (1976)
$CHO + HO_2 = CH_2O + O_2$	$1. \times 10^{14}$	0	3.	Engleman (1976)
$CHO + N = CH + NO$	1.0×10^{14}	0	48.6	Engleman (1976); estimate
$CHO + N = HCN + O$	1.0×10^{14}	0	0	Engleman (1976)
#$CHO + N = CO + NH$	2.0×10^{11}	.50	2.	Engleman (1976)
#$CHO + NO = CO + HNO$	2.0×10^{11}	.50	2.	Engleman (1976); estimate
$CHO + O = CO + OH$	6.31×10^{11}	1.0	0.5	Engleman (1976); (2.)
#$CHO + O = CO_2 + H$	3.16×10^{11}	0	0	Engleman (1976)
$HCN + OH = CN + H_2O$	2.0×10^{11}	.60	5.	Engleman (1976)
$HCN + N = CH + N_2$	2.5×10^{11}	0	16.	Benson et al (1975); (2.5); estimate
$HCN + O = CH + NO$	1.0×10^{14}	0	72.	Benson et al (1975); estimate

Table 2e. $K_f = AT^N \exp(-E/RT)$ (cm^3; mole; sec units)

REACTION	A	N	E(kcal/mole)	COMMENTS*
$CN + CO_2 = NCO + CO$	3.72×10^{12}	0	0	Morley (1976); estimate
#$CN + OH = HCN + O$	3.16×10^{12}	0	3.	Engleman (1976)
$CN + OH = NCO + H$	6.2×10^{13}	0	0	Morley (1976); estimate
$CN + H_2 = HCN + H$	6.2×10^{12}	0	5.3	Morley (1976); estimate
#$CN + NH = CH + N_2$	1.0×10^{14}	0	40.	Benson et al (1975); estimate
#$CN + NO = CO + N_2$	3.0×10^{11}	0	0	Engleman (1976)
$CN + O = CO + N$	6.31×10^{11}	.50	0	Benson et al (1975); estimate
#$CN + O_2 = CO + NO$	3×10^{11}	0	0	Engleman (1976)
$NCO + H = NH + CO$	$5. \times 10^{11}$	.50	6.87	Estimate; Tunder et al (1967) method
$CO + HNO = CO_2 + NH$	$1. \times 10^{11}$	.50	7.	Estimates; Tunder et al (1967) method
$CO + OH = CO_2 + H$	1.51×10^{7}	1.3	-.765	Baulch and Drysdale (1974)
#$CO + HO_2 = CHO + O_2$	3.0×10^{12}	0	37.1	Benson et al (1975); estimate
#$CO + O_2 = CO_2 + O$	3.16×10^{12}	0	50.	Engleman (1976)
#$CO_2 + N = CO + NO$	2.0×10^{11}	.50	25.	Engleman (1976)
$H + HNO = H_2 + NO$	1.0×10^{13}	0	2.5	Engleman (1976)
#$H + HNO = NH + OH$	2.0×10^{11}	.50	23.	Engleman (1976)
$H + OH = H_2 + O$	2.71×10^{17}	-.94	14.69	Schott et al (1972); exp't

Table 2f. $K_f = AT^{N} \exp(-E/RT)$ (cm^3; mole; sec units)

REACTION	A	N	E(kcal/mole)	COMMENTS*
$H + HO_2 = OH + OH$	2.50×10^{14}	0	1.9	Engleman (1976); evaluation
$H + N_2O = OH + N_2$	8.0×10^{13}	0	15.	Engleman (1976)
$H + N_2O = NH + NO$	1.0×10^{11}	.50	30.	Engleman (1976); estimate
$H + NO_2 = OH + NO$	3.16×10^{14}	0	1.5	Engleman (1976)
#$HNO + HNO = N_2O + H_2O$	1.0×10^{10}	.50	41.55	Estimate; Tunder et al (1967) method
$HNO + OH = H_2O + NO$	1.0×10^{12}	0	1.0	Engleman (1976)
#$HNO + NO = OH + N_2O$	2×10^{12}	0	26.	Engleman (1976); evaluation
$HNO + O = OH + NO$	5.0×10^{11}	.50	0	Engleman (1976); estimate
$HNO + O = NH + O_2$	1.0×10^{11}	.50	7.	Engleman (1976)
$OH + H_2 = H + H_2O$	2.5×10^{13}	0	5.2	Baulch et al (1972); evaluation
$OH + OH = H_2O + O$	6.0×10^{12}	0	1.	Baulch et al (1972); evaluation
$OH + N_2O = HO_2 + N_2$	3.16×10^{13}	0	15.	Engleman (1976)
$OH + O = H + O_2$	6.31×10^{11}	.50	0	Benson et al (1975); estimate
$HO_2 + H = O_2 + H_2$	2.5×10^{13}	0	.70	Engleman (1976)
$HO_2 + OH = H_2O + O_2$	5.0×10^{13}	0	1.	Engleman (1976)
$HO_2 + O = OH + O_2$	5.0×10^{13}	0	1.	Engleman (1976)
$N + OH = NO + H$	6.31×10^{11}	.50	0	Benson et al (1975); estimate
$N + NO = N_2 + O$	3.10×10^{13}	0	.334	Engleman (1976)

Table 2g. $k_f = AT^N \exp(-E/RT)$ (cm^3; mole; sec units)

REACTION	A	N	E(kcal/mole)	COMMENTS*
#$N + NO_2 = N_2 + O_2$	1.0×10^{12}	0	0	Engleman (1976)
#$N + NO_2 = NO + NO$	4.0×10^{12}	0	0	Engleman (1976)
$N + O_2 = NO + O$	6.0×10^{9}	1.	6.3	Engleman (1976); evaluation
$NH + H = N + H_2$	6.31×10^{11}	.50	8.0	Benson et al (1975); estimate
$NH + OH = H_2O + N$	5.0×10^{11}	.50	2.	Engleman (1976); estimate
$NH + OH = NO + H_2$	5.0×10^{11}	.50	2.	Presently used
	1.6×10^{12}	.56	1.5	Sarofim et al (1973)
#$NH + O = N + OH$	1.7×10^{10}	.70	.10	Presently used
	8.4×10^{12}	.70	.10	Sarofim et al (1973); estimate
	3.16×10^{11}	.50	8.	Engleman (1976); estimate
	1.0×10^{12}	.50	.10	Bahn (1968); estimate
$NH + O = NO + H$	6.31×10^{11}	.50	0	Benson et al (1975); estimate
#$NH + N = H + N_2$	6.0×10^{11}	.50	0	Engleman (1976); estimate
#$NH + NH = N_2 + H_2$	3.6×10^{11}	.55	1.9	Sarofim et al (1973)
#$NH + NO = N_2 + OH$	2.4×10^{12}	0	0	Sarofim et al (1973)
$NH_2 + H = NH + H_2$	1.4×10^{11}	.67	4.3	Sarofim et al (1973)
$NH_2 + OH = NH + H_2O$	3.0×10^{10}	.68	1.3	Sarofim et al (1973)
$NH_2 + O = NH + OH$	9.2×10^{11}	.50	0	Presently used

Table 2h. $K_f = AT^N \exp(-E/RT)$ (cm^3; mole; sec units)

REACTION	A	N	E(kcal/mole)	COMMENTS*
$NH_2 + O_2 = NH + HO_2$	1.0×10^{13}	0	50.5	Estimate; Tunder et al (1967) method
$NH_2 + NH_2 = NH_3 + NH$	1.7×10^{11}	.63	3.6	Sarofim et al (1973)
$NH_2 + NO = N_2 + H_2O$	5.0×10^{12}	0	0	See Kaskan and Hughes (1973); Fenimore (1975 Duxbury and Pratt (1975); Lesclaux et al (1975) Results of Lesclaux (1975) and Fenimore (1976) strongly weighted.
$NH_3 + OH = NH_2 + H_2O$	1.26×10^{10}	68	1.10	Sarofim et al (1973); (.32); Adjusted to "match" results of Zellner and Smith (1974) Perry et al (1975); Dove and Nip (1974)
$NH_3 + H = NH_2 + H_2$	1.9×10^{11}	.67	3.4	Sarofim et al (1973)
$NH_3 + O = NH_2 + OH$	1.5×10^{12}	0	6.	Baulch et al (1972 & 1973)
$NH_3 + O_2 = NH_2 + HO_2$	5.0×10^{11}	.50	56.	Estimate; Tunder et al (1967) method
#$N_2O + O = N_2 + O_2$	1.0×10^{14}	0	28.	Engleman (1976)
#$N_2O + O = NO + NO$	1.0×10^{14}	0	28.	Engleman (1976)
#$NO + OH = HO_2 + N$	5.0×10^{10}	.50	96.5	Estimate; Tunder et al (1967) method
$NO + HO_2 = NO_2 + OH$	5.0×10^{11}	.50	3.52	Estimate; Tunder et al (1967) method
#$NO + N_2O = NO_2 + N_2$	2.0×10^{14}	0	50.	Engleman (1976)

Table 2i. $K_f = AT^N \exp(-E/RT)$ (cm^3; mole; sec units)

REACTION	A	N	E(kcal/mole)	COMMENTS*
#$NO + NO_2 = N_2O + O_2$	1.0×10^{12}	0	60.	Engleman (1976)
#$NO_2 + O = NO + O_2$	1.0×10^{13}	0	1.	Engleman (1976)
#$CH + CH_3 = CH_2 + CH_2$	3.2×10^{12}	0	8.	Engleman (1976); estimate

* Number in parenthesis indicates factor by which original rate was multiplied.

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HETEROGENEOUS PROCESSES INVOLVED IN THE CONTROL OF NITROGEN OXIDE FORMATION IN FOSSIL FUEL FLAMES

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SECTION 1

INTRODUCTION

The general philosophy and overall objectives of the FCR* program have been described elsewhere (1). This program involves the planning and direction of several projects whose overall goal is to provide the EPA/CRB with the necessary understanding of the fundamental behavior of combustion systems to develop control technology which will minimize the emission of both NO_x and associated pollutants from stationary sources. The program is focused on well-defined priority target areas, and the research effort is directed towards providing engineering solutions to specific problems within a time frame consistent with the technology development programs. Neither the time nor resources are limitless, and the program has been planned to provide products which can be realized in both the near and far-term. Information is being generated now which can either be directly transferred to "technology development" programs, or used in the development of empirical engineering models to aid the designer of low NO_x combustion systems. Projects with a long-term payoff, which are in the minority, are associated with the development of numerical models capable of describing pollutant formation in complex combustors.

The FCR program is primarily concerned with the basic mechanisms associated with the formation and destruction of nitrogen oxides in fossil fuel flames. However, some effort has been initiated relating to the formation of soot and fine particulate matter, as well as the mechanisms of sorbent extraction of SO_2 in flames. Reviewing the sources of anthropogenic NO_x emissions, it can be seen that approximately 50 percent can be attributed to stationary combustion; and of this, 50 percent greater than 55 percent is associated with the combustion of nitrogen-containing fuels which are mainly

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*Fundamental Combustion Research Applied to Pollution Control coal or oil. Thus, the primary initial objective was to focus upon pollutant production in one-atmosphere turbulent diffusion flames burning pulverized coal or residual oil and radiating to cold walls. Since the increased use of coal is one of the nation's methods of achieving energy independence, this initial objective has considerable relevance because any increase in the use of coal or coal-derived fuels without the application of necessary control technology will probably result in an increase in NO_x emissions.

A key element of the FCR program is the establishment of the lower bounds set on NO_x emissions under various limiting situations and constraints. It is important when assessing control strategies to know that for a particular set of process requirements that there exists a limit on the level of control achievable by combustion modifications and set by these requirements. Thus, the value of studies leading to the establishment of lower bounds is not only that they provide a yardstick by which to measure the effectiveness of other control schemes, but they also provide strong guidance in the development of advanced control techniques.

The generation of nitrogen oxides during the combustion of pulverized coal and residual oil in turbulent diffusion flames involves the complex interaction of several physical and chemical phenomena. Transport processes involving heat or mass, gas phase kinetics, and heterogeneous processes are all involved in the formation and destruction of NO in these flames. This paper describes projects included in the FCR program, both ongoing and planned for the future, which can be classified as heterogeneous processes. Projects associated with mass transfer phenomena and homogeneous gas phase kinetics are discussed in two other papers.

SECTION 2

FCR APPLICATIONS

The purpose of the FCR program is to provide development engineers with information and tools which will aid in the application of NO_x control technology to stationary combustion sources. More specifically, the primary objective involves large water-wall combustors burning pulverized coal or residual fuel oil. The ultimate goal is to combine information generated from the three major program elements in order to describe pollutant formation in large industrial flames. However, in this the second year of the program, the potential applications are much more restricted, and are more concerned with the direct transfer of information to aid in the interpretation of development results.

The program element concerned with heterogeneous processes can be placed in context by considering the experimental results presented in Figures 1 and 2. These data were generated in programs designed to generalize low NO_x burner technology for solid and liquid fuels, and to determine the role of fuel composition on NO_x emissions. Figure 1 presents a composite plot showing the conversion of fuel nitrogen to NO_x as a function of weight percent nitrogen in the fuel on a dry, ash-free basis. The results were generated in two different furnaces with different but similar burner systems. Minimum NO_x emissions obtained with the same fuels for a simple staging system are shown in Figure 2. The results are somewhat unexpected, but because they are of great practical importance, they clearly demonstrate the need for further interpretation through this FCR program element. Only then can their general impact be recognized and translated to practice in the field.

The observables presented in Figures 1 and 2 can be summarized by:

- In overall lean conditions fuel nitrogen conversion to NO_x for liquid fuels appears to depend very strongly on the weight percent nitrogen in the fuel. This is not unexpected. However, for solid fuels there is apparently some other parameter controlling fuel nitrogen oxidation, and NO_x does not appear to depend primarily on coal N content. FCR will help identify this other parameter.

- There are secondary parameters involved in fuel nitrogen formation in liquid fuels which are probably associated with the volatility of the fuel nitrogen compounds (2).
- Fuel nitrogen conversions in alternate liquid fuels are higher than those for solid fuels with similar nitrogen contents.
- Under staged conditions minimum NO_x emissions appear to be less dependent upon fuel nitrogen content, although both coal and oil properties appear to influence minimum NO_x levels.
- There is a strong effect of the particle/droplet size. Minimum NO_x emissions under staged combustion conditions for the same coal vary by over 30 percent when coal is burned with a particle size of 165 μm or size less than 39 μm. Smaller particles give lower emissions staged, but higher emissions unstaged. Similarly, with liquid fuels minimum NO_x emissions increase from 110 to 130 ppm as the mean droplet size varies from 20 to 180 μm.

These experimental results were obtained from specific simple combustors, described elsewhere (2). It is the function of this FCR program element to determine if, why, and when they hold in general, especially under advanced combustor design conditions. Interpretation of these results is complicated because of both fuel effects and fuel/air contacting effects. One goal of the heterogeneous program element is to ascertain under which conditions these two factors play a dominant role.

The combustion of liquid or solid fuels involves several processes. Before heat release can occur the fuel must undergo some physical transformation, i.e., pulverization or atomization, to provide for efficient fuel/air mixing and minimize combustion time. The coal particles or droplets are heated either by convection from the surrounding gases, or by radiation from the chamber walls or adjacent flames. During heating the fuel decomposes producing light gases, tars, and leaving a solid char. The tars may themselves pyrolyze and the gases produced either directly or from this secondary pyrolysis process are burned in premixed or diffusion controlled heat release zones. The char remaining after devolatilization and any solid produced by pyrolysis reactions in the gas phase are then oxidized. Several questions can be raised concerning the fate of fuel nitrogen during these processes which, if answers were available, might well help to explain some of the results presented in Figures 1 and 2. These questions are:

- Do fuel properties affect the distribution of nitrogen between the light gases, tars and char formed during thermal decomposition?
- Do fuel properties affect the rate of nitrogen loss as a function of temperature, gaseous environment, and particle droplet size?
- Is the speciation of nitrogen evolved during thermal decomposition fuel-dependent?
- What is the fate of nitrogen remaining in the char?
- Under what condition do NO, NH_3 and HCN react with solids?
- How does particle size control particle temperature and its subsequent devolatilization?

One of the goals of the FCR program is to define lower bounds on NO_x emissions, and in concluding this section on potential applications it is worthwhile considering a control scheme whose limits are set by the kinetics of heterogeneous processes. Assuming that char nitrogen converion to NO_x is finite, then one low NO_x concept could involve the design of a combustor with the following features:

- A rich, high temperature zone to extract nitrogen from the solid phase.
- A hold up zone to maximize N_2 production by homogeneous or heterogeneous reactions.
- Burnout in a diffusion flame with the required composition to maximize HCN, NH_3, NO conversion to N_2.

The information required to design such a combustor is an example of what will be generated in the heterogeneous process program element.

SECTION 3

HETEROGENEOUS PROCESSES — AN FCR PROGRAM ELEMENT

Figure 3 presents a schematic showing the relationship between the heterogeneous processes program element and the other FCR program elements:

- Homogeneous Kinetics
- Transport Processes
- Measurement System Assessment/Development
- Numerical Model Development

The various projects under this program element can be classified under three major headings which are:

- Thermal Decomposition
- Gas Solid Reactions
- Reactor Studies

Figure 3 shows the Principle Investigators associated with the projects in each of the areas.

THERMAL DECOMPOSITION STUDIES

During the initial stages of a flame liquid fuel droplets and pulverized coal particles are heated rapidly, causing both physical and chemical changes to occur which affect pollutant formation. Two projects have been initiated which are concerned with the fate of fuel nitrogen during the thermal decomposition process. Axworthy is conducting an investigation of the volatility of nitrogen compounds present in fossil fuels, and Solomon has just begun a project to characterize four coals during thermal decomposition.

A quartz two-stage pyrolysis reactor was developed by Rocketdyne under EPA Contract 68-02-1886 (3). Liquid or solid fuels are pyrolyzed rapidly under inert conditions in the small volume first stage reactor. The volatile pyrolysis products are swept by helium carrier gas into a second stage stirred flow reactor where they can be (1) pyrolyzed further in helium at a different temperature; (2) mixed with oxygen and undergo oxidative pyrolysis and oxidation; or (3) condensed and collected for chemical analysis. This reactor was used to establish that (1) most of the HCN forms from the secondary pyrolysis of volatile primary pyrolysis products; (2) the fuel nitrogen in coal liquids and shale oils are apparently more volatile than nitrogen in conventional fuels; and (3) the volatility of fuel nitrogen in coals varies considerably from coal-to-coal. The objective of the program being carried out by Axworthy is to measure and compare the volatility characteristics of reactive fuel nitrogen in liquid and solid fuels. This information is needed to both qualitatively explain observations described in Section 2, as well as provide information on the rate of evolution of volatile nitrogen from various fuels in order to develop a semi-empirical model of the conversion of fuel nitrogen to NO and N_2 in flames. The fuels to be studied in this program are those that have been used in other CRB development programs.

Figure 4 presents an example of some of the initial data comparing the volatility of convertible fuel nitrogen for a variety of fuels as a function of first stage pyrolysis temperature. It can be seen that the shale and shale-derived diesel fuel have large fractions of volatile fuel nitrogen compounds which are evolved at low temperatures. Greater than 60 percent of the initial fuel nitrogen can be converted to HCN at pyrolysis temperatures greater than 300°C. This can be compared with the results presented for snythol, a coal-derived liquid which shows a similar behavior but only 40 percent of the fuel nitrogen is converted to HCN. The data for the three petroleum-derived residual fuels shows a more gradual evolution of nitrogen from the oil, but also that different oils have different characteristics. Although the final conversions for the Gulf Coast and Alaskan oils are similar, the effect of temperature on volatile nitrogen evolution is very different. The Gulf Coast oil appears to have a large component of refractory nitrogen.

Axworthy's experiments were designed to provide a rapid screening tool to identify large differences in the volatility of fuel nitrogen compounds for a wide range of fuels in order to select those more suitable for more detailed study. A different project has been initiated at the United Technologies Research Center under the direction of Solomon which will involve the use of vacuum distillation equipment (4) and a high temperature furnace to characterize the thermal decomposition of four coals using infrared analysis. The characterization includes the definition of the coal structure including sulfur and nitrogen groups, and the determination of the rates and products of thermal decomposition. The investigation will also include a measurement of nitrogen group decomposition in tars. This rate will be measured by thermally decomposing tar in a high temperature furnace with in situ infrared analysis of products which will be capable of detecting HCN and NH_3. The information on the rates of these thermal decomposition processes will be incorporated in the coal combustion model. Given the time/temperature history of a coal particle, prediction of the volatile yield and volatile composition (including sulfur and nitrogen distribution) will be possible. This information can then feed directly into a combustion model for pulverized coal which include gas phase combustion kinetics, char kinetics, heat and transport processes.

Coal particles undergo both chemical and physical changes during thermal decomposition. Physical effects such as swelling, shattering, and method of off-gasing, etc., will have a significant influence upon the formulation of any model which attempts to describe pollutant formation during the combustion of pulverized coal particles. A proof-of-principle experiment was carried out with Trolinger of Spectron Development Laboratories to determine whether holography could be used to observe coal particles during thermal decomposition in flames. Success of the technique would depend upon its ability to distinguish particles whose size is the same as those used in practice, and in a thermal environment similar to a turbulent diffusion flame. The physical behavior of coal particles during heat up has been observed photographically in the past. However, these experiments involved larger coal particles heated either upon grids or platinum ribbons. Holography provides the opportunity of producing high resolution images of individual particles in a dynamic particle field array, i.e., under typical combustion conditions.

Holography has been applied to the study of several combustion phenomena (5) with varying degrees of success. One of the principle problems is associated with loss of resolution caused by the imaging through a turbid medium associated with combustion, and it was found that the application of certain optical and mechanical techniques allowed the observation of burning coal particles in free flight with nearly diffraction-limited capability. Although holographic interferometry has been used extensively to study flow fields and density gradients in gases, the primary problem in this application of interferometry is the high sensitivity required because the distances involved are so small. The holo camera developed by Trolinger used in this investigation is shown in Figure 5. The required high resolution was achieved by (1) magnifying with high quality lenses before recording; (2) using near image plan holography to further relax hologram requirements; and (3) precisely aligning the hologram during reconstruction. Coal particles of approximately 75 μm mean size were injected into the combustion products of a methane/air flat flame through a rectangular slit. Holograms were produced under a wide variety of conditions and at various locations above the injection point. Holographic interferometry was used to examine phase characteristics of the region around coal particles in the flame. This included double pulse, double exposure, double plate, and sheared wave front hologram interferometry (5). Double-pulsed hologram interferometry proved especially useful for examining dynamics, while double exposure proved useful for high sensitivity flow visualization. In other of these cases the gross phase shift created by the methane/air flat flame was removed from the final interferogram, a desired feature of hologram interferometry.

As stated earlier, the main objective of the study was to determine the utility of holography for viewing burning particles, and from this viewpoint the experiment was an unqualified success. Phenomena observed included:

- Single particles down to 4 μm
- Evolution of high molecular-weight gases from single coal particles

- Formation of a sphere of small particles (soot) around single particles and separation of the coal particle from the sphere probably due to relative motion of the gas and coal particle
- Coal particle swelling
- Coal particle disintegration
- Production of particles with a high length-to-diameter ratio which are probably soot caused by pyrolysis of the gaseous devolatilization products.

A program has been planned to continue with the use of this technique to investigate both chemical and physical effects during the thermal decomposition of both liquid and solid fuels.

GAS SOLID REACTIONS

At this time the FCR program is primarily interested in two heterogeneous processes concerning gas solid reactions which affect NO production. These are the fate of char-bound nitrogen and the reduction of NO_x on particulate matter yielding N_2. Some activity at MIT touches on the former subject, and it is planned to expand the study of char nitrogen oxidation in the near future.

De Soete at the Institut Francais du Pétrole is currently investigating the reduction of nitrogen oxides by particulate matter in the presence of combustion products. Beér et al. (6) have demonstrated that NO can be reduced by char in fixed bed experiments. This phenomenon may prove to be of practical importance as an NO_x control technique. Preliminary work by De Soete (7) indicated that the reduction mechanism was enhanced by the presence of hydrogen and CO and inhibited by the presence fo small quantities of oxygen. De Soete also measured the decay of NO when NO/Ar mixtures were injected downstream of the flame front of a sooting flame. Typical results are presented in Figure 6 showing that the NO reduction mechanism can be significant. Currently, De Soete is working on a project which involves investigation of adsorption and desorption rates of nitric oxide on solid particles as well as determining the kinetic rates for decomposition by several different particles, e.g., flame-generated soot, fly ash, etc. One of the initial findings was that the presence of carbon was not mandatory, and NO could be reduced by the high temperature refractory walls of the experimental reactor. These results have already been transferred to the developmental programs, and have been used both to design the proper experimentation for the programs and to interpret ensuing data.

REACTOR STUDIES

The principle goal of the reactor studies is to provide information on the fate of fuel nitrogen during the combustion of solid and liquid fuels in well-defined fluid dynamic conditions. The information generated in the thermal decomposition and gas solid reaction investigations will provide rate data to allow interpretation of the results generated by the reactor studies provided the fluid mechanical conditions are well-stirred or plug flow (or combinations of the two). Thus, the reactor studies will not only provide experimental information but a proof of simple engineering models which can later be applied to more complex combustion systems. A project is underway at Acurex under the direction Tong to determine the fate of coal nitrogen as a function of particle size, air/fuel ratio, temperature and residence time in a well-stirred reactor. The study of Overley at Battelle involves a similar goal with liquid fuels. It should be recognized that these experiments involve complex design problems in order to ensure that the gas phase is well-mixed, and that the residence time of the solid or liquid phase is known. These problems are complicated because residence times of interest are of the order of 20 to 100 msec rather than 1 or 2 msec.

To date, both projects have progressed to the point which allows combustion studies to begin with well-characterized reactors. Tracer studies have been employed by both investigators to measure the residence time distribution of both phases.

SECTION 4

SUMMARY

This paper has discussed the heterogeneous processes program element of the FCR program. Several projects have been initiated to determine the fate of fuel nitrogen during the combustion of both solid and liquid fuels. Three programs are concerned with the chemical and physical effects occurring during thermal decomposition. One program is underway to investigate NO reduction by solids in the presence of combustion products, and two reactor studies have been initiated to investigate fuel nitrogen conversion under well-backmixed conditions. Two additional programs are planned. One concerned with the oxidation of char nitrogen, and the other a series of reactor studies to provide time-resolved nitrogenous species under controlled mixing history conditions with both solid and liquid fuels. The information generated by these programs is currently being applied to interpret data generated by several development programs as well as aiding in the development of empirical engineering tools.

To date, the FCR program has concentrated upon nitrogen oxide formation. Future effort in the heterogeneous processes program element will include investigations directed toward the formation of fine particulate matter from inorganic material in coal, the formation of soot, and the absorption of sulfur specie by calcium and sodium-containing sorbents.

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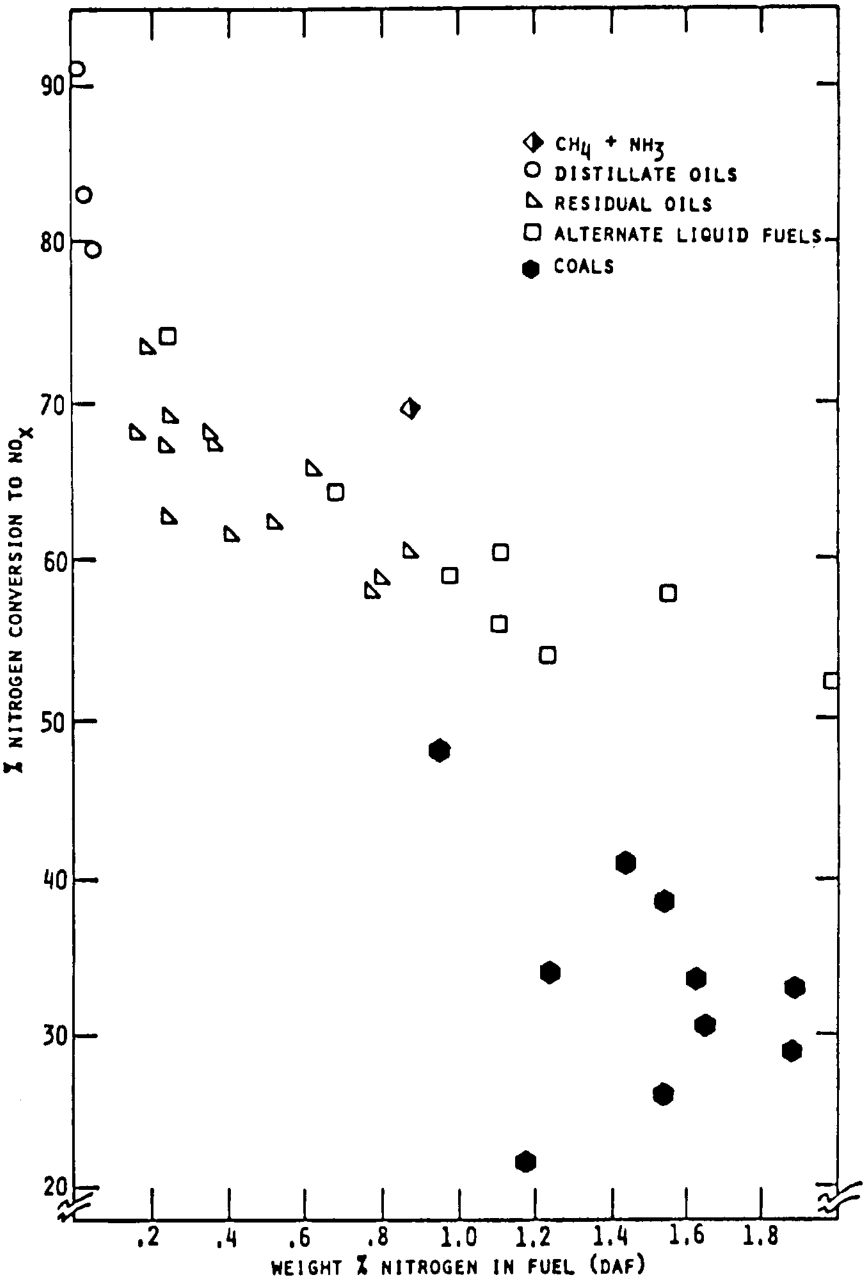

Figure 1. Conversion of Fuel Nitrogen to NO_X for Various Fuels

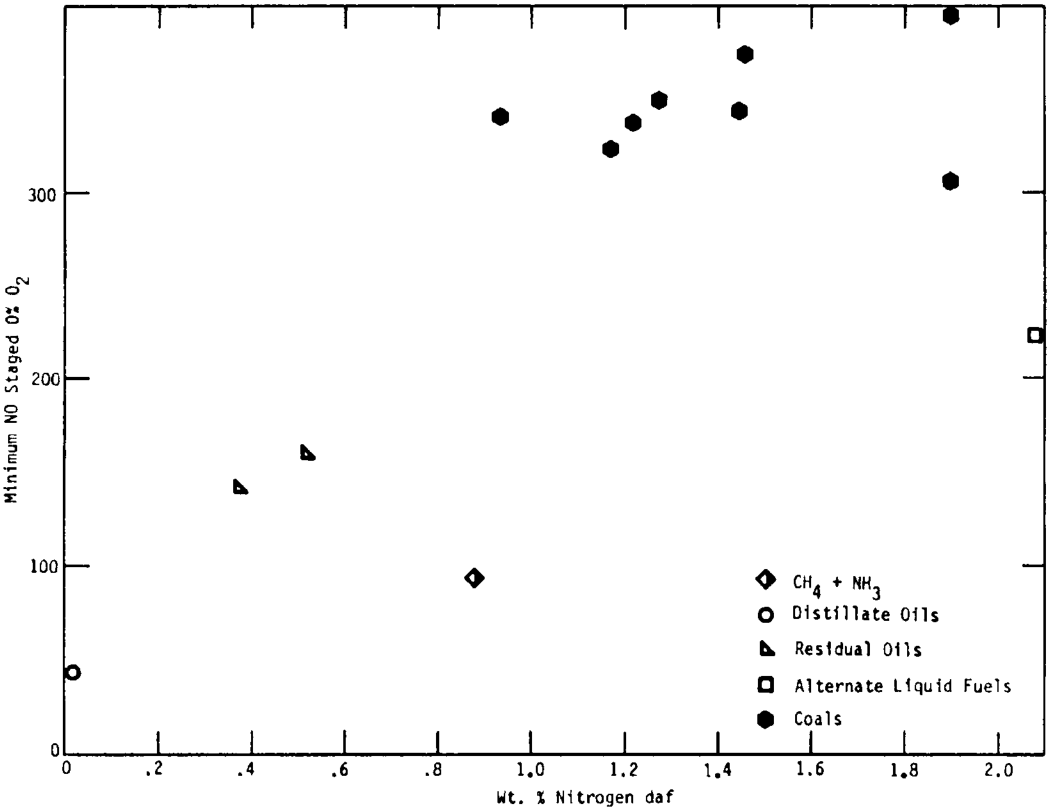

Figure 2. Minimum NO Emissions Obtained Under Staged Combustion Conditions for Various Fuels in a Bench-Scale Reactor

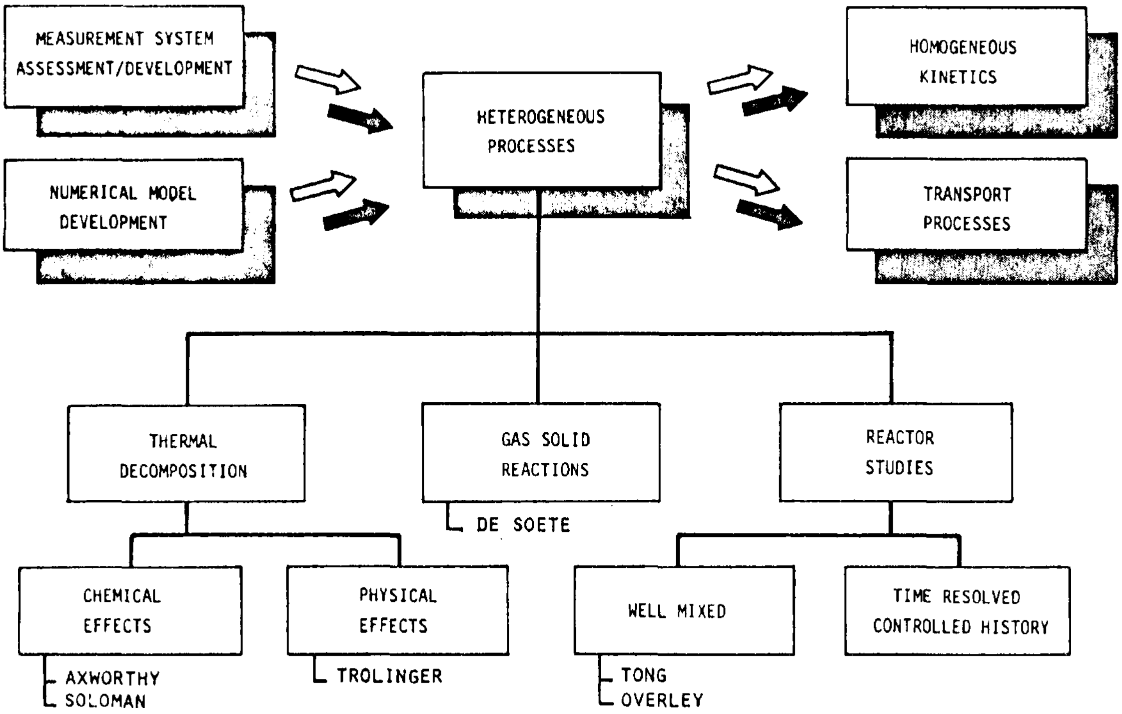

Figure 3. Heterogeneous Processes — Project Organization

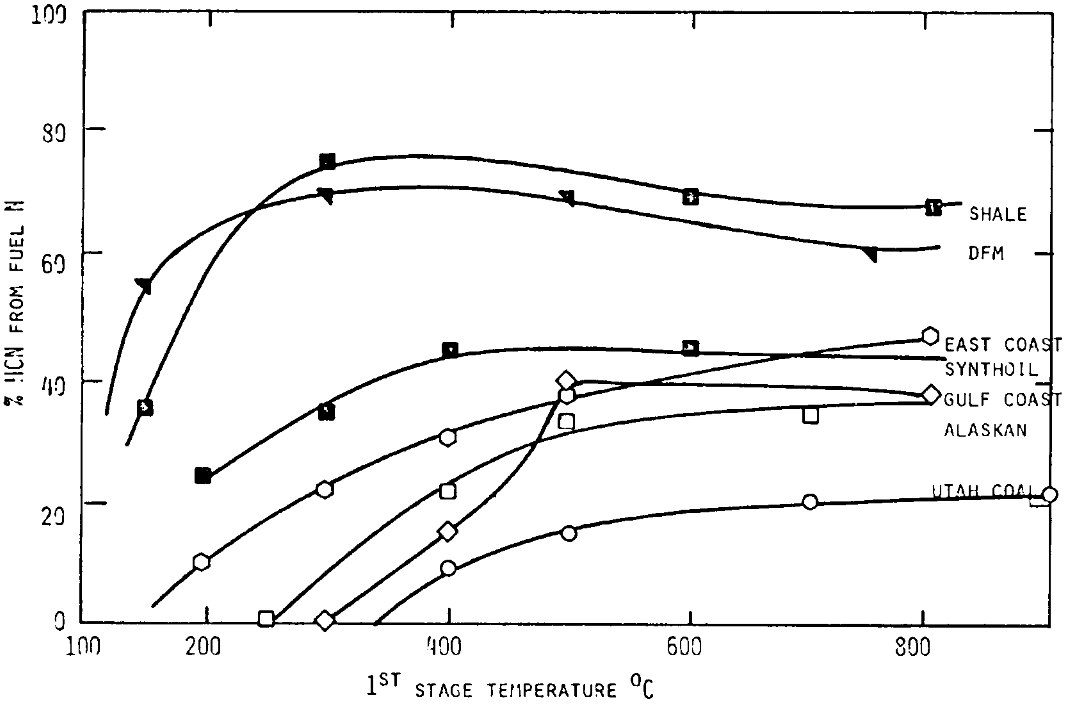

Figure 4. Composite Plot Showing the Volatility of Convertible Fuel Nitrogen for Several Fuels as Measured by Axworthy

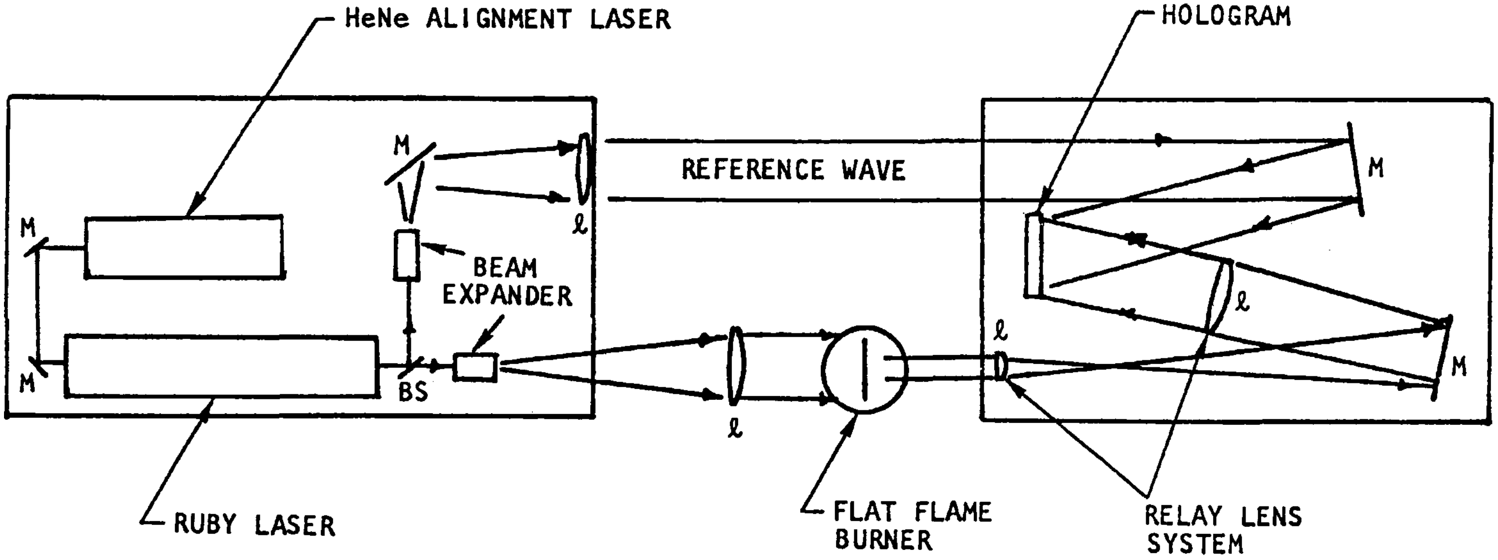

Figure 5. Holographic System Layout Used by Trolinger

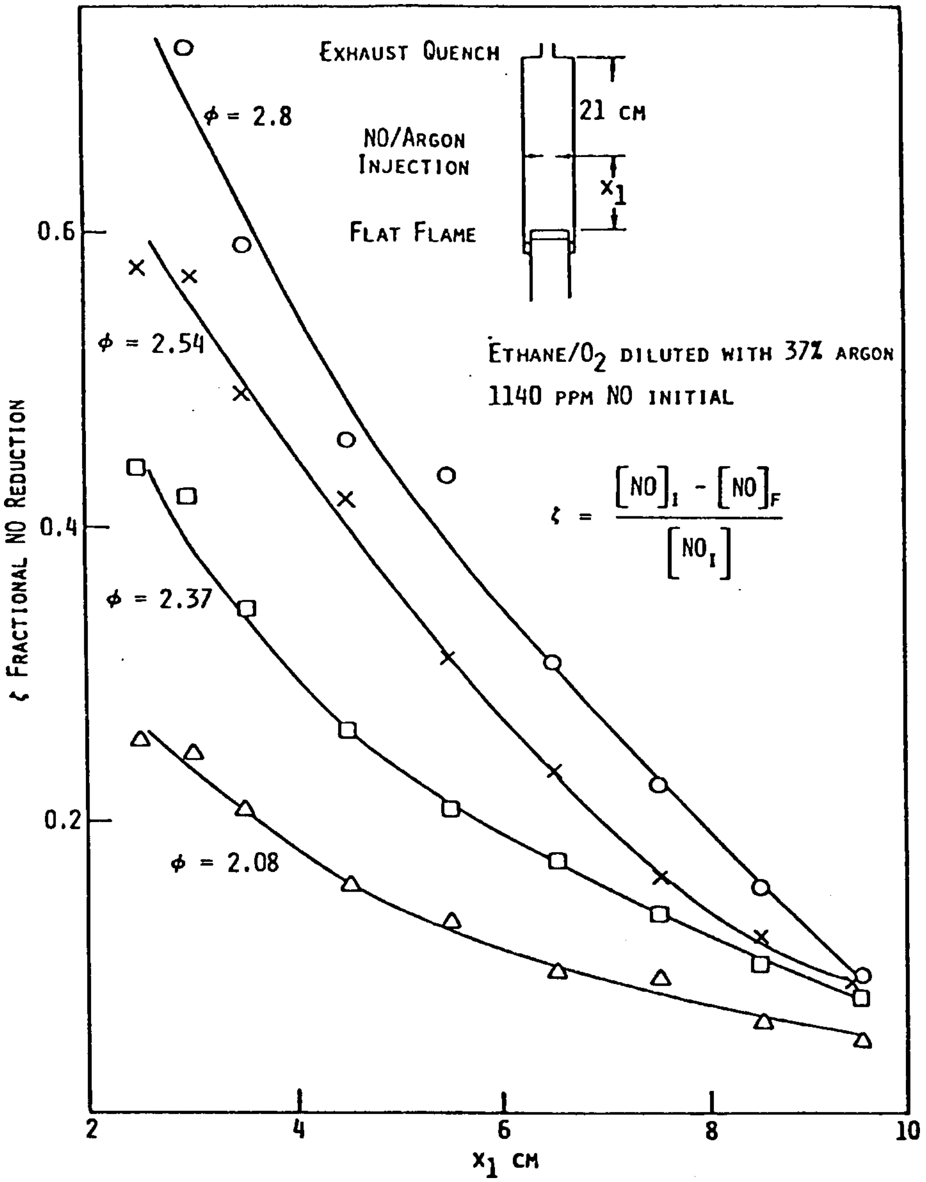

Figure 6. NO Reduction by Soot (after De Soete[6]) Produced in a Premixed Flat Flame

TRANSPORT PROCESSES AND NUMERICAL MODEL DEVELOPMENT — FCR PROGRAM ELEMENTS

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SECTION 1

INTRODUCTION

The FCR program has two major objectives. These are:

- To provide guidance to development programs concerned with the application of low NO_x combustion systems to stationary sources.
- To gain insight into the fundamental phenomena controlling the production of NO_x in these devices in order to define potential advanced control techniques.

One major aspect of the program involves the presentation of basic information in such a way as to be of the most benefit to the development engineer. This information may be transferred directly or in the form of a model which can be used as a design tool, thereby cutting the cost and delay time associated with empirical development programs.

Two fuels, coal and residual oils, when burned in large turbulent diffusion flames confined by relatively cold walls produce the major fraction of NO_x emissions from stationary combustion sources. Two previous papers have discussed the dominant homogeneous and heterogeneous kinetic processes associated with the production of nitric oxide in these combustion systems. However, these papers did not consider the detailed physics involved in the turbulent mixing process associated with fuel/air contacting in real combustors. This paper discusses two other elements of the FCR program; those concerned with numerical model development, and transport processes which serve the key function of synthesizing information generated in the other program elements in order to provide an understanding of the basic mechanisms limiting NO_x formation in practical combustion devices.

In the FCR program elements concerned with homogeneous kinetics and heterogeneous processes the dominant physical and chemical mechanisms pertinent to NO_x production during the combustion of clouds of oil droplets or coal particles will be defined. Several experiments have been planned which, in conjunction with the development of numerical models, will provide a predictive capability capable of describing NO_x production in simple reactor systems. Two of these programs are concerned with solid and liquid fuels, and were described in an earlier paper. Two other experimental programs, one being carried out by Myerson at Exxon and the other by Clark at EER, are directed towards the generation of data which will allow the verification of an adequate kinetic mechanism capable of describing NO_x production from simple fuel nitrogen compounds during the combustion of hydrocarbon fuels. This predictive capability will be refined and verified by comparison with measurements made in these simple combustion reactors. Once confidence has been established in the predictive capability, it can be used to analyze the behavior of staged combustion reactors in a rational and comprehensive search for those reactor combinations which yield the lower limit of NO_x emission set by the basic physics and chemistry of fossil fuel combustion.

Simple zero- and one-dimensional reactors do not completely reflect the detailed physics and chemistry associated with turbulent diffusion flames burning in real furnaces. Consequently, an additional effort has been planned which will parallel the reactor studies and thoroughly characterize turbulent diffusion flame phenomena pertinent to NO_x formation and destruction. Two general classes of turbulent diffusion flames can be recognized; those which involve rapid fuel/air mixing and are dominated by near-field behavior. The second group of turbulent diffusion flames are far-field dominated and can be described as long coaxial jet flames. Several tasks have been initiated in the FCR program which are directed towards understanding the basic turbulent diffusion layer structure in these general flame types. These investigations are concerned with particle transport, both ballistic and turbulent, macroscale turbulent transport of energy and matter, the persistence of coherent structures in large-scale flames, and the detailed processes occurring within these coherent structures.

Once the capability has been developed to model the microscale behavior of oil droplets and coal particles, and after verifying the model by comparison of prediction and observations, it is appropriate to use this model in a search for lower bounds on NO_x emissions dictated by the basic physics of turbulent transport. The model will aid the understanding of NO_x production and destruction in basic flame elements such as turbulent shear layers, well-backmixed zones, and plug flow zones. This understanding can then be transferred to a modular model capable of describing all the complexities of the fuel/air contacting processes in turbulent diffusion flames The generation of experimental data to allow this modular model to be developed represents a major subtask of the transport processes program element, and focuses on the macroscale flame behavior in an attempt to establish how burner combustion chamber designs and operating parameters affect the manner in which diffusion zones and well-mixed zones are established and interact. Once the gross features of the flow field have been defined the production and destruction of pollutants on a microscale can be analyzed in an overlay fashion. Having synthesized the physical and chemical processes associated with NO_x production and destruction with the capability to describe the mass transfer in combustion systems, this model can be used to establish the scaling characteristics of low NO_x devices. The definition of scaling criteria represents one of the most important goals of the FCR program, and provides the major driving force towards the description of NO_x production in two-phase turbulent diffusion flames by a hierarchy of models. It should be recognized that in the near-term these models will contain many empirical subelements. However, their modular nature will allow for a more complete mathematical description as the relevant physical and chemical phenomena are defined and quantified.

It is readily apparent that both the development of an understanding of transport processes and the development of numerical models play an important role in the achievement of the FCR program goals. Not only do they provide a predictive capability, they also establish a rationale whereby the effectiveness of NO_x control techniques can be compared against that expected from the lower bounds set by the various physical and chemical constraints. In addition, the development of numerical models provides a tool with which to extract the maximum amount of information from the various experimental programs associated with homogeneous kinetics and heterogeneous processes program elements of the FCR program.

SECTION 2

MODELING OF SIMPLE REACTOR SYSTEMS

Idealized reactor systems offer the opportunity to examine the physics and chemistry of pollutant formation from fossil fuels under two extreme conditions. A well-stirred reactor is the extreme of the backmixed system; one reactant composition and temperature characterizing the total system. In the well-stirred reactor there is a distribution of reactant lifetimes whereas in the other idealized reactor system a plug flow reactor all reactants have identical residence times. Three investigations have been planned to study both gaseous and heterogeneous systems under well-stirred conditions. The existence of a numerical model offers the maximum opportunity to extract information from these experimental investigations.

GAS PHASE REACTORS

Current activities in this area include:

- analysis of experimental data,
- development of a screening methodology and reaction mechanism analysis,
- exploratory numerical studies for planning purposes.

One basic goal of the homogeneous kinetic program element is the validation of a kinetic mechanism capable of describing the conversion of fuel nitrogen compounds to either XN specie (NO, NH_3, HCN) or N_2 during the combustion of hydrocarbon fuels. The development of such a mechanism requires both a numerical modeling capability and experimental data with which to verify the kinetic mechanism. In the homogeneous kinetic program element two investigations are being carried out which will provide the necessary data. The current reaction set for methane/air combustion was developed without a knowledge of the total XN concentration in rich combustion systems. Myerson is currently providing data on the generation of nitrogenous species from ammonia in a well-stirred reactor fired by methane, propane and ethylene for various initial ammonia concentrations and reactor temperatures. A high temperature plug flow reactor is being used to generate time-resolved profiles under isothermal conditions to examine the decay of XN species in fuel-rich mixtures under controlled isothermal conditions. The EER kinetics analysis code is being used to determine the key reaction path associated with fuel nitrogen conversion in these simple reactors. The code has a sensitivity analysis capability which allows the influence of variations in reaction rate upon specie production or energy release to be assessed. The code has also been used to evaluate the current methane/air mechanism by comparing ignition times against those measured in shock tube studies.

Although the methane/air reaction set has not been completely validated, it has been used in a series of numerical investigations as an aid in the planning of future work. These exploratory studies include the following.

- An examination of the influence of quench rate and reactant stoichiometry on XN decay during staged combustion.
- An evaluation of the use of artificial oxidants for determination of fuel nitrogen conversion. Experiments have been carried out using argon, oxygen, carbon dioxide mixtures in an attempt to eliminate thermal NO production, and thereby determine fuel nitrogen conversion directly. Numerical studies suggest that the use of these oxidants affects fuel nitrogen conversion, particularly under fuel-rich conditions.
- An examination of the effect of initial fuel nitrogen compound on the formation of XN specie.
- The interaction of SX and NX specie during fuel-rich combustion.
- A preliminary analysis of the influence of higher hydrocarbons on fuel nitrogen conversion.
- The development of a preliminary reaction set for acetylene as the hydrocarbon gas.

- Analysis of microscale unmixedness in stirred reactors. One potential problem associated with the use of well-stirred reactors is the degree of mixedness and a series of numerical investigations have been carried out to assess the effect of this unmixedness on the performance of a stirred reactor.

HETEROGENEOUS REACTORS

The previous paper described the projects being carried out in the heterogeneous process element of the FCR program. Two of these projects involved experimental investigations of the fate of fuel nitrogen in both solid and liquid fuels burning in well-backmixed conditions. A general heterogeneous well-stirred plug flow model is currently being developed to aid in the interpretation of these results. The model uses the gas phase model with a series of subelements which describe the evolution of hydrocarbon gases and fuel nitrogen specie from the coal particles or liquid droplets, as well as a heterogeneous heat release model. Naturally, in its current stage the model includes considerable empiricism. However, information being generated on the thermal decomposition of both coal and liquid fuels, char nitrogen oxidation, and the reduction of NO by solids will be fed into the model as it becomes available.

The modeling of the fate of fuel nitrogen in heterogeneous reactors requires information on the following:

- the dependence of devolatilization characteristics on the particle temperature and gaseous environment.
- the molecular consistency of the devolatilization products and both the rate and order in which they are evolved.
- particle droplet heat up transients and temperature overshoots as dictated by heterogeneous reactions and energy release in the diffusion layer surrounding the particle/droplet.
- the division of fuel nitrogen between heavy molecular weight gaseous components and the char, and the kinetics of char nitrogen conversion.

- particle/droplet relative Reynolds number effects on all transport processes.

Once the model is available it can be used to examine the influence of those processes listed above on the fate of fuel nitrogen, as well as providing a basis to define under which conditions fuel nitrogen conversion to NO is minimized.

SECTION 3

FLUID MECHANICS AND MODELING OF DIFFUSION FLAMES

Pulverized coal and residual fuel oil are burned in turbulent diffusion flames (i.e., the fuel and oxidant are injected into the combustion chamber separately) and the rate of heat release is normally controlled by the rate of fuel oxidant mixing. Combustion and pollutant formation is complicated by the turbulent mixing process, and currently there does not exist an adequate model for gaseous systems let alone one involving solid or liquid fuels. One aspect of the approach being taken in the FCR program is to examine the influence of various types of molecular diffusion controlled reaction zones on pollutant formation since these could represent the full range of reaction zones likely to be embedded within real turbulent diffusion flames. In addition, the understanding gained from studying simple flame systems provides validation of the kinetic mechanism under conditions that are very different from those used in its development.

MOLECULAR DIFFUSION FLAMES

A generalized diffusion kinetics analysis code has been developed which allows several flame systems to be modeled which involved molecular diffusion. The utility of such models is associated with the computational time required to carry out meaningful calculations. The current code utilizes operator splitting techniques for those situations which are path dependent, and fully implicit techniques involving the inversion of block tridiagonal matrices for conditions which have an asymptotic solution. The generalized code includes the following options:

- strained flames
- steady state particle/droplet flames
- transient confined particle/droplet diffusion flames
- transient spherical gas pockets
- free shear layer flames

- coaxial jet flames
- flat premixed flames

The code has been used to date to examine flat premixed flames, coaxial jet flames, and strained opposed jet diffusion flames. The strained flame provides one link between the modeling being carried out on molecular diffusion flames and turbulent diffusion flames, since the coherent flame structure model assumes that reaction takes place in diffusion layers separating the fuel and the oxidant. Computations have been carried out on the effect of strain rate on flame thickness, flame temperature, thermal NO production and fuel NO production from ammonia. These computations are currently being used by Broadwell and Marble in a model of NO production in a simple turbulent diffusion flame.

DIFFUSION EFFECTS IN PARTICLE/DROPLET COMBUSTION

The conversion of fuel nitrogen to NO in coal and oil flames may depend upon diffusion controlled processes which occur during thermal decomposition, and are associated with the physical effects of particle droplet heating. Experimental data on fuel nitrogen conversion in premixed fuel-lean coal flames suggests that approximately 30 percent of the total fuel nitrogen is converted to NO. Taking account of the division of fuel nitrogen between gas and char components, conversion on the order of 60 percent of the volatile component can be expected. These are similar to conversions measured with liquid fuels of similar nitrogen contents. However, in a fuel-lean premixed gaseous system, fuel nitrogen conversions on the order of 90 percent would be expected. Therefore, any model which assumes that nitrogenous species released from the particle/droplet are immediately completely mixed with the surrounding bulk gases will provide conversion rates which are higher than those encountered in practice. Thus, reaction in a diffusion-controlled layer might well be a necessary submodel for heterogeneous systems.

Nitrogen species may be driven from a coal particle as a jet, or feed some zone around the particle which then reacts in a layer surrounding the particle rather than in the bulk gas phase. Numerical experiments are planned to compare fuel nitrogen conversion in diffusion layers of these types (i.e., mantle, wake or envelope) to that which would occur in the bulk gas phase. Reaction in the diffusion layer will also control particle temperatures which may yield particle temperatures well in excess of the mean bulk flow and thus have a strong influence on devolatilization rates.

FLUID MECHANICS AND MODELING OF TURBULENT DIFFUSION FLAMES

Broadwell and Marble are developing a coherent flame structure model for gaseous turbulent diffusion flames. In addition there are several experimental studies either planned or in progress. They will provide information which will later be fed into a model of turbulent diffusion flames. The tasks currently underway are:

- Wendt and Hahn at the University of Arizona are measuring the conversion of ammonia to NO in a methane/air opposed jet diffusion flame representative of strained flamelets which may dominate the internal behavior of turbulent flames.
- Vranos at UTRC is currently investigating the combustion of heavy oil droplets in a free shear layer separating oxidant from high temperature combustion products.
- A study will be initiated shortly with IBM to use high-speed cinematography to ascertain whether coherent structures play a significant role in large-scale turbulent diffusion flames.

A subcontract effort is planned to characterize in detail long turbulent diffusion flames of both pulverized coal and heavy fuel oil at various scales.

SECTION 4

FLUID MECHANICS AND MODELING OF FLOW FIELD AND FUEL/AIR CONTACTING IN LARGE COMBUSTORS — MACROSCOPIC BEHAVIOR

Low NO_x combustion systems for pulverized coal and heavy oil flames can be classified into two major groups:

- Low NO_x burner designs. The objective of the development of low NO_x burners is to provide a burner system which will be accommodated by existing combustion chamber designs. Thus, its implementation will require the minimum degree of combustion chamber modification.
- Divided chamber systems. The advanced NO_x control techniques (i.e., those capable of achieving emission levels on the order of 20 ppm) will involve a completely zoned combustion chamber which will allow the control of temperature and optimize XN decay in a rich section, as well as minimizing NO formation during the second stage combustion process.

The FCR program is currently planning investigations which will aid in the development of these systems. The program involves a parallel experimental and modeling task whose goal is to provide a model which links burner combustion chamber design and operational parameters with flow field characteristics such as the size and strength of recirculation zones, the rate of fuel/air mixing, the influence of energy release on flow patterns, etc. This model can then be used in conjunction with the other flame element models to provide a tool which will be used to suggest control strategies.

Four basic flow field types have been identified. These include:

- Intensely swirl-stabilized: recirculation zone closed on the centerline, near-field dominated, energy release primarily in the free shear layer enclosing the recirculation zone. Initial fuel deposition can be distributed between the recirculation zone and the outer shear layer.

- Weakly swirl-stabilized: recirculation zone toroidal and open on the centerline with high momentum fuel passing downstream through the recirculation zone. Flow is dominated by the far-field behavior with energy release distributed well-downstream. Some fuel is initially deposited or swept into the recirculation zone to provide stability.
- Nonswirling long flames: stability provided by furnace-scale recirculation and the impingement of neighboring flames on the flame root.
- Divided chamber physically staged burner: particular attention here is given to modeling the interstage or secondary stage mixing behavior (the desire here is to minimize thermal NO formation and NO formed by oxidation of nitrogen intermediates).

The initial experimental task will concentrate upon the near-field of an intensely swirl-stabilized flame and the influence of the following independent parameters on the flow field will be ascertained:

- radial distribution of swirl and axial velocities at the burner throat;
- the length-to-diameter ratio and the area ratio of the burner divergent section;
- the degree of burner confinement or proximity to neighboring burners; and
- the fuel dispersion and resulting energy release distribution (this involves the deposition of fuel in particular parts of the flow field and will be accomplished by the use of multiple fuel injection ports or fuel dispersion rakes).

In addition to conventional flame diagnostics, use will be made of stimulus response tracer techniques to assist in mapping the flow field and determining turbulent transport intensity.

The parallel model development effort will concentrate on intensely swirl-stabilized systems. Weakly stabilized systems will be modeled by a modified version of a coaxial long turbulent diffusion flame code. Currently a program is underway at TRW where Fendell is evaluating available elliptic codes for use in flow field prediction.

SECTION 5

SUMMARY

This paper has reviewed the effort which is currently underway or planned in the FCR program elements concerned with numerical model development and transport processes. One key feature of the overall approach is the use of limit-case models to evaluate the lower bounds on NO_x production which are set by practical constraints. Examples of such limit-case studies are provided by the use of simple gas phase reactors with a suitable reaction set in order to evaluate the optimum time/temperature stoichiometry history of staged combustion systems. Figure 1 provides an example of one such study. The decay of XN specie in a fuel-rich combustor is kinetically-limited and the optimum combustor will be a compromise between volume and pollutant emissions. Thus it is necessary to maximize the rate of XN decay in a fuel-rich zone. The example shown in Figure 1 illustrates how distributed air addition to a fuel-rich region can maximize this decay rate. Further calculations of this type are planned involving heterogeneous as well as gaseous systems.

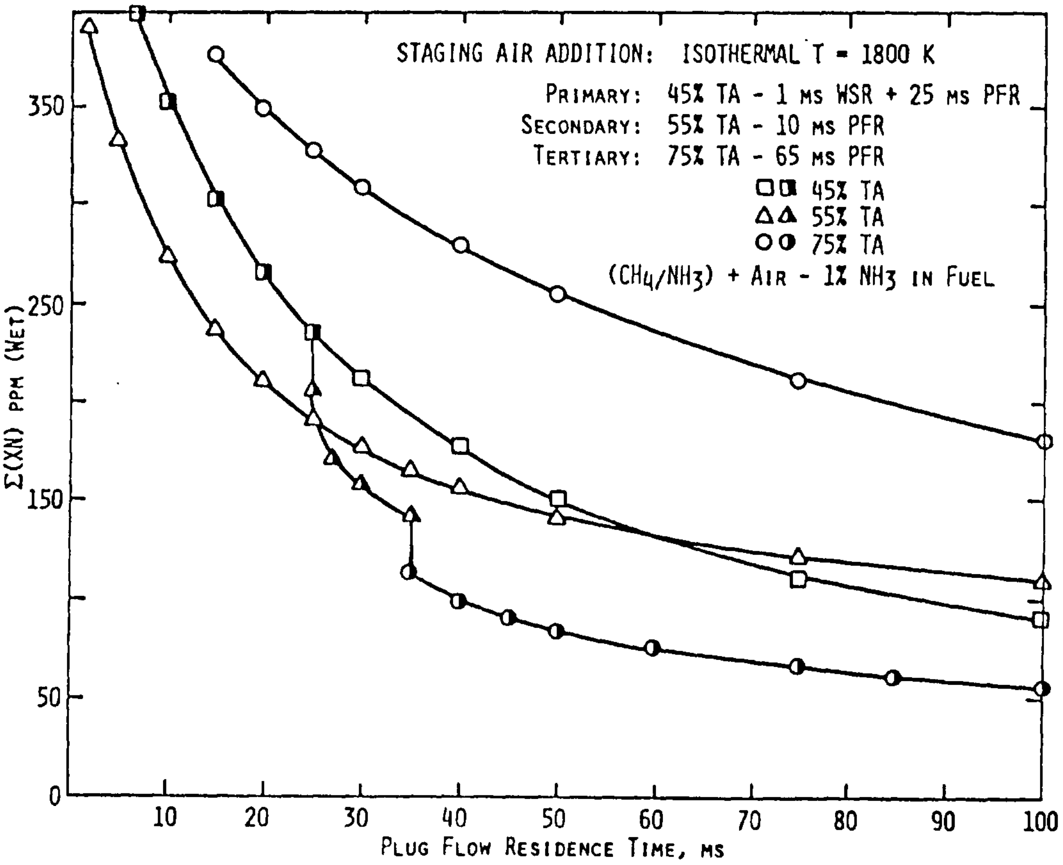

Figure 1. Decay Rate of Total XN Species in Isothermal Plug Flow Reactor as a Function of Stoichiometry and Temperature Showing that Distributed Addition Maximizes Decay Rate

SESSION VII

ENVIRONMENTAL ASSESSMENT

WADE H. PONDER
SESSION CHAIRMAN

SURVEY OF PROJECTS CONCERNING CONVENTIONAL COMBUSTION ENVIRONMENTAL ASSESSMENTS

by

W. E. Thompson

November 1978

ABSTRACT

The work reported on is part of the overall Conventional Combustion Environmental Assessment (CCEA) program being conducted by EPA. A nationwide survey has been made to identify projects that are relative to one or more of the environmental assessment elements of the methodology recently developed. The information necessary to compare CCEA-related projects has been defined. Comprehensive forms have been devised to elicit the information. Literature searches were carried out for the years 1970 to 1976. Institutions doing relevant work were identified. Research identified centered on kinds of pollutants emitted and their control and impact. The record of projects sponsored by EPA's Industrial Environmental Research Laboratory/Research Triangle Park (IERL/RTP) was examined. Extensive research is being conducted by IERL/RTP on emissions characterization, control processes (SO_x, NO_x, particulates), and economics.

Major sources surveyed for governmental research were: the Interagency Energy-Environment Research and Development Program Report, in which the computer search turned up 1,000 projects of which 246 were deemed relevant, and the Inventory of Federal Energy-Related Environment and Safety Research, from which 150 projects were selected from the 2,500 citations.

Further information on what is being done and by whom was obtained by attending national technical meetings and by visiting organizations for technical discussions. Present work centers on the development of a computerized system for the storage of the information so that it may be retrieved in a form that will facilitate management decisions.

This is part of the overall CCEA program being conducted by EPA's Industrial Environmental Research Laboratory/Research Triangle Park (IERL/RTP). The program is limited to studies relating to stationary conventional combustion processes.

From the beginning of the program, one of the major questions was: What constitutes an "environmental assessment"? This question has been answered by the methodologies developed by the Energy Assessment and Control Division of IERL/RTP and more particularly for the CCEA program by the Mitre Corporation. The Mitre methodology, shown in figure 1, contains approximately 70 elements used as the basis for classifying project activity.

In order to carry out an environmental assessment analysis on CCEA-related projects, information on the following subjects is necessary:

1. Fuel characterization,
2. Combustion process,
3. Effluent characterization,
4. Control techniques evaluation,
5. Health and ecological evaluation,
6. Quantification of pollution impacts, and
7. Environmental goals and objectives comparisons.

Very early in the course of work on this assignment, discussions were held with personnel of the Process Measurements Branch of the Industrial Processes Division of IERL/RTP. Their position was that projects requiring environmental assessment data could be compared for overlap or gaps only by a detailed analysis which included information on:

1. The specific source types being considered,
2. The points in the process at which samples were being taken,
3. The sampling procedures used, and
4. The analytical procedures used.

In order to elicit the information needed, a comprehensive set of forms have been developed by RTI. The forms cover the following details:

1. Project administrative data,
2. CCEA element checklist,

3. CCEA burner/fuel category identification,
4. Identification of sampling and analysis techniques,
5. Pollutant control methods checklist,
6. Health effects methods checklist, and
7. Ecological effects checklist.

A major portion of the Research Triangle Institute (RTI) work assignment was to obtain information with as much detail as possible on activities sponsored by government, industry, universities, and other organizations related to the environmental assessment of conventional combustion processes. This information was to be analyzed to determine its significance relative to the CCEA program. The effort was structured to obtain information on a broad nationwide basis on the scope of CCEA-related projects. It should be emphasized here that the effort was aimed at gathering information on the type of projects and the organization carrying them out. No numerical data or research results were gathered or evaluated. In other words, the effort was aimed at descriptions of "who is doing what?"

The information was collected by various methods, e.g., telephone contacts, a computer data base literature search, published project inventory data, contractor reports, information from technical symposia, and discussions with researchers at their respective institutions.

Initially a number of telephone calls were made to organizations that, based on RTI's past experience, were known to be performing CCEA task-related work. However, telephone calls were found to be a poor method of eliciting any details.

Literature searches were carried out for RTI by the North Carolina Science and Technology Research Center (a NASA Industrial Applications Center). The information produced was then evaluated by RTI technical personnel for relevance. The data files searched for published CCEA research projects are shown in table I. The search was keyed on air pollution associated with fuel combustion, and sought articles and reports published from 1970 to 1976.

From these citations several items of interest were distilled. The first was a long list of domestic organizations involved in such research. The next item of interest was the subjects addressed in the research. These were categorized by major assessment elements as shown in table II.

It should be pointed out that the sum of the right-hand column of table II exceeds 477 because many of the articles and reports dealt with several assessment element topics. Discussions on pollution control received the largest attention, with the identification of pollutants and determination of pollutant loadings coming next. Fuel and source characterization were next.

The third item of interest was the comparison of activity in the sectors addressed over the period of the survey. This was obtained by a census of articles by sectors/media: utility/air, industrial/air, and residential/air. The commercial institutional sector did not appear to be covered at all. A very large amount of activity was in the relationship of pollutants and control methods for the emissions associated with various fuel types. The results of this crude census are shown in figure 2. In this figure it may be seen that fuel-related CCEA research has been consistently strong. Research reported on air emissions and controls for utilities peaked in 1973 and 1974. Research on air emissions and controls for industrial sources has overtaken and passed that for utilities. Compared to the other categories, research on residential source emissions and controls has been low key.

We may conclude from this study that from 1970 to 1976 a large number of domestic organizations were involved in research on what kinds of pollutants are emitted, how they can be controlled, and what their impacts might be. Further, it seems that the tempo of the research has increased as public and institutional awareness has increased and as Federal and State pollution regulations have been promulgated.

A well-defined data base for CCEA activity is provided by the records of projects sponsored by EPA's Industrial Environmental Research Laboratory. Up until mid-1975, IERL program activities were primarily directed to process characterization and pollution control development directed to air pollution from stationary sources. Following the reorganization of EPA's Office of Research and Development (ORD) on June 10, 1975, IERL's pollution control activities began to span a wider range. A multimedia approach was taken, which was concerned with pollution in air, water, solid waste, thermal discharge, and energy conservation. In addition, cooperative efforts with other EPA laboratories and other Federal agencies have been undertaken to build programs that consider and include all aspects of environmental assessment in order to make explicit the alternative approaches in balancing the demands of minimal environmental quality degradation, economic constraints, and energy constraints. This growth into a broader outlook can be followed by tracing the topics dealt with by IERL project reports. The projects are organized in the following categories:

1. Reports on emissions characterization, methodology and measurements (75 projects),
2. Reports on SO_2 control processes for conventional combustion sources (110 projects),
3. Reports on NO_x control processes for conventional combustion sources (35 projects),
4. Reports on particulate matter controls for conventional combustion sources (60 projects), and
5. Reports on economic, energy, and resource recovery or conservation factors (35 projects).

Another important source of information is the Interagency Energy-Environment Research and Development Program Report, published under the guidance of ORD/EPA. For FY1975 and FY1976, these program abstracts were published in bound volumes. These reports were categorized into pollutant characterization, measurement and monitoring, environmental transport and fate, health effects, ecological effects, integrated assessment, and nine classes of control technology. This arrangement facilitated analysis. However, for FY1977 the information was entered on a computer but not published. Computer searching of the system was complicated by the fact that the ORD Information System report listed approximately 6,000 key words. In order to make a search, we limited the number of key words used to 25. Approximately 1,000 projects were received on the computer printouts. Upon analysis, 246 were deemed to be relevant to the CCEA program. The breakdown is shown in table III.

The system contains project-level descriptions of nearly all of the $100 million in research and development funded by the EPA-coordinated Interagency and Energy-Environment R&D program.

An advantage of the published abstracts was that they were grouped by agencies. Project descriptions are coded from Notice of Research Projects forms prepared by the appropriate laboratories and agencies using the Smithsonian Science Information Exchange format. This data base is limited to five agencies: EPA, the Energy Research and Development Administration (ERDA), the Department of the Interior, the Tennessee Valley Authority, and the Department of Agriculture.

Perhaps the most important single source of information is the Inventory of Federal Energy-Related Environment and Safety Research, the so-called ERDA-DOE Inventory. The purpose of the inventory is to provide a data base for overviews of federally funded, energy-related environment and safety research projects. The inventory is designed to be used to assist planning for future research by aiding in the determination of the adequacy of current environmental, health, and safety research programs to meet the needs of developing energy technology. The Energy Reorganization Act of 1974, PL93-438, authorizes the ERDA administrator to establish programs to minimize the adverse environmental effects of energy development and use. It further directs that these programs will use research and developmental efforts supported by other Federal agencies in a cooperative manner to avoid unnecessary duplication. A comprehensive plan was required to be submitted to Congress by the Federal Non-Nuclear Energy Research and Development Act of 1974, PL93-577, Section 6. The inventory complies with these requirements. Fourteen Federal agencies provided information for the inventory in response to form 294, which was approved by the Office of Management and Budget. Table IV gives the name of each agency, the number of projects for each agency, and the FY1976 funding level for research in biomedical and environmental research, environmental control technology, and operational safety for this particular fiscal year. About 84 percent of the total Federal funding is represented by the sum of the budgets of ERDA, the Nuclear Regulatory Commission, EPA, and the Department of Commerce. The field of biomedical and environmental research is divided into five categories. These are:

1. Characterization, measurement, and monitoring;
2. Environmental transport, physical and chemical processes, and effects;
3. Health effects;

4. Ecological processes and effects; and
5. Integrated assessment.

Table V shows a technology funding distribution for each of these categories. Table VI shows the breakdown of funding by technology areas for projects on environmental control technology. Note that EPA dominates the fossil fuel area and ERDA the nuclear area. The inventory summarizes approximately 2,500 projects, of which approximately 150 were identified as relevant in our survey of the 1976 inventory. The FY1977 inventory is now being surveyed.

A visit was made to the Electric Power Research Institute (EPRI) where discussions were held with a number of technical personnel. These discussions provided an overview of the extensive research programs being carried out under EPRI funding. Some idea of the magnitude of this effort can be obtained by considering the proposed 1977-1981 EPRI budget, shown in table VII. For example, the proposed combined expenditures in fossil fuel controls and environmental assessment over the 5-year period amount to about $143 million for 13 percent of the entire EPRI budget for the period. Since our visit, EPRI has provided us with numerous projects abstracts and planning documents. An analysis was made of the entire EPRI research program in terms of projects relevant to the CCEA program.

We have found attendance at symposia and meetings to be an excellent low-cost method of adding to our program information data bank. Some of the most valuable appeared to be:

1. EPA Stationary Source Combustion Symposia;
2. EPA Symposia on Flue Gas Desulfurization;
3. EPRI Symposia; and
4. Air Pollution Control Association meetings, both national and regional.

The most detailed information was gathered by visits to various organizations involved in combustion research for direct discussions with the researchers. This yields very satisfactory information. Unfortunately, this is the most expensive method. In most cases, however, the results obtained were satisfactory. For example, detailed information was gathered on the entire program at Pennsylvania State University, the

Princeton University combustion research operation, combustion research at the University of California at Berkeley, and the well-known analytical work being conducted at the University of California, Livermore.

All of the mass of data collected has been reduced to tables giving project title, organization, funding organization, budget, and other administrative information. In addition, a great number of abstracts of projects have been presented in special reports. However, it is doubtful that so much information can be readily prepared for analysis of such things as overlaps and gaps in programs. Therefore, we are at present engaged in a study of the feasibility of using a computer storage and retrieval and display system. This is being designed to give the greatest possible flexibility for management information needs that we can design. The problem of using all of the information on projects scattered throughout a great number of organizations in order to yield a true environmental assessment of conventional combustion processes is yet to be solved.

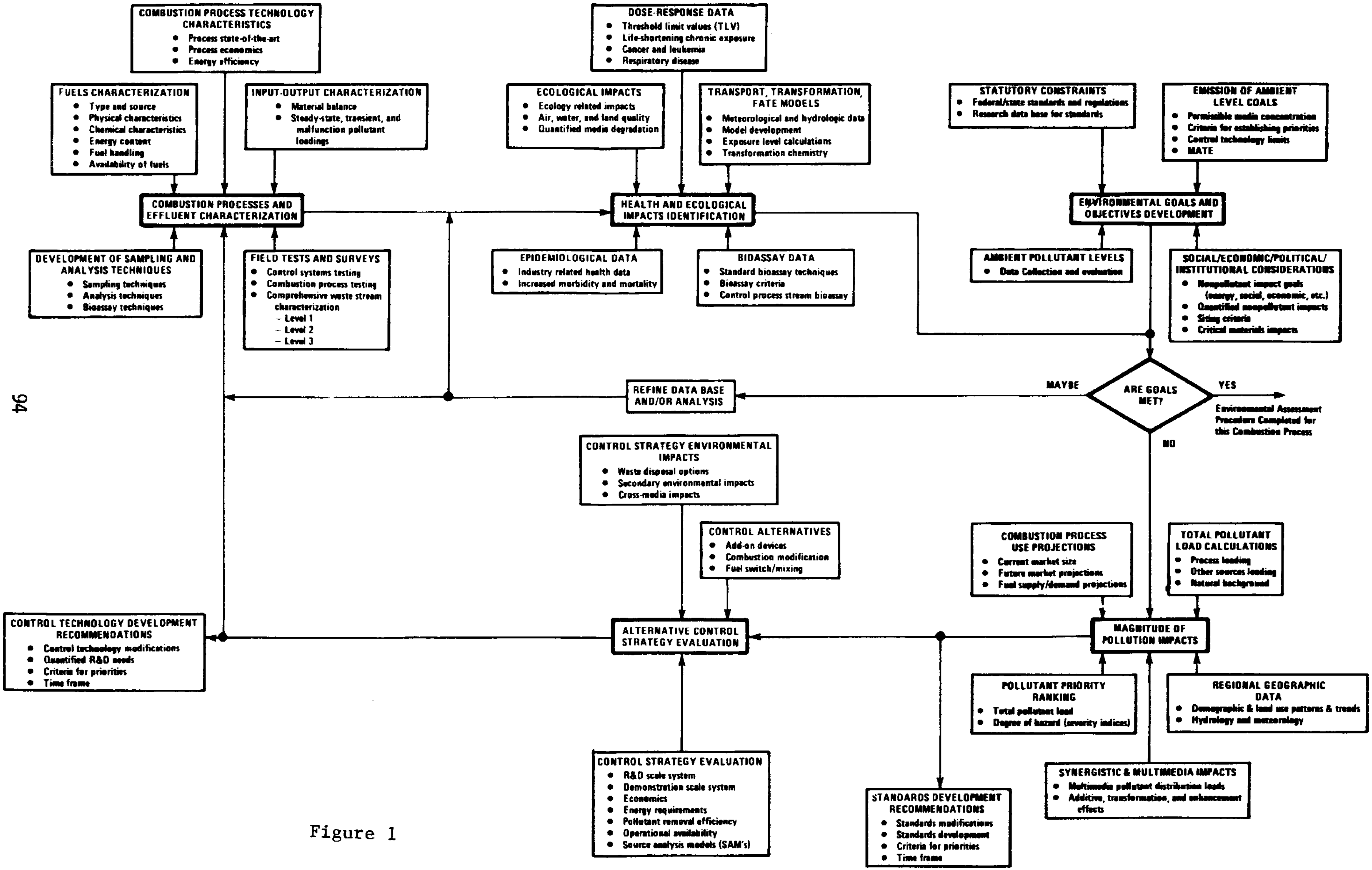
COMBUSTION PROCESS TECHNOLOGY CHARACTERISTICS
Process state-of-the-art
Process economics
Energy efficiency
FUELS CHARACTERIZATION
Type and source
Physical characteristics
Chemical characteristics
Energy content
Fuel handling
Availability of fuels
INPUT-OUTPUT CHARACTERIZATION
Material balance
Steady-state, transient, and malfunction pollutant loadings
COMBUSTION PROCESSES AND EFFLUENT CHARACTERIZATION
DEVELOPMENT OF SAMPLING AND ANALYSIS TECHNIQUES
Sampling techniques
Analysis techniques
Bioassay techniques
FIELD TESTS AND SURVEYS
Control systems testing
Combustion process testing
Comprehensive waste stream characterization
– Level 1
– Level 2
– Level 3
DOSE-RESPONSE DATA
Threshold limit values (TLV)
Life-shortening chronic exposure
Cancer and leukemia
Respiratory disease
ECOLOGICAL IMPACTS
Ecology related impacts
Air, water, and land quality
Quantified media degradation
TRANSPORT, TRANSFORMATION, FATE MODELS
Meteorological and hydrologic data
Model development
Exposure level calculations
Transformation chemistry
HEALTH AND ECOLOGICAL IMPACTS IDENTIFICATION
EPIDEMIOLOGICAL DATA
Industry related health data
Increased morbidity and mortality
BIOASSAY DATA
Standard bioassay techniques
Bioassay criteria
Control process stream bioassay
STATUTORY CONSTRAINTS
Federal/state standards and regulations
Research data base for standards
EMISSION OF AMBIENT LEVEL GOALS
Permissible media concentration
Criteria for establishing priorities
Control technology limits
MATE
ENVIRONMENTAL GOALS AND OBJECTIVES DEVELOPMENT
AMBIENT POLLUTANT LEVELS
Data Collection and evaluation
SOCIAL/ECONOMIC/POLITICAL/ INSTITUTIONAL CONSIDERATIONS
Nonpollutant impact goals (energy, social, economic, etc.)
Quantified nonpollutant impacts
Siting criteria
Critical materials impacts
MAYBE
ARE GOALS MET?
YES
Environmental Assessment Procedure Completed for this Combustion Process
NO
REFINE DATA BASE AND/OR ANALYSIS
CONTROL STRATEGY ENVIRONMENTAL IMPACTS
Waste disposal options
Secondary environmental impacts
Cross-media impacts
CONTROL ALTERNATIVES
Add-on devices
Combustion modification
Fuel switch/mixing
COMBUSTION PROCESS USE PROJECTIONS
Current market size
Future market projections
Fuel supply/demand projections
TOTAL POLLUTANT LOAD CALCULATIONS
Process loading
Other sources loading
Natural background
CONTROL TECHNOLOGY DEVELOPMENT RECOMMENDATIONS
Control technology modifications
Quantified R&D needs
Criteria for priorities
Time frame
ALTERNATIVE CONTROL STRATEGY EVALUATION
MAGNITUDE OF POLLUTION IMPACTS
POLLUTANT PRIORITY RANKING
Total pollutant load
Degree of hazard (severity indices)
REGIONAL GEOGRAPHIC DATA
Demographic & land use patterns & trends
Hydrology and meteorology
CONTROL STRATEGY EVALUATION
R&D scale system
Demonstration scale system
Economics
Energy requirements
Pollutant removal efficiency
Operational availability
Source analysis models (SAM's)
STANDARDS DEVELOPMENT RECOMMENDATIONS
Standards modifications
Standards development
Criteria for priorities
Time frame
SYNERGISTIC & MULTIMEDIA IMPACTS
Multimedia pollutant distribution loads
Additive, transformation, and enhancement effects

Figure 1

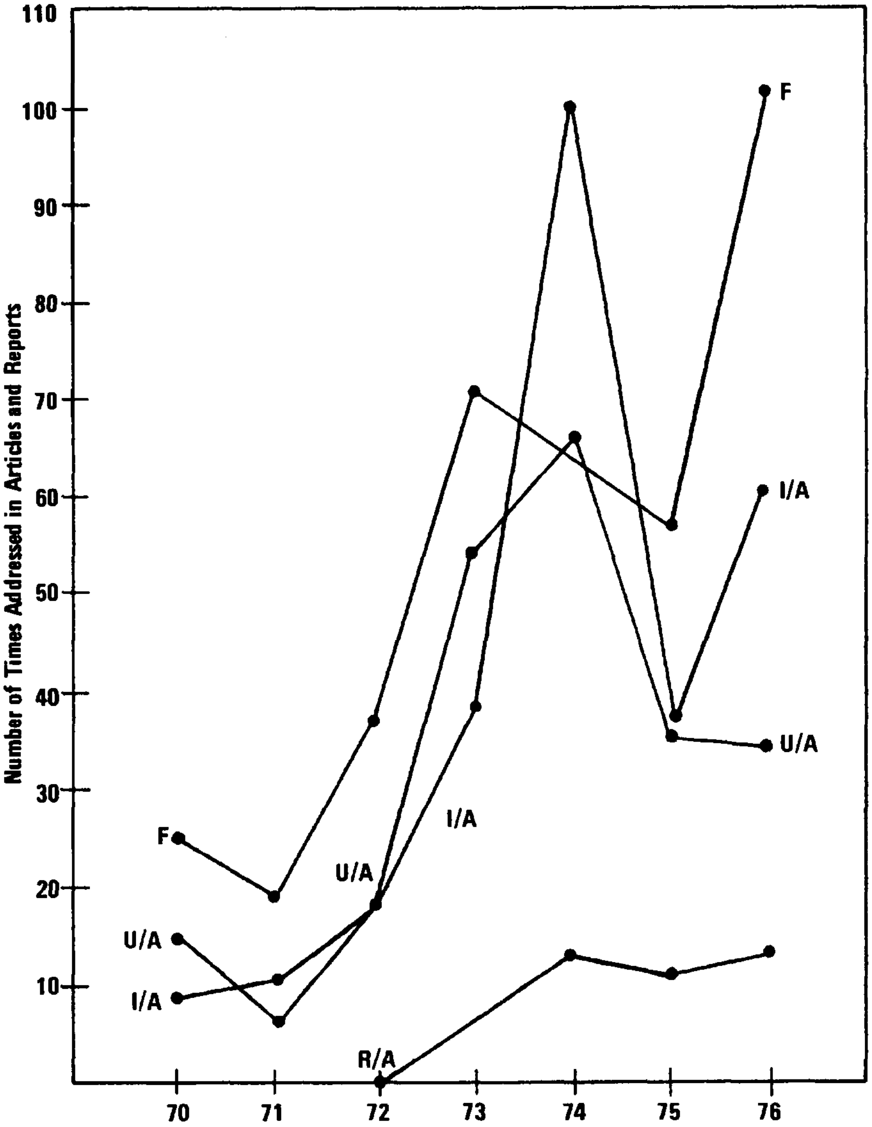

Figure 2. Results of citation census for CPA research in categories of utility/air (U/A), industry/air (I/A), residential/air, (R/A), and pollutants and controls related to various fuel types (F).

TABLE I. DATA FILES SEARCHED FOR PAST CPA RESEARCH ACTIVITY

Data Base Name	Subject and Source	Coverage From	Number of Citations
Engineering Index (compendex)	Worldwide engineering literature (3,500 publications)	1970	500,000
Energy Data Base	Complete energy information (ERDA)	1974	100,000
Pollution	Pollution and environment (pollution abstracts)	1970	37,700
Smithsonian Science Information Exchange	Research projects in progress; emphasizes federally funded projects and includes many privately funded projects	1966	200,000

TABLE II. DISTRIBUTION OF ARTICLES AND REPORTS BY ASSESSMENT ELEMENT CATEGORY

Assessment Element	Number of Articles and Reports
Source characterization	70
Determination of material inputs	60
Identification of pollutants	93
Identification of media for each pollutant	11
Determination of pollutant loadings	83
Fugitive emission analysis	4
Operating parameter sensitivity analysis	71
Controls	342
Combined effects assessment	3
Cross-media effects assessment	1
Environmental conversion assessment (secondary pollutants)	5
Health effects	1
Ecological effects	15
Energy analysis	28
Economic analysis	28

TABLE III. RELEVANT CCEA PROGRAM PROJECTS

Category	No. of Projects
Fuels	9
Sampling and Analysis	62
Emissions--Effluents	26
Controls--General	3
Controls--Particulates	20
Controls--NO_x	12
Controls--SO_2	12
Transport and Fate	23
Health	49
Ecology	26
Integrated Assessment	4

TABLE IV. FEDERAL AGENCY RESPONSES

Agency	No. of Projects Reported	Funding by Agency ($ in millions)
Department of Agriculture	7	7.6
Department of Commerce	93	41.0
Department of Defense	3	1.4
Department of Health, Education, and Welfare	263	22.6
Department of Housing and Urban Development	1	<0.05
Department of the Interior	80	25.9
Department of Transportation	9	.4
Environmental Protection Agency	305	63.0
Energy Research and Development Administration	1,467	197.5
Federal Energy Administration	20	1.7
National Science Foundation	18	1.2
National Aeronautics and Space Administration	5	1.3
Nuclear Regulatory Commission	200	77.5
Tennessee Valley Authority	65	11.8
Total	2,536	452.9

TABLE V. BIOMEDICAL AND ENVIRONMENTAL RESEARCH SUBCATEGORY FUNDING BY FEDERAL AGENCY, FY 1976 ($ in millions)

Energy Technology	BER Subcategory					
	Characterization, measurement, and monitoring	Environmental transport	Health effects	Ecological effects	Integrated assessment	Total
DOA	0.3	0.8	-	1.8	0.9	3.8
DOC:						
OEA	-	-	-	-	0.2	0.2
NBS	1.9	<0.05	0.1	<0.05	-	2.0
NOAA	4.3	8.5	0.2	19.0	6.3	38.2
DOD	-	-	-	-	-	-
HEW:						
NIOSH	0.9	-	1.0	-	-	1.9
NIEHS	<0.05	<0.05	13.2	0.5	0.1	13.8
NCI	-	-	6.7	-	-	6.7
HUD	-	-	-	-	<0.05	<0.05
DOI:						
FWS	0.2	-	-	2.3	<0.05	2.5
BLM	-	-	-	-	-	-
USGS	7.4	4.2	-	2.5	3.6	17.8
RECLAM	0.1	-	-	0.1	-	0.2
BPA	<0.05	<0.05	-	<0.05	0.3	0.4
DOT	0.1	-	<0.05	-	-	0.1
EPA	5.6	1.9	4.6	3.9	3.1	19.1
ERDA	20.8	21.3	78.4	19.6	13.7	153.8
FEA	0.2	0.1	<0.05	0.2	1.1	1.6
NSF/RANN	0.2	0.3	<0.05	0.3	0.2	1.1
NASA	0.2	0.2	<0.05	0.1	0.1	0.6
NRC	1.6	3.5	0.6	0.7	1.0	7.4
TVA	1.2	1.3	<0.05	1.9	1.5	5.9
Total	45	42.1	104.8	52.9	32.1	277.1

TABLE VI. ENVIRONMENTAL CONTROL TECHNOLOGY FUNDING (ENERGY TECHNOLOGY BY FEDERAL AGENCY), FY 1976 ($ in millions)

	Technology															
Agency	Fossil general	Coal	Oil and gas	Oil shale	Bio-mass	Nuclear general	Fission	Fusion	Geo-thermal	Solar	Hydro-electric	Conser-vation	Multi-tech	General science	Other	Total
DOA	2.9	0.5	-	0.2	-	0.1	-	-	-	-	-	-	-	-	-	3.7
DOC:																
OEA	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NBS	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOAA	-	-	0.1	-	-	-	-	-	-	<0.05	<0.05	<0.05	-	-	-	0.2
DOD	0.1	-	-	-	-	-	-	-	-	-	-	1.3	-	-	-	1.4
HEW:																
NIOSH	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NIEHS	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NCI	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
HUD	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DOI:																
FWS	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BLM	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
USGS	-	2.8	0.3	0.3	-	-	-	-	-	-	-	0.2	-	0.4	0.1	4.1
RECLAM	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BPA	-	<0.05	<0.05	-	-	-	-	-	-	-	0.1	-	-	-	-	0.1
DOT	-	-	-	-	-	-	-	-	-	-	-	-	0.1	-	-	0.1
EPA	3.5	27.7	3.3	0.8	0.9	<0.05	-	-	0.4	0.4	-	2.6	3.1	0.4	0.7	43.9
ERDA	0.1	2.4	1.1	0.1	-	30.5	0.7	0.2	0.7	<0.05	-	0.3	0.5	0.2	0.2	36.9
FEA	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NSF/RANN	-	-	-	-	-	-	-	-	-	-	-	-	-	-	<0.05	<0.05
NASA	-	0.2	-	<0.05	-	-	-	-	<0.05	-	-	-	0.4	-	-	0.7
NRC	-	-	-	-	-	1.3	<0.05	-	-	-	-	-	-	-	-	1.3
TVA	0.8	4.0	-	-	-	-	-	-	-	-	0.1	0.5	-	0.3	<0.05	5.7
Total	7.4	37.6	4.8	1.4	0.9	31.9	0.7	0.2	1.1	0.4	0.2	4.9	4.1	1.3	1.0	98.1

TABLE VII. EPRI SUMMARY OF PROPOSED PROGRAM PLAN ($ in millions)*

Program	1977	1978	1979	1980	1981	Total
FOSSIL FUEL AND ADVANCED SYSTEMS						
Fluidized combustion and coal cleaning	4.8	8.1	8.8	9.4	10.0	41.1
Air quality control	14.3	10.2	10.2	10.4	10.8	55.9
Water quality control and heat rejection	1.9	2.4	2.6	2.6	2.7	12.2
Fossil plant performance and reliability	2.4	2.8	3.0	4.1	4.4	16.8
TOTAL--Fossil fuel power plants	23.4	23.5	24.6	26.5	27.9	126.0
Clean gaseous fuels	11.1	9.5	10.0	10.0	10.0	50.5
Clean liquid and solid fuels	14.9	14.8	14.5	14.5	14.5	73.3
Power generation	5.8	7.0	7.5	9.5	10.5	40.3
Power plant requirements and analysis	0.7	1.0	1.0	1.0	1.0	4.7
TOTAL--Advanced fossil power systems	32.5	32.3	33.0	35.0	36.0	168.8
Fusion	4.7	3.4	3.8	4.3	4.4	20.6
Solar	4.4	3.4	3.7	4.0	4.3	19.8
Geothermal	2.2	2.0	2.0	2.2	2.3	10.7
TOTAL--New energy resources	11.3	8.8	9.5	10.5	11.0	51.1
Energy storage	5.2	7.1	9.0	8.9	8.2	38.3
Fuel cells and chemical energy conversion	9.0	8.5	6.7	6.6	7.8	38.7
Energy utilization and conservation technology	1.0	1.4	2.3	2.5	3.0	10.1
TOTAL--Energy management and utilization technology	15.2	17.0	18.0	18.0	19.0	87.1
TOTAL--FOSSIL FUEL AND ADVANCED SYSTEMS	82.4	81.6	85.1	90.0	93.9	433.0
NUCLEAR POWER						
Water reactor system technology	14.8	18.8	17.9	18.0	17.9	87.4
Reliability, availability, and economics	14.1	16.4	16.9	16.0	13.9	77.3
Fuels, waste, and environment	8.0	9.0	9.7	10.7	12.2	49.6
Developing application and technology	9.1	7.0	9.0	11.8	15.0	51.9
TOTAL--NUCLEAR POWER	46.0	51.2	53.5	56.5	59.0	266.2
ELECTRICAL SYSTEMS						
AC transmission	7.0	7.5	7.9	8.3	8.7	39.4
Underground transmission	7.5	7.5	8.0	8.4	8.8	40.2
DC transmission	10.9	4.4	3.9	4.0	4.2	27.4
Distribution	5.2	6.4	6.7	7.3	7.6	33.2
Systems planning, security, and control	1.9	2.7	2.9	3.1	3.2	13.8
Rotating electrical machinery	0.5	2.8	3.2	3.4	3.5	13.4
TOTAL--ELECTRICAL SYSTEMS	33.0	31.3	32.6	34.5	36.0	167.4
ENERGY ANALYSIS AND ENVIRONMENT						
Environmental assessment	10.4	12.5	14.8	17.0	20.1	74.8
Demand and conservation	2.1	2.7	2.6	2.6	2.6	12.2
Supply	3.1	3.8	3.7	3.7	3.7	18.0
Systems	1.5	1.6	1.7	1.7	1.7	8.2
Electric utility rate design study	.8	.3	-	-	-	.3
TOTAL--ENERGY ANALYSIS AND ENVIRONMENT	17.9	20.9	22.8	25.0	28.1	113.5
TOTAL FUNDS ALLOCATED	179.3	185.0	194.0	206.0	217.0	981.3
Nonprogrammed expenditure	-	5.0	9.0	28.0	61.0	103.0
TOTAL INSTITUTE	179.3	190.0	203.0	234.0	278.0	1084.3

*Funding entries represent planned contractor expenditures stated in current dollars including an adjustment for inflation.

EMISSIONS ASSESSMENT OF CONVENTIONAL COMBUSTION SYSTEMS

By

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ABSTRACT

The Emissions Assessment of Conventional Combustion Systems (EACCS) is a sampling and analysis program for comprehensive emissions characterization and environmental assessment of stationary conventional combustion processes in the following principal categories: electricity generation-external combustion, electrical generation and industrial-internal combustion, industrial-external combustion, commercial/institutional, and residential.

The EACCS program uses the EPA-IERL Level 1/Level 2 phased approach which is designed to provide comprehensive emissions information on all process waste streams in a cost effective manner. Level 1 uses semiquantitative techniques of sampling and analysis to provide preliminary information on emission to identify potential problems. Level 2 sampling and analysis techniques are specific and quantitative for problem emissions identified by Level 1.

All sources in the residential, electricity generation and industrial-internal combustion, and gas-and-lignite-fired categories have been completed and draft reports written.

SECTION 1

INTRODUCTION

The Emissions Assessment of Conventional Combustion Systems (EACCS) Program is a sampling and analysis program for comprehensive emissions characterization and environmental assessment of stationary conventional combustion processes (SCCP). It is currently the largest EPA-funded program of its type.

SCCP under consideration are grouped into five principal categories:

- Electricity generation - external combustion
- Industrial - external combustion
- Electricity generation and industrial - internal combustion
- Commercial/institutional - space heating
- Residential - space heating

Within these five principal categories, 50 source categories were defined based on combustion method (external, internal), firebox design (e.g., pulverized dry bottom, cyclone), and fuel type (e.g., gas, residual oil, anthracite).

The objective of the EACCS Program is to produce environmental assessments of pollutant emissions by source category. The scope of the EACCS Program includes the following major activities:

- Review and evaluate existing emissions data covering each of the 50 source categories in the five principal categories

- Acquire new emissions data by using Level 1 sampling and analysis methodology from 170 test site covering the 50 source categories

- Conduct 21 Level 2 test activities, as required, by application of the EPA/IERL philosophy of phased sampling and analysis

- Develop estimates of total multimedia pollutant emissions by source category in order to perform the required environmental assessments.

Because the EACCS program is based on the EPA/IERL phased approach to environmental assessment (Reference 1), the sampling and analysis methodology comprises a set of detailed procedures (Reference 2) designed to provide internally consistent and comparable data.

The phased approach to environmental assessments is designed to provide comprehensive emissions information on all process waste streams in a cost effective manner. To achieve this goal, two distinct sampling and analysis levels are being employed in this program. Level 1 utilizes semiquantitative (± a factor of 3) techniques of sample collection and laboratory and field analyses to: provide preliminary emissions data for waste streams and pollutants not adequately characterized; identify potential problem areas; and prioritize waste streams and pollutants in those streams for further, more quantitative testing. Using the information from Level 1, available resources can be directed toward Level 2 testing which involves specific, quantitative analysis of components of those streams which do contain significant pollutant loadings. The data developed at Level 2 is used to identify control technology needs and to further define the environmental hazard associated with each process stream. A third phase, Level 3, which is outside the scope of this program, employs continuous or periodic monitoring of specific pollutants identified at Level 2 so that the emission rates of these critical components can be determined exactly as a function of time and operating conditions.

Level 1 results are compared with a variety of evaluation criteria, e.g., Source Severity Factors (Reference 3) and MEG/MATE values (Reference 4). Emissions with a Source Severity Factor of 0.05 or greater or which exceed MEG/MATE values are flagged as potential problems or recommended for Level 2 analysis for further definition.

The first program activity was reviewing and evaluating existing emissions data for each of the categories covered by the program. Preliminary results from this evaluation were reviewed by EPA, and recommendations were made for selecting the Level 1 test sites. (As Level 1 data are reviewed, the same process is used to select Level 2 test activities).

All sources in the residential principal category have been tested, and a draft final report is in review (Reference 5). A draft report on the internal combustion category (Reference 6) is in review. Data on lignite- and gas-fired utilities sites have been reviewed. This paper will discuss results from these sources.

SECTION 2

CONCLUSIONS

GAS- AND OIL-FIRED RESIDENTIAL SOURCES

The following conclusions were drawn from the emissions assessment of gas- and oil-fired residental sources tested (Reference 5).

- Gas-fired and oil-fired residential heating source categories do not constitute a major environmental hazard. Source severity factors for all pollutants calculated from emissions data are well below 0.1. Source severity factors lower than 0.1 are considered to be indicative that pollutant emissions are not hazardous.

- Criteria pollutant emissions are variable and often not in agreement with either EPA emission factors or existing data. The variability in the data is probably because of natural variations in residential combustion units, the semiquantitative nature of Level 1 measurements, and, in the case of hydrocarbons, differences in pollutant definition relating to measurement technique. Severity factors for criteria pollutants are higher for oil-fired systems than for gas-fired systems.

- SO_3 emission levels per unit of fuel sulfur, based on a limited number of analyses, are slightly in excess of those normally found in utility systems. This finding, for which there is some precedent, may be a real effect or the result of experimental error at low total sulfur concentrations.

- Trace element emissions are extremely low for gas-fired systems. Trace elements from oil-fired systems are emitted to a greater extent than from gas combustion but are largely comprised of transition elements. Severity factors for all elements are well below 0.1.

- POM emissions are essentially nonexistent from gas-fired residential sources. Some POMs are emitted from oil-fired combustion. However, the most hazardous POM constituents; i.e., benzo(a)pyrene, were not detected and degree of hazard factors, defined as the ratio of stack concentrations to MATE values, for those POM compounds detected were well below 0.1.

- On the basis of the above conclusions, no further sampling and analysis is required for these sources. No Level 2 investigation of any pollutant is required.

- Hydrocarbon and POM emissions were not significantly affected by the change in burner cycle mode from 50 minutes on/10 minutes off to 10 minutes on/20 minutes off. The effect of cycle on emissions noted by other investigators is undoubtedly a real effect but the change in emissions was not detectable in this Level 1 sampling and analysis program.

INDUSTRIAL AND UTILITY INTERNAL COMBUSTION SOURCES

The following conclusions were drawn from the emissions assessment of industrial and utility internal combustion sources (Reference 6).

- NO_x emissions from internal combustion sources are a potential environmental problem. These emissions account for approximately 20 percent of the total NO_x emissions from stationary sources. Of the NO_x emissions from internal combustion sources, more than 80 percent are contributed by the industrial reciprocating gas engine category.. Source severity factors for NO_x emissions from gas turbines and reciprocating engines range from 0.17 to 7.1.

- Emissions of hydrocarbons from internal combustion sources contribute significantly to the national emissions burden. These emissions account for approximately 9 percent of the total hydrocarbon emissions from stationary sources. More than 80 percent of the hydrocarbon emissions from internal combustion sources are contributed by the industrial reciprocating gas engine category. Source severity factors for hydrocarbon emissions range from 0.01 for industrial gas-fueled gas turbines to 1.7 for industrial reciprocating gas engines.

- CO emissions from internal combustion sources are not an environmental concern. Source severity factors for CO emissions from internal combustion sources are all well below 0.05. Total CO emissions from these sources account for approximately 1 percent of CO emissions from all stationary sources. More than 80 percent of the CO emissions from internal combustion sources are contributed by the industrial reciprocating gas engine category.

- Emissions of SO_2 and particulates from internal combustion sources contribute only an insignificant fraction of the emissions of these pollutants from stationary sources. Source severity factors for SO_2 and particulate emissions are well below 0.05, with the exception of SO_2 emissions from diesel engines. Source severity factors for SO_2 emissions from industrial and electricity generation diesel engines are 0.08 and 0.10, respectively.

- Combination of emissions data from this measurement program and the existing data base provides adequate characterization of emissions of criteria pollutants from internal combustion sources.

- SO_3 emissions from oil-fueled internal combustion sources are a potential environmental problem. Source severity factors for SO_3 emissions range from 0.05 to 0.23. For distillate oil-fueled gas turbines, an average of 3.8 percent of the sulfur present in the fuel is converted to SO_3. For diesel engines, an average of 1.4 percent of the fuel sulfur is converted to SO_3. The percent of fuel sulfur converted to SO_3 is lower for diesel engines because of the lower oxygen level in reciprocating engines.

- For distillate oil-fueled gas turbines, the data base for SO_3 emissions is adequate. For distillate oil reciprocating engines, the data base for SO_3 emissions could be improved by additional field tests.

- Emissions of trace elements from gas-fueled internal combustion sources are negligible when compared with emissions of trace elements from oil-fueled sources. For oil-fueled internal combustion sources, emissions of copper, nickel, and phosphorus have source severity factors greater than 0.05.

- The data base for trace element emissions from diesel engines is adequate. For distillate oil-fueled gas turbines, trace elements for which the emissions data base is inadequate include nickel, phosphorus, and silicon. The emissions data base for these trace elements may be improved by analysis of additional fuel samples.

- Emissions of individual organic species from internal combustion sources are environmentally insignificant. Analyses of organic samples have indicated that organic emissions from oil-fueled internal combustion sources consist mainly of saturated and unsaturated aliphatic and aromatic hydrocarbons. The most prevalent organic species present are saturated straight chain and branched hydrocarbons. Substituted benzenes are the second most abundant organic species emitted. Source severity factors for these organic emissions are well below 0.05.

- POM emissions from internal combustion sources are not at levels of environmental concern. POM emissions from gas- and oil-fueled gas turbines were at levels too low to be differentiated from blank values. For diesel engines, the POMs emitted were mostly naphthalenes and substituted naphthalenes, with source severity factors well below 0.05. POM compounds known to be carcinogenic, such as benzo(a)pyrene and dibenz(a,h) anthracene, were not found above the detection limit of 0.05 $\mu g/m^3$. Benzo(a)pyrene, the only POM compound with MATE value below the detection limit, is unlikely to be present, as no other POM compounds of molecular weight greater than 202 were found.

GAS-FIRED UTILITY SOURCES

From the gas-fired utility source tests, the following conclusions have been drawn.

- Inorganic emissions are not a problem
- Particulate emissions are well below NSPS requirements
- Emissions of polycyclic organic materials (POMs) are not a problem, as no POMs were found.
- CO data were scattered, and additional data may be necessary
- Hydrocarbon emissions for two non-tangential sites were scattered. Acquisition of additional data is not recommended at this time.

LIGNITE-FIRED UTILITY SOURCES

The following conclusions were drawn from the emission assessment of lignite-fired utility sources.

- Particulate emissions vary widely depending on control technology used.
- ESPs effectively control particulate emissions.
- Present NO_x and SO_x data are suspect because of problems with Level 1 methodology; sufficient data may be available from AP-42.
- Ba, Ni, Cu, Ca, Be, and F exceed source severity standards in the controlled sites.
- Organic emissions are generally high and vary widely but lower than AP-42 data. Additional Level 2 testing is recommended.
- Significant amounts of organic material were found in all fly ash, bottom ash, and water samples.
- Organic material was primarily aliphatic and aromatic hydrocarbons; sufficient esters and oxygenated compounds were not present to distinguish them from the blanks.
- SO_3 and particulate sulfate data is needed.
- Additional lignite data are necessary on all levels. Large units in Texas should be considered.

SECTION 3

TESTING

SOURCES TESTED

Gas- and Oil-Fired Residential Sources

Residential space heating systems consist of combustion units burning natural gas, liquid petroleum gas (LPG), distillate oil, coal, and wood and electric heating systems. The EACCS program focussed on gas (natural and LPG) and oil, as they are the most important residential space heating fuels representing, respectively, 60 percent and 38 percent of 1975 consumption.

Residential oil- (distillate) and gas-fired space heating equipment is subject to a number of design variations relating to burners, combustion chambers, excess air, heating medium, etc. Gas-fired systems are inherently less complex and easier to maintain than oil-fired systems because the fuel is cleaner and atomization is not required. Residential systems operate only in an on/off mode. There are no other variations in fuel input rate in contrast to load modulation encountered with larger commercial, industrial, and utility sources.

Air emissions from the blue gas stack are the only significant emissions from oil- and gas-fired residential heating units. Because these fuels are relatively clean, the concentrations of air pollutants emitted from these sources are low in contrast with those emitted from other combustion sources to be evaluated during this program. However, because these sources are numerous and have a high source-receptor relationship, they may be of environmental importance.

Evaluation of existing emissions data on these sources indicated a strong need for additional data, particularly an emissions of organic compounds. Therefore, five representative gas- and oil-fired residential space heating units each were tested.

Internal Combustion Sources

Stationary internal combustion sources for electricity generation and industrial applications are grouped into two categories: gas turbines and reciprocating engines. Gas turbines are classed into three general types of cycles: simple open cycle, regenerative open cycle, and combined cycle. Regenerative open cycle turbines constitute only a very small fraction of the total gas turbine population. Emissions from identical gas turbines used in the combined and simple cycle modes are the same. Thus, only emissions from simple open cycle gas turbines were evaluated.

Reciprocating internal combustion engines are classified according to the method of ignition: spark and compression (diesel). Both spark and compression ignition engines are further classified into two groups: four-cycle and two-cycle. Most of the large bore, high power engines for utility and industrial applications are four-cycle compression ignition engines designed to operate as diesel fuel and two-cycle or four-cycle spark ignited gas engines.

The principal application areas for gas turbines and reciprocating engines are: electricity generation, oil and gas transmission, natural gas processing, and oil and gas production and exploration. In 1976 the installed capacity of gas turbines was 46,570 MW in electrical utilities and 8,800 MW for industrial applications. In 1976, the installed capacity of reciprocating engines was 5,300 MW in electric utilities and 18,870 MW for industrial applications.

Air pollution control equipment is generally not installed on gas turbines or reciprocating engines. However, there is evidence that water and steam injection are valid techniques for controlling NO_x emissions from gas turbines.

Evaluation of existing emissions data on gas turbines indicated that the data base on distillate oil fired turbines was inadequate for trace elements, particulate sulfate, and organics. For distillate oil reciprocating engines, the data base for SO_3, particulate sulfate, and organic emissions was found to be inadequate. Emissions data for gas fired turbines and reciprocating engines were adequate. To fill the deficiencies in the data base, one gas turbine, five distillate oil turbine, and five distillate oil reciprocating engine sources were tested.

Gas- and Lignite-Fired Utility Sources

Gas-fired utility sources were classified by combustion source type: non-tangential and tangential firing. Evaluation of existing emissions data indicated a need for additional data. Therefore, four non-tangential and 3 tangential fired heaters were tested using Level 1 methods.

Lignite-fired utility sources were also classified by combustion source type:

- pulverized dry bottom (front fired)
- cyclone
- spreader stoker

Evaluation of existing emissions data indicated a need for further testing of lignite-fired heaters. Consequently, three pulverized dry bottom, one cyclone, and two spreader stoker sources were tested.

SAMPLING AND ANALYSIS

Field Testing

Field testing procedures were on Level 1 environmental assessment methods (Reference 1). The Source Assessment Sampling System (SASS) was used to collect particulate, organic, and trace metal samples. The SASS train is a high volume, 0.14 m^3/min (5 scfm), system designed to extract particulates and gases from the stack, separate particulates into four size fractions, trap organics in an absorbent, and collect volatile trace metals in liquid solutions. A high volume system is required to collect adequate quantities of trace materials for subsequent laboratory analyses. The SASS train is operated for a time sufficient to collect 30 m^3 of stack gases.

Stack gas is drawn into the SASS train through a stainless steel probe. Particulates are collected by a series of three cyclones (>10μ, 3-10μ, >3μ) and a filter > 0.1μ. The cyclone and filter are in a heated oven maintained at 150°C (300°F). From the cyclone oven, stack gas passes through the organic vapor sorbent trap which cools the gas to 20°C and quantitatively traps organic compounds boiling above 100°C. The trapping medium is XAD-2 resin, a styrene-divinylbenzene copolymer. The sample stream is then drawn through a series of four impingers. The first impinger contains hydrogen peroxide, H_2O_2, which stabilizes stack gas components by oxidation. The second impinger contains a solution of ammonium peroxydisulfate $(NH_4)_2S_2O_8$, and silver nitrate, $AgNO_3$, to trap volatile trace metals and organometallic compounds. The third impinger is a backup to the second and contains a solution of ammonium peroxydisulfate. The fourth impinger contains silica gel to remove moisture.

Compounds with boiling points (<100°C) too low to be retained by the sorbent trap are analyzed in the field by gas chromatography. Gas samples were collected in Tedlar bags using a reciprocating pump and stainless steel probe. A cooling chamber was used between the stack and the Tedlar bag. Bag samples were analyzed for C_1 to C_6 alkanes by gas chromatography with flame ionization detection. Inorganic gases CO_2, O_2, N_2 and CO were also separated by gas chromatography but a thermal conductivity detector was used. Standard gas mixtures were used to quantify the measurements.

Analyses of flue gases for NO_x were conducted at gas-fired sites electrochemically. At oil-fired sites NO_x emissions were sampled and analyzed using U.S. EPA Method 7. Grab samples for NO_x were collected in evacuated flasks containing a dilute sulfuric acid-hydrogen peroxide absorbing solution. Samples were analyzed in the laboratory colorimetrically using the phenoldisulfonic acid procedure.

A Bacharach smoke spot tester was also used in the field.

Testing, reagents, and sample handling were in accord with Level 1 procedures. The recovery of samples and washing of the SASS train and sample containers were all performed in the laboratory. All working surfaces were washed with isopropyl alcohol prior to any contact. All containers and handling equipment were cleaned according to Level 1 specifications. Filters were desiccated 24 hours in clean desiccators prior to any weighings.

Residential Sources--

Field tests were conducted at five gas- and five oil-fired residential sites, using a stove pipe extension to provide a sampling port for the SASS train. In all tests a 3-foot probe with a 5/8-inch nozzle was used. Sampling was conducted at one point approximately in the center of the 8-inch stack. The residential furnaces were operated on a cycle of 50 minutes on and 10 minutes off. Sampling was conducted simultaneously with the furnace operating period. At gas-fired sites, sampling time was about 3 hours (30 m^3 of gas were sampled) while at oil-fired sites the sampling duration was about 10 hours (90 m^3 of gas were sampled). The SASS train cyclones were not used because the level of particulate emissions was very low. The filter was, however, used.

Internal Combustion, Gas and Lignite Utility Sites--

Tests at the internal combustion and gas-fired utility sites were conducted without the SASS train cyclones because of the low concentrations of particulates and their characteristic small particle diameters. The SASS train filter (spectrograde^R glass fiber) was used. Cyclones were used at the lignite-fired utility sites.

Field tests were conducted at 11 internal combustion units. Seven of the units had sampling ports located in the stack. The other four units were tested by use of a 3-foot SASS probe fitted with a vertical nozzle adaptor. The SASS probe was positioned approximately six inches above the stack at a point where the vertical adaptor sampled down into the stack at a traverse point of average stack velocity. Multiple-point traverses were used to obtain blue gas samples at the seven gas and six lignite utility sites.

Smoke spot numbers were determined using a Bachrach Smoke Spot Tester. Visible emissions (percent opacity) were determined by a trained operator.

Water, solid waste and fuel samples were collected according to Level 1 SASS procedures. Limited water analyses were carried out in the field as specified in the procedures manual.

Laboratory Analyses

Inorganic Analyses--

The Level 1 analysis (References 1 and 2) scheme was used for all inorganic analyses. This scheme was designed to identify all elemental species in the SASS train fractions and to provide semiquantitative data on the elemental distributions and total emission factors. The primary tool for the Level 1 analysis scheme is the Spark Source Mass Spectrograph (SSMS). The

SSMS was chosen for Level 1 for its capability of detecting 70 elements simultaneously with sub-ppm sensitivity. The SSMS data are supplemented with atomic absorption spectrometry (AAS) data for Hg, As, and Sb and with standard method determinations for chlorides.

The following SASS train sample types were analyzed for their elemental composition: (1) the particulate filter (PF), (2) the XAD-2 resin (XR), and (3) a composite sample containing portions of the condensate, the HNO_3 module rinse, and the first impinger (CI). In addition, for the oil-fired sources, the fuel was also analyzed. Most of these sample types require some preparation prior to analysis. The XAD-2 resin and the fuel oil samples were prepared for analysis by a Parr oxygen bomb combustion of the materials according to the Level 1 procedures manual. The particulate filter samples were prepared by an aqua regia extraction of the inorganic materials using a soxhlet apparatus according to the EACCS procedures manual. The composite samples require no special preparation prior to analysis.

Organic Analyses--

Level 1 organic analysis is a technique designed to identify organic compounds beyond a total hydrocarbon equivalent analysis. It provides qualitative and quantitative data on volatile and nonvolatile organic compounds (note that gaseous organics are measured in the field) collected in the SASS train. Organics are recovered from all SASS train components. Stainless steel components including the tubing are carefully cleaned with methylene chloride or methylene chloride/methanol solvent to recover organics. Organics in the condensate trap and XAD-2 resin are recovered by methylene chloride extraction.

Because all samples are too dilute to detect organic compounds by the majority of instrumental techniques employed, the first step is to concentrate the samples from as much as 1000 ml to 10 ml in a Kuderna-Danish apparatus. Methylene chloride is evaporated while the organics of interest are retained. Kuderna-Danish concentrates are then evaluated by gas chromatography (GC), infrared spectrometry (IR), liquid chromatography (LC), gravimetric analysis, and sequential gas chromatography/mass spectrometry (GC/MS).

All samples are analyzed by GC/MS for specific polycyclic organic materials (POM); i.e., compounds containing two or more ring structures. The mass peak output data from the MS are evaluated by computer for all polycyclic organic materials for which identification data are available. The detection limit is about 0.9 μg/mℓ of solution injected; in the specific residential tests about 0.3 μg/m^3. Accuracy is within a factor of ±2.

GC analyses conducted in the field for gaseous compounds with boiling points in the C_1-C_6 range ($<100°C$) are supplemented by laboratory analyses for volatile organics (C_8-C_{17}, 90 to 290°C) and nonvolatile organics ($>C_{17}$, $>290°C$). Separate analyses are also conducted for C_8 (110°C to 140°C), C_9 (140°C to 160°C), C_{10} (160 to 180°C), C_{11} (180 to 200°C) and C_{12} (200 to 200°C) organics. Except for the nonvolatiles which are measured gravimetrically after evaporation all analyses are performed with GC using flame ionization detection.

The results of the above analyses are used to determine the next step in the analysis. If the total organics (volatile and nonvolatile) indicate a stack gas concentration below 500 $\mu g/m^3$ then the procedure ends. If the organics are above 500 $\mu g/m^3$ then a class separation by liquid chromatography is conducted. Liquid chromatography is carried out in water-jacketed columns in order to maintain homogeneity in column packing and assure reproducibility. A class separation of the sample placed on the column is accomplished with 6.5 gm of silica gel packing. A gradient elution of various compounds is accomplished by sequential addition of solvents as indicated in Table 16.

After separation into eight fractions by liquid chromatography, volatiles are measured by gas chromatography if the earlier determination indicated a total concentration above 50 $\mu g/m^3$. The nonvolatile portion of each fraction is determined gravimetrically after evaporation.

Infrared spectrometry is used to analyze each LC fraction for functional group in order to further specify the types of compounds in each fraction. Samples are evaporated to dryness on KBr plates and analyzed with a grating spectrophotometer. The use of KBr plates eliminates potential organic interferences. Each spectrograph is standardized against polystyrene film.

The overall accuracy and precision of these analyses are well within a factor of ±2; i.e., if a number is reported as 50 μg, one can be 95 percent confident that the true value is between 25 and 100 μg. Most of these analyses are more accurate than ± factor of 2 with the exception of GC/MS.

SECTION 4

RESULTS

RESIDENTIAL SITES

Gas-Fired Residential Sites

Basic flue gas composition data are shown in Table I for the gas-fired residential sites. Measured particulate loadings were over 10 times lower than the EPA emission factor (Reference 7) and comparable to those reported by TRC (Reference 8). NO_x emissions were lower by a factor of 3 than existing EPA data (Reference 7). This has been timed to the sampling method. Although not reported on Table I, opacity measurements and the smoke spot index were zero for all five units.

Results of SSMS analysis for trace elements in filters and other SASS train components were very low, reflecting the low contaminant levels in natural gas. Trace element results from better catches were at the lower detection limit of the SSMS and were equivalent to those observed in the blanks for most elements.

Analyses for As, Hg, and Sb were performed by AAS. Mercury was found only in the XAD-2 resin at concentrations ranging from 0.03 $\mu g/m^3$ to 4 mg/m^3. Antimony was found at about 4 $\mu g/m^3$ at only one site in the composite of the condensate, module wash, and H_2O_2 impinger. Arsenic was found at the detection limit in all five sites and ranged from <0.16 to <0.56 $\mu g/m^3$.

Emission concentrations of gaseous, volatile, and nonvolatile organic compounds were determined, and the results are presented in Table II. The C_8-C_{12} functions varied from site-to-site and were generally present in larger amounts than in the oil-fired residential sites. Virtually all volatile organic compounds were found in the XAD-2 resin. Nonvolatile compounds were found primarily in the walls of the sorbent trap module rather than in the resin.

No POM compounds were found in the gas-fired residential site samples other than naphthalene, dihydronaphthalene, and methyltetrahydronaphthalene, which are so closely related to the resin itself (copolymer of styrene and divinylbenzene) that these may have been artifacts of the sampling rather than emitted compounds.

Oil-Fired Residential Sites

Basic flue gas composition data are shown in Table III for the oil-fired residential test sites. Measured particulate loadings were similar to those found in the gas-fired residential sites and are roughly half those reported by Battelle and recently adopted by EPA. NO_x emission results were questionable because of analysis difficulties. SO_x data were not necessary.

Results of SSMS analyses for trace elements in filters and other SASS train components were very low. Measured emissions of trace elements were lower in almost all cases than those calculated from fuel analyses. Source severity factors for trace elements were well below levels of concern.

Emission concentrations of gaseous, volatile, and nonvolatile organic compounds were determined. Results are given in Table IV. Compounds in the C1-C3 range (measured in the field) predominated, generally representing more than 60% of the totals. Volatile compounds (C_8-C_{17}) were considerably lower than gaseous and nonvolatile compounds.

Results of GC/MS analyses for POM compounds are presented in Table V, which shows only compounds found above the detection limit of 0.3 $\mu g/m^3$. If no value is given, the compound was not detected.

INDUSTRIAL AND UTILITY INTERNAL COMBUSTION SITES

Table VI presents source characteristics (source type, operating load, and fuel used) and O_2, particulate, SO_x, and smoke number results. NO_x and CO emissions were not measured because the data base for these species was adequate. SO_x emissions data in Table VI were calculated from fuel sulfur content and not measured in the field.

Particulate emissions determined from filter weights correlate well with the Bachrach smoke readings, i.e., higher particulate emissions normally correspond to higher smoke numbers. Particulate emissions from distillate oil engines were much higher than from distillate oil turbines. SO_x emissions were low because of the low sulfur content of the fuels and the large amounts of excess air generally present in the combustion gases from turbines and reciprocating engines.

Table VII presents a summary of results of inorganic analyses. Mercury, arsenic, and antimony emissions were all quite low. These three elements were found primarily in the XAD-2 resin. SSMS analysis found the major elements (0.3 mg/DSCM) present in all sites to be: Al, B, Ba, Ca, Cu, Fe, R, Mg, Na, Ni, P, Pb, S, Si, and Zn. Additionally, Mn was found at significant levels in those sites (111, 306, and 307) using fuel containing an organomanganese additive.

Table VIII presents a summay of analysis results for gaseous (C1-C6), volatile (C7-C16), and nonvolatile (>C17) organic compounds. There was large variation in concentrations of C1-C6 compounds among the oil-fired turbines. The total concentration of compounds in the C7-C16 range varied from 200 to 3000 $\mu g/m^3$ among the samples from the gas and oil fired turbines.

The C7-C16 hydrocarbon content of samples from the diesel oil fired engines ranged from about 10 to 20 $\mu g/m^3$. On average, the diesel burning engines emitted approximately 15 times more C7-C16 compounds than the gas or oil fired turbines.

The nonvolatile organic content of samples from the diesel oil fired sources were about 25 times greater than those from the gas or oil fired turbines. The average total organic content of samples from gas or oil fired turbines was 6 mg/m^3, and the average total organic content of samples from the diesel fired engines was 88 mg/m^3.

No POM compounds were found in samples from the oil and gas fired turbine sites; the detection limit for these samples was 0.08 $\mu g/m^3$. Samples from the diesel oil fired sites contained substantial amounts of hydrocarbon oils which made POM quantitation difficult; however, the results presented in Table IX are considered adequate because the levels of POMs found were several orders of magnitude below levels of concern.

GAS AND LIGNITE - FIRED UTILITY SOURCES

Gas-Fired Utility Sites

Basic flue gas composition data are shown in Table X for the gas-fired utility sites. Measured SO_x and particulate emissions both were well below NSPS requirements. Carbon monoxide results were scattered, and more data may be required.

Because natural gas has minimal inorganic content, inorganic analyses of samples from the gas-fired utility sites were not necessary.

Table XI presents emission concentration of gaseous, volatile and nonvolatile organic compounds from the gas-fired utility sources tested. Measured hydrocarbon emissions were highly variable from all three groups of compounds, and additional data should be acquired. No POM compounds were found at a detection limit of 0.3 $\mu g/m^3$.

Lignite-Fired Utility Sites

Basic flue gas composition data are shown in Table XII for the lignite-fired utility boilers. Sites 314, 315, and 316 had multiclone control units with design efficiencies of 84%, 84%, and 89.5%, respectively, for particulates. Sites 318, 316, and 319 had electrostatic precipitator units with design efficiencies of 98.5%, 99.05%, and 99.82%, respectively, for particulates. Results in Table XII show that particulate emissions varied widely with the control device used and that ESP units controlled particulate emissions effectively. NO_x and SO_x data were acquired but were insufficiently accurate to draw useful conclusions. Adequate data are, however, available.

Inorganic analyses of samples from these sites showed problem emissions for many elements from those units with multiclone central devices. Table XIII shows, by element, numbers of sites with source severity factors in several ranges. A source severity factor in excess of 0.1 indicates a problem emission. Results in Table XIII show that ESP units are considerably more effective at reducing emissions than are multiclone central devices.

Table XIV presents results of organic analyses of samples from the lignite-fired sites. Emissions of gaseous, volatile, and nonvolatile compounds are generally high in comparison to other sites tested but are lower than AP-42 data on lignite-fired sites. Organic material was primarily aliphatic and aromatic. Esters and other oxygenated compounds were not found. Additionally, significant amounts of organic material were found in all fly ash, bottom ash, and water samples from these sites. POM emissions were below levels of interest.

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TABLE I. FLUE GAS COMPOSITION DATA FROM GAS-FIRED RESIDENTIAL SITES

Site No.	O_2 %	CO_2 %	CO PPM	Particulate Emmissions		NO_x Loading	
				$\mu g/m^3$	$lb/10^6 Btu$	$\mu g/m^3$	$lb/10^6$ Btu
100	16.7	6.4	<500	0.46	0.00097	25.3	0.054
101	12.9	1.4	<500	0.40	0.00048	9.4	0.011
102	19.5	3.0	<500	0.49	0.00069	18.8	0.027
103	19.1	1.7	<500	0.64	0.0013	12.5	0.026
104	16.8	1.1	<500	0.62	0.00075	9.3	0.011

TABLE II. GASEOUS, VOLATILE AND NONVOLATILE ORGANIC EMISSIONS FROM GAS-FIRED RESIDENTIAL SYSTEMS, $\mu g/m^3$

Site	Gaseous*						Volatile							Nonvolatile	Total organics†
	C_1	C_2	C_3	C_4	C_5	C_6	C_8	C_9	C_{10}	C_{11}	C_{12}	Total C_8-C_{12}	C_8-C_{17}	$>C_{17}$	C_1-C_6, C_8-C_{17}, $>C_{17}$
100	0*	0	0	0	0	0	<10	<10	1,490	560	60	2,110	-	400	~2,500
101	0	0	0	0	0	0	<10	<10	<10	<10	<10	<10	-	1,240	~1,240
102	0	0	0	0	0	0	-	-	-	-	-	-	-	780	>780
103	39,400	37,800	55,500	0	0	0	<10	<10	770	680	<10	1,450	-	480	~1,900
104	0	0	0	0	0	0	<10	<10	1,960	2,680	370	5,010	-	920	~5,900
Average							<10	<10	1,060	980	110	2,150	-	760	~2,500

*Less than 1000 $\mu g/m^3$, C_1-C_6 gases.

†Not including C_1-C_3.

TABLE III. FLUE GAS COMPOSITION DATA FROM OIL-FIRED RESIDENTIAL SITES

Site No.	O_2 %	CO_2 %	CO %	Particulates mg/m^3	Particulates $lb/10^6$ Btu	Smoke Spot Index
300	17.2	3.8	<0.2	2.3	0.0082	2
301	17.4	3.7	<0.2	1.2	0.0038	1
302	19.6	1.2	<0.2	2.2	0.013	0.5
303	17.3	2.9	<0.2	2.5	0.011	3
304	17.5	2.6	<0.2	1.9	0.013	1.5

TABLE IV. GASEOUS, VOLATILE AND NONVOLATILE ORGANIC EMISSIONS FROM OIL-FIRED RESIDENTIAL SYSTEMS, $\mu g/m^3$

Site	Gaseous						Volatile							Nonvolatile	Total organics
	C_1	C_2	C_3	C_4	C_5	C_6	C_8	C_9	C_{10}	C_{11}	C_{12}	Total C_8-C_{12}	C_8-C_{17}	$>C_{17}$	C_1-C_6, C_8-C_{17}, $>C_{17}$
300	9,600	1,700	< 200	<300	<300	<400	6.3	4.9	46	25	1.3	84	170	650	12,000 to 13,000
301	2,700	1,900	4,400	<300	<300	<400	1.2	3.0	14	6.6	33	58	180	1,800	11,000 to 12,000
302	2,000	400	< 200	<300	<300	<400	7.5	9.0	26	44	45	131	560	290 to 560	3,000 to 4,700
303	1,800	<100	< 200	<300	<300	<400	1.2	15	43	47	65	171	560	1,200 to 1,400	3,600 to 5,100
304	2,800	140	< 200	<300	<300	<400	5.2	7.3	43	49	81	186	320	6,000	9,300 to 10,500
Average	3,800	850	<1,000	<300	<300	<400	4.3	7.8	34	34	45	126	360	2,000 to 2,400	7,800 to 9,100

TABLE V. POLYCYCLIC ORGANIC MATTER RESULTS, OIL-FIRED RESIDENTIAL SYSTEMS, µg/m^{3}*

Compound	Site 301		Site 302		Site 303	Site 304	
	XAD-2 module rinse	XAD-2 resin	XAD-2 module rinse	XAD-2 resin	XAD-2 resin	Condensate	XAD-2 resin
Acenaphthene		9.3					
Acetonaphthone		2.3					0.47
Anthracene					1.5		
Azulene or naphthalene		20					
Benzo(c)cinnoline		1.2					
Biphenyl		23		1.0			
Butyl-phenanthrene							20
Dimethyl naphthalene				6.0	2.5		
Dimethyl phenanthrene				0.4			
Ethyl naphthalene		23					6.5
Fluorenone	4.2[†]	4.7				0.67	
Methyl anthracene		2.4					
Methyl-dibenzo thiophene				0.10			
Methyl naphthalene					7.6		15.4
Methyl phenanthrene				0.2			
Octyl phenanthrene							3.7
Phenanthrene	0.46	4.7	0.08	3.0		1.67	
Phenanthrene quinone	4.2[†]	1.2	0.13				

*Other compounds were below the detection limit of about 0.3 µg/m^{3}.

[†] Fluorenone or phenanthrene quinone.

TABLE VI. PARTICULATE AND SO_x EMISSIONS FROM INTERNAL COMBUSTION SOURCES TESTED

Combustion Source Type	Site No.	Operating Load	O_2 %	Particulate Emissions		SO_x Emissions		Bachrach Smoke No.
				mg/m^3	kg/GJ	ppm	kg/GJ	
Gas Turbine	#110	19.5 MW	18.50	ND	ND	ND	ND	0
Distillate Oil Turbine	#111	18.0 MW	19.40	6.71	0.0214	3.4	0.0285	3.5
	#112	22.5 MW	17.50	2.91	0.0042	7.9	0.0306	3.0
	#306	14.5 MW	14.97	2.46	0.0021	<1.9	<0.0042	3.0
	#307	14.5 MW	13.45	3.85	0.0026	<2.3	<0.0042	4.0
	#308	20.2 MW	16.48	4.37	0.0049	<1.4	<0.0042	5.0
Distillate Oil Reciprocating Engine	#309	2.5 MW	11.11	21.02	0.0110	60	0.0831	6.5
	#310	2.5 MW	13.70	29.41	0.0208	81	0.1531	7.0
	#311	2.5 MW	15.82	33.15	0.0330	58	0.1531	6.5
	#312	2.5 MW	11.30	12.44	0.0066	43	0.0612	ND
	#313	2.5 MW	12.88	15.71	0.0100	44	0.0743	6.0

TABLE VII. SUMMARY OF RESULTS FROM SPECIFIC INORGANIC ANALYSES

Combustion Source Type	Site No.	Mass Emissions (mg/DSCM)						
		Hg	As	Sb	SO_4*	Cl	F	NO_3*
Gas Turbine	110	0.0091	<0.0014	<0.0016	-	0.89	-	-
Distillate Oil Turbine	111	0.00018	<0.0056	<0.0046	-	4.9	0.010	0.029
	112	0.0014	<0.0033	0.013	0.23	2.5	0.049	0.018
	306	<0.00074	<0.00009	0.0017	0.035	-	-	-
	307	0.0016	<0.00011	0.0019	0.018	-	-	-
	308	<0.00033	<0.00019	<0.00016	0.068	-	-	-
Distillate Oil Reciprocating Engine	309	0.00016	<0.00012	<0.00020	0.74	-	-	-
	310	0.00077	<0.00017	<0.0019	0.74	-	-	-
	311	<0.00091	<0.00020	<0.00024	0.98	-	-	-
	312	<0.00003	<0.00011	<0.00030	0.50	-	-	-
	313	<0.0011	<0.00011	<0.00019	0.74	-	-	-

*Values are from particulate samples only.

TABLE VIII. VOLATILE AND NONVOLATILE ORGANIC EMISSIONS FROM INTERNAL COMBUSTION SYSTEMS

							Combination Source Type							
	Gas Turbine		Distillate Oil Turbine					Distillate Oil Reciprocating Engines						
Site	110	111	112	306	307	308	309	309-2	310	311	312	312-2	313	313-2
Volatile Organic Gases Analyzed in Field, µg/m^3														
C_1	BL*	BL	BL	BL	BL	BL	1000	500	1570	2570	3285	800	4000	1100
C_2	BL	BL	BL	67620	15130	2275	7765	700	10380	5970	17540	1900	26015	1700
C_3	BL	BL	BL	BL	BL	BL	3535	700	3065	1140	705	BL	745	BL
C_4	BL	BL	BL	BL	BL	BL	BL	BL	BL	BL	BL	BL	BL	BL
C_5	BL	BL	BL	BL	BL	BL	BL	BL	BL	BL	BL	BL	BL	BL
C_6	BL	BL	BL	BL	BL	BL	BL	BL	BL	BL	BL	BL	BL	BL
Volatile Organic Materials Analyzed in Laboratory by GC-TCO Procedure: µg/m^3														
C_7 (B.P. 90-110°C)	483	32	29	100	82	BL	24	10	214	98	585	90	87	BL
C_8 (B.P. 110-140°C)	1202	100	147	52	27	BL	251	370	328	497	251	400	154	560
C_9 (B.P. 140-160°C)	444	137	200	7	5	BL	685	850	633	683	565	1100	301	1290
C_{10} (B.P. 160-180°C)	727	927	613	17	14	99	1488	2410	1516	1228	1704	1800	1034	2120
C_{11} (B.P. 180-200°C)	23	BL	21	89	12	BL	1945	2890	2292	1265	2159	2120	682	2580
C_{12} (B.P. 200-220°C)	BL	84	152	6	15	25	2916	3230	2512	1438	2663	2450	1267	3120
C_{13} (C.P. 220-240°C)	29	BL	56	28	BL	12	4919	3000	3827	2899	3970	2330	1742	2810
C_{14} (B.P. 240-260°C)	BL	BL	BL	210	BL	11	3632	3580	3810	1933	2413	2200	1509	3100
C_{15} (B.P. 260-280°C)	BL	BL	46	484	1	38	3103	2760	4192	1810	2389	2250	1771	3010
C_{16} (B.P. 280-300°C)	BL	BL	457	783	8	71	2606	2290	3746	1941	2149	1680	937	2350
Nonvolatile Organic Matter >C16 From Laboratory Gravimetric Analysis, µg/m^3:	310	6800	3710	440	1400	1270	56180	55380	53880	43040	63590	55040	46680	66340
Total Organics, mg/m^3	3.22	8.08	5.43	69.8	16.7	3.80	89.0	76.8	92.0	66.5	104	71.5	86.9	87.3

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*BL Concentration of the species is below the limit of detection of the instrument; 1 ppm (=1000 µg/m^3) per C_1-C_6 and 0.001 ppm (=0.5 µg/m^3) per C_7-C_{16}.

TABLE IX. POM EMISSIONS FROM DIESEL ENGINE SITES, $\mu g/m^3$

	309		310		311		312		313	
	Possible Range†	Best Est.	Possible Range†	Best Est.	Possible Range†	Best Est.	Possible Range†	Best Est.	Possible Range†	Best Est.
Naphthalene	32-15	16	22-16	18	61-33	36	-	-	5-1	3
Methyl Naphthalenes	-	-	26-20	22	-	-	-	-	-	-
Dimethyl Naphthalenes	60-28	30	14-11	12	110-58	64	-	-	-	-
Biphenyl	5-2	2	7-6	6	17-9	10	-	-	26-7	15
C_3 Substituted Naphthalene	16-7	8	5-4	4	-	-	-	-	-	-
Dibenzothiophene	10-5	5	2-1	2	-	-	-	-	-	-
Methyl Dibenzothiophene	-	-	1-0.7	0.8	-	-	-	-	-	-
Phenanthrene	16-7	8	3-2	3	-	-	-	-	-	-
Methyl Phenanthrenes	40-19	20	10-7	8	102-55	60	120-70	77	270-70	150
Dimethyl Phenanthrenes	8-4	4	1-0.7	0.8	41-22	24	72-42	46	110-28	58
Trimethyl Phenanthrenes	-	-	3-2	2	-	-	18-11	12	27-7	15
Detection Limit of 0.2 μg	0.2-0.07	0.08	0.1-0.07	0.08	0.1-0.07	0.08	0.1-0.07	0.08	0.3-0.07	0.1

*POM's were only found in the XAD-2/XAD-2 module rinse sample.

†This range is given because of analysis problems (see text).

TABLE X. FLUE GAS COMPOSITION DATA FROM GAS-FIRED UTILITY SITES

Combustion Source Type	Site No.	O_2 %	SO_2 Emissions ppm	CO Emissions ppm	Particulate Emissions $\mu g/m^3$
Non-Tangential	106	5.85	<1	<500	4,420
	108	9.08	<1	<500	<32
	116	7.88	<1	42	531
	117	6.47	<1	31	<3.9
Tangential	113	4.81	<1	<10	306
	114	4.62	<1	311	168
	115	8.64	<1	481	41

TABLE XI. EMISSIONS OF GASEOUS, VOLATILE, AND NONVOLATILE ORGANIC COMPOUNDS FROM GAS-FIRED UTILITY BOILERS

Combustion Source Type	Site No.	Organic Emissions $\mu g/m^3$			Total Organic Emissions $\mu g/m^3$
		$C_1 - C_6$	$C_7 - C_{16}$	$>C_{16}$	
Non-Tangential	106	34,360-45,200	33,100	No Data	>67,460
	108	No Data	8,600	7,400	No Data
	116	21,500-30,680	2,034	679	24,200-33,390
	117	<9,460	409	383	790-10,260
Tangential	113	<6,380	42	1,846	1,888-8,266
	114	<12,760	38	902	940-13,700
	115	<12,760	474	2,246	2,720-15,480

TABLE XII. FLUE GAS COMPOSITION DATA FROM LIGNITE-FIRED UTILITY SOURCES

Source Type	Site No.	O_2 %	CO Emissions, % m	Particulate Emissions <1 μm	1 - 3 μm	>10 μm	Total mg/m^3	Control Device, Efficiency, %
Pulverized Dry Bottom (Front Fired)	314	4.94	< 500	2.1%	6.6%	56.5%	8480	Multiclone, 84%
	315	4.70	< 500	1.1%	8.6%	50.9%	4625	Multiclone, 84%
	318	11.9	< 500	-	-	-	2.83	ESP, 98.5
Cyclone	316	7.0	< 500	-	-	-	1.14	ESP, 99.53 (Tested)
Spreader Stoker	317	10.9	< 500	22.3%	4.9%	59.2%	1630	Multiclone, 89.5%
	319	*	*	-	-	-	1.2	ESP, 99.82%

*No data were acquired

TABLE XIII. SOURCE SEVERITY FACTORS FOR INORGANIC ELEMENT EMISSIONS FROM LIGNITE FIRED SOURCES*

			Source Severity Factor Range					
Element	> 2.0		2.0 - 0.5		0.5 - 0.05		Total Sites	
Al			2	(2)	1	(1)	3	(3)
As					2	(2)	2	(2)
B					2	(2)	2	(2)
Ba	2	(2)			3	(1)	5	(3)
Be			3	(2)	2	(1)	5	(3)
Ca	2	(2)	1	(1)	1		4	(3)
Cd					1	(1)	1	(1)
Cl					2	(1)	2	(1)
Co					2	(2)	2	(2)
Cr					2	(2)	2	(2)
Cu			2	(2)	2		4	(2)
F					4	(2)	4	(2)
Fe	2	(2)			1	(1)	3	(3)
Hg					1	(1)	1	(1)
K			1	(1)	1	(1)	2	(2)
Li			2	(2)			2	(2)
Mg	2	(2)			1	(1)	3	(3)
Mn					2	(2)	2	(2)
Na	2	(1)	1	(1)	1	(1)	4	(3)
Ni	1	(1)	3	(1)	1	(1)	5	(3)
P	2	(2)	1	(1)	2		5	(3)
Pb			2	(2)			2	(2)
Si			2	(2)	1	(1)	3	(3)
Sr			2	(2)	1	(1)	3	(3)
Ti					2	(2)	2	(2)
V					2	(2)	2	(2)
Zn					1	(1)	1	(1)

*( ) indicates number of sites with multiclone emission control devices

TABLE XIV. EMISSIONS OF GASEOUS, VOLATILE, AND NONVOLATILE ORGANIC COMPOUNDS FROM LIGNITE-FIRED SITES

		Organic Emissions			Total
Combustion Source Type	Site No.	$C_1 - C_6$ µg/m^3	$C_7 - C_{16}$ µg/m^3	C_{16} µg/m^3	µg/m^3
Pulverized Dry Bottom (Front Fired)	314	39,020- 44,520	434	9,800	49,300- 54,800
	315	5,340- 17,430	936	6,930	13,200- 25,300
	318	4,000- 13,000	558	64	4,600- 13,600
Cyclone	316	10,680- 22,770	382	2,410	13,500- 25,600
Spreader Stoker	317	1,780- 13,870	643	1,745	4,200- 16,300
	319	No Data	26.9	332	No Data

ENVIRONMENTAL ASSESSMENT OF COAL AND OIL FIRING IN A CONTROLLED INDUSTRIAL BOILER

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SECTION 1

INTRODUCTION

The industrial nations of the world are being forced to simultaneously deal with two very difficult and contradictory problems. The relatively cheap and convenient sources of energy are rapidly being depleted while the need for increasingly stringent control of pollution is making the environmentally acceptable use of the energy sources that are available more difficult. One response to these dual needs has been to use the more abundant high polluting fuels in combustion systems that have sophisticated pollution controls. The technologies that are used to control pollution are new relative to combustion technology. Therefore, the subtle short- and long-term effects of these new technologies are not yet completely known.

The objective of this program is to conduct a comparative, multimedia environmental assessment of oil versus coal firing in controlled industrial and utility boilers and to draw conclusions about the comparative environmental, energy, and societal impacts of firing oil versus firing coal.

This report presents the comparative assessment of controlled industrial boilers. The major technical input for this assessment was feed stream and emissions characterization data collected as part of the Conventional Combustion Emission Assessment Program. These data were derived from rigorous sampling and analysis and specify the types and quantities of solid, liquid, and gaseous pollutants in each of the inlet and outlet streams of a controlled oil- and coal-fired industrial boiler. A comprehensive assessment of each fuel type in the controlled industrial boiler was accomplished to determine:

- The types and amounts of pollutants that are released during coal and oil combustion in an uncontrolled boiler;
- The types and amounts of pollutants that are released during the combustion of each fuel in a controlled boiler;

- The effectiveness of the controls with respect to each controlled pollutant;
- If the control devices modify pollutants that pass through the controls;
- If the controls themselves create pollutants.

The comprehensive assessment results for the oil- and coal-fired industrial boiler were then used in a comparative assessment to determine the differences in the types and quantities of pollutants released.

The results of the industrial comparative emission assessments were then evaluated to determine what conclusions could be drawn about the oil versus coal firing. The comparative impacts identified were summarized by environmental, energy, economic, and societal categories.

It should be kept in mind that the conclusions presented are based on tests conducted on only one industrial boiler, one type of coal, and one type of oil. It should not be assumed that these conclusions apply to all industrial boilers under all circumstances. The results of this program should, perhaps, best be thought of as a good indication of the impact differences between coal and oil firing and as a set of guidelines on which future work can be based.

SECTION 2

CONCLUSIONS

Uncontrolled emissions of criteria pollutants produced by this boiler during coal firing correspond well with emission factors from AP-42. This observation does not generally hold true for oil-fired emissions. Full load NO_x emissions from oil firing were 19% lower than the AP-42 emission factor, although they appear to be within the normal range for similar industrial units. CO emissions from oil firing were nearly 63% lower than the AP-42 emission factor. Oil-fired SO_2 and total hydrocarbons correspond well with their respective AP-42 emission factors. Particulate emissions from oil firing, in the absence of coal ash contamination, are approximately twice the value tabulated in AP-42.

NO_x emissions increased with increasing load for both coal and oil firing, as expected. Available data indicate that for boiler loads between 90 and 100%, NO_x emissions from coal firing are approximately three times greater than from oil firing.

Uncontrolled SO_2 emission rates during coal and oil firing were 1112 ng/J (2.59 lb/MM Btu) and 993 ng/J (2.31 lb/MM Btu), respectively. Removal data indicate an average scrubber removal efficiency of 97% during both coal and oil firing. Controlled SO_2 emissions for coal and oil firing were 36.3 ng/J (0.08 lb/MM Btu) and 26.8 ng/J (0.06 lb/MM Btu), respectively, which are lower than either existing or proposed NSPS limitations.

Particulate loadings prior to scrubbing were 2951 ng/J (6.86 lb/MM Btu) during coal firing and 59.0 ng/J (0.14 lb/MM Btu) during oil firing, in the absence of coal ash contamination. Scrubbing removed 99% of the coal-fired particulates and 75% of the oil-fired particulates. The lower removal efficiency obtained during oil firing is attributed to the increased fraction of particles smaller than 3 μm; at least 21% of the uncontrolled oil-fired particulates are less than 3 μm in diameter while substantially less than 1% of uncontrolled coal-fired particulates are under 3 μm.

There appeared to be a net increase in emission rates across the scrubber for coal fired particulates less than 3 μm in size. This net increase can be attributed to the poor removal efficiency of the scrubber for fine particulates, and to the sodium bisulfate ($NaHSO_4$) and calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2\ H_2O$) particulates generated by the scrubber. Both $NaHSO_4$ and $CaSO_3 \cdot 1/2\ H_2O$ have been identified at the scrubber outlet but not at the inlet. Although a very slight increase in oil-fired particulates in the 1-3 μm range was observed, a net decrease in particulates less than 3 μm was observed during oil firing. Based on the results of coal firing tests, it appears reasonable that scrubber generated particulates were present in the scrubber outlet stream during oil firing but that the high fine particulate loading associated with oil firing masked detection of these materials.

Of the 22 major trace elements analyzed in the flue gas stream during coal firing, 18 exceed their MATE values at the scrubber inlet and four at the scrubber outlet. Similarly, for oil firing, 11 exceeded their MATE values at the scrubber inlet while five exceeded their MATE values at the scrubber outlet. Elements exceeding their MATE values at the scrubber outlet and which are common to both fuels are arsenic, chromium and nickel. Additionally, iron exceeded its MATE value at the scrubber outlet during coal firing as did cadmium and vanadium during oil firing. The overall removal of trace elements across the scrubber is 99% for coal firing and 87% for oil firing.

The fraction of fuel sulfur converted to SO_3 during oil firing was 50 to 75% higher than during coal firing. In contrast, the fraction of fuel sulfur converted to sulfates during coal firing was twice that during oil firing.

Sulfates are more efficiently removed than SO_3 (60% removal for oil firing and 88% for coal firing). This indicates that $SO_4^=$ is probably associated with the larger particulates, which are more efficiently removed than smaller particulates. The higher sulfate removal from the coal flue gases is explained by the higher particulate loading during coal firing.

Polycyclic organic material (POM) was not found in the scrubber inlet or outlet at detection limits of 0.3 ug/m^3 for either coal or oil firing.

MATE values for most POM's are greater than this detection limit. However, since the MATE values for at least two POM compounds - benzo(a)pyrene and dibenz(a,h)anthracene - are less than 0.3 $\mu g/m^3$, additional GC/MS analyses at higher sensitivity would be required to conclusively preclude the presence of all POM's at MATE levels.

Organic emissions for coal and oil firing were very similar. Total organic emissions were less than 9 ng/J (0.02 lb/MM Btu) for both tests, and these emissions appear to be primarily C_1 to C_6 hydrocarbons and organics heavier than C_{16}. While uncontrolled emission rates for both coal and oil firing are low, emissions of these organics were further reduced by about 75 to 85% in the scrubber unit.

The combined waste water stream from the boiler operation may not pose an environmental hazard in terms of organic materials since the discharge concentrations of organics are well below their MATE values for both coal and oil firing. The same conclusion may be drawn for inorganic compounds with the exception of cobalt, nickel, copper and cadmium for coal firing and nickel and copper for oil firing since these metals may exceed their MATE values.

The scrubber cake produced when either fuel is burned contains concentrations of trace elements high enough to exceed most MATE values. Because of these high concentrations the scrubber cake must be disposed of in specially designed landfills.

The difference in environmental insult expected to result between coal and oil combustion emissions from a single controlled 10 MW industrial boiler is insignificant. This is because: 1) there are only slight differences in the emissions levels of the pollutants, or 2) the absolute impact of either fuel use is insignificant. The environmental impacts of emissions from a cluster of controlled 10 MW industrial boilers are potentially significant. The impacts include health effects, material damages, and ecological effects from high levels of SO_2, NO_x and suspended particulate matter; health effects and ecological damage due to trace metal accumulation in soils and plants; and aesthetic degradation from visibility reduction and waste disposal sites.

The environmental acceptability of a cluster of controlled industrial boilers is more dependent on site specific factors (e.g., background pollution levels, location and number of other sources) than type of fuel utilized. Careful control of the site specific factors can avert potential environmental damages and generally compensate for any differential effects arising between the use of coal or oil.

Coal firing appears to produce a greater enrichment of trace elements in the flue gas desulfurization cake than oil firing produces. However, the scrubber cake resulting from either coal or oil firing contains sufficient amounts of heavy metals and toxic substances that it must be disposed of in specially designed landfills.

Based on the Lundy/Grahn Model for health effects associated with suspended sulfate levels, regional emissions levels from controlled oil or coal-fired industrial boilers would not be expected to cause a significant impact on regional health. Emissions from uncontrolled boilers would result in substantially greater levels of regional suspended sulfate levels, and the associated health effects would be an order of magnitude greater.

The health impact of solid waste generation on health is essentially the same for controlled coal firing and oil firing, provided suitable land disposal techniques are employed to assure minimal leaching rates and migration of trace elements to groundwater and the terrestrial environment.

The potential for crop damage from either controlled coal firing or oil firing depends greatly on ambient levels of NO_x, SO_2, or trace element soil concentrations. If such levels are presently high, localized plant damage would be expected to occur within a 1 to 2 km range from a controlled boiler cluster. Leaf destruction from SO_2 exposure would be expected to be slightly more severe in the vicinity of a cluster of controlled boilers which are coal fired as opposed to oil fired. For boilers uncontrolled for NO_x emissions, plant damage would be expected to be significantly greater in the vicinity of the coal-fired cluster, owing to higher levels of ambient NO_x produced. The likelihood of damage occurring in plants due to emissions of trace elements from either controlled oil or coal firing is remote, with the possible exception of injury due to elevated levels of molybdenum and cadmium in plant tissue resulting from coal firing and oil firing, respectively.

The impact of boiler emissions on corrosion in the local area near a cluster of controlled industrial boilers would be significant. The corrosion rate would be slightly greater when the boilers are coal-fired. However, the extent of this overall impact (oil or coal) is minor compared to that which occurs when industrial boilers are uncontrolled.

The differential direct economic impact between emissions from coal firing and oil firing is generally insignfiicant with the possible exception of some differences occurring in a limited localized area near clusters of boilers. The extent of the incremental direct economic impacts is proportional to the extent of the incremental environmental damages.

Differential second order economic impacts, such as changes in hospital employment, alteration of taxes, or changes in income, are expected to be insignificant between emissions from controlled oil and coal-fired industrial boilers.

At the present time, the comparative assessment of the effects of emissions from controlled oil and coal-fired industrial boilers tends to support the national energy plan for intensified utilization of coal. The fuel choice of oil or coal is a relatively minor issue concerning the environmental acceptability of controlled industrial boilers; other site specific and plant design factors exert a greater effect on environmental damages. While it was shown that fuel choice caused significant differences in impacts to occur when the boiler is uncontrolled for NO_x emissions, these differences may be mitigated by the addition of NO_x control technologies with minimal overall cost impact.

SECTION 3

TEST AND ANALYSIS

The test unit used for this assessment is a dual fuel industrial process steam boiler operated by the Firestone Tire and Rubber Company in Pottstown, Pennsylvania. The 10 megawatt equivalent boiler is equipped with a pilot FMC, Inc. flue gas desulfurization (FGD) unit that is designed to treat approximately one-third of the flue gas produced by the boiler when it is operating at full load (3 megawatt equivalent). The boiler was originally designed to burn coal but was later modified to burn either high volatile eastern bituminous coal or Number 6 fuel oil. Table 1 presents a list of the major boiler parameters. The boiler has no NO_x controls.

The boiler and associated equipment produce four liquid waste streams: boiler feed water pretreatment waste, steam drum blowdown, mud drum blowdown and cooling water. All liquid waste streams except the cooling water are mixed with process waste water from elsewhere in the plant. This combined stream is then pumped directly into the municipal sewerage system. The boiler cooling water is pumped directly into the municipal sewerage system without mixing with other plant waste streams.

The pilot FGD unit is a double alkali scrubber that produces only a solid cake as a waste product. The scrubber does not produce a liquid waste stream. It is designed as a sulfur dioxide (SO_2) and particulate control device, and will operate on either fuel without modification.

Sampling and analysis of gaseous, liquid, and solid pollutants were conducted according to the EPA Level 1/Level 2 criteria, except that both Level 1 and Level 2 sampling were conducted simultaneously because of program time constraints. Level 1/Level 2 analysis procedures were followed except Level 2 analysis was conducted prior to receiving the results of Level 1 analysis in those cases where sample degradation was anticipated. Figure 1 shows the sampling locations.

SECTION 4

COMPREHENSIVE ASSESSMENTS

Table 2 summarizes the annual emissions resulting from coal and oil firing. The table presents estimates of air emissions both before and after the scrubber. Liquid effluent and solid waste rates are presented for both the controlled and uncontrolled cases.

Outlet emissions were determined on the basis of 100 percent of the flue gas being treated by the scrubber. It was assumed that additional scrubber modules, identical to the existing one, could be added such that all of the flue gas was processed in exactly the same manner as the fraction that actually passed through the scrubber. In this way, emissions from the pilot scrubber were scaled up to represent the total flue gas flow. All emissions data and conclusions are based on this assumption.

COMPREHENSIVE ASSESSMENT OF COAL FIRING

Criteria Pollutants

Uncontrolled emissions of criteria pollutants generally corresponded well with values reported in AP-42. Although NO_x emissions were slightly higher than the average AP-42 value, they appear to be within the normal range for similar industrial units.

NO_x reductions varying from approximately 0 to 24 percent were measured across the scrubber. However, the magnitude of NO_x reductions could not be correlated to changes in variables monitored during the test period (i.e., temperature, gas flow rate, liquid/gas ratio, boiler load, etc.). For this reason, it is believed that observed NO_x reductions are a sampling phenomenon, perhaps related to leaks in the sample train.

Sulfur dioxide removal data indicated an average scrubber efficiency of 97 percent. Controlled SO_2 emissions were 36.3 ng/J (0.08 pounds/MM Btu) which is less than either existing or proposed NSPS limitations for utility boilers.

Mass balance data indicate that the multiclone unit upstream of the scrubber was removing little or no fly ash during the test period. The scrubber was found to remove 99.4 percent of the inlet particulate.

Inorganics

Although the removal efficiency for total particulates is high, there appears to be a net increase in emission rates across the scrubber for particulates less than 3 μm in size. This net increase can be attributed to the poor removal efficiency of the scrubber for fine particulates, and to the sodium bisulfate ($NaHSO_4$) and calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2\ H_2O$) particulates generated by the scrubber. Both $NaHSO_4$ and $CaSO_3 \cdot 1/2\ H_2O$ have been identified at the scrubber outlet but not at the inlet.

The relatively poor removal efficiency (approximately 30%) for SO_3 across the scrubber is an indication that SO_3 is either present at very fine aerosols in the scrubber inlet, or is converted to very fine aerosols as the flue gas stream is rapidly cooled inside the scrubber.

Analysis has shown that while there may be higher surface concentrations of sulfur-containing compounds in the particulates emitted from the scrubber, most of the sulfur-containing compounds are probably present as solid sulfates and sulfites. Thus, it is conceivable that sulfuric acid vapor is condensed and deposited on the particulates emitted, whereas sodium bisulfate and calcium sulfite hemihydrate are emitted as fine, solid particulates.

The overall sulfur balance indicates that over 92 percent of the fuel sulfur is emitted as SO_2, less than 1 percent of the fuel sulfur is emitted as SO_3, and approximately 3 percent of the fuel sulfur is emitted as $SO_4^{=}$.

The overall removal efficiency for trace elements across the scrubber is 99.5 percent. Of the 22 major trace elements, 18 exceed their MATE values at the scrubber inlet and four at the scrubber outlet. The four trace elements in the scrubber flue gas that pose a potential hazard are arsenic, chromium, iron, and nickel. In addition, the emission concentration of beryllium at the scrubber outlet is equal to its MATE value. The relative removal efficiency for trace elements across the scrubber can be explained by enrichment theory. In general, trace elements that occur as element vapors or form volatile compounds at furnace temperatures are more concentrated in the smaller particulates, as a result of subsequent condensation and surface adsorption. These are the same trace elements that are removed less efficiently by the scrubber.

Mass balance closure for most of the trace elements have been found to be in the 75 to 107 percent range. This closure instills confidence on the validity of the sampling and analysis data for trace elements.

Organics

Total organic emissions were generally less than 9 ng/J (0.02 pound/MM Btu) and these emissions appear to be primarily C_1 to C_6 hydrocarbons and hydrocarbons heavier than C_{16}. While uncontrolled emission rates for C_7 to C_{16} and higher hydrocarbons are low, emissions of these organics were further reduced by 21 to 35 percent in the scrubber unit.

Polycyclic organic material (POM) was not found in the scrubber inlet or outlet at detection limits of 0.3 $\mu g/m^3$. MATE values for most POM's are greater than this detection limit. However, since the MATE values for at least two POM compounds - benzo(a)pyrene and dibenz(a,h)anthracene - are less than 0.3 $\mu g/m^3$, additional GC/MS analyses at higher sensitivity would be required to conclusively preclude the presence of all POM's at MATE levels.

Liquid Effluents

The combined wastewater stream generated from the boiler operation may not pose an environmental hazard, since the discharge concentrations of most inorganics and organics are all well below their MATE values. However, based on the uncertainty in SSMS analyses, cobalt, cadmium, nickel and copper may exceed their MATE values based on ecological considerations.

Solid Waste

The scrubber cake produced contains a significant amount of coal fly ash. With the exception of boron, trace element concentrations in the scrubber cake far exceeded their MATE values. Because the trace elements may leach from the disposed scrubber cake, these solid wastes must be disposed of in specially designed landfills.

COMPREHENSIVE ASSESSMENT OF OIL FIRING

Criteria Pollutants

Uncontrolled emissions of criteria pollutants do not generally correspond with emission factors from AP-42. NO_x emissions were nearly 23 percent lower than the AP-42 emission factor, although they appear to be within the normal range for similar industrial units. CO emissions were nearly 63 percent lower than the AP-42 emission factor. SO_2 and total hydrocarbons corresponded well with their respective AP-42 emission factors. Particulate emissions, in the absence of coal ash contamination, are approximately twice the value tabulated in AP-42.

Sulfur dioxide removal data indicated an average scrubber efficiency of 97 percent. Controlled SO_2 emissions were 26.8 ng/J (0.06 lb/MM Btu) which is less than either existing or proposed NSPS limitations for utility boilers.

Inorganics

Particulate removal data indicate that, on the average, scrubber efficiency was 84 percent during the test period. However, based on particulate catches essentially free of coal ash contamination, the scrubber efficiency was approximately 75 percent for oil firing particulates.

When emissions are uncontrolled, over 90 percent of the sulfur in the fuel feed is emitted as SO_2, less than 1 percent as SO_3, and 1.5 percent as $SO_4^=$.

SO_2 is efficiently removed by the scrubber (97 to 98 percent efficiency). The SO_3 removal efficiency (28 to 29 percent) suggests that SO_3 is associated with fine particulates or aerosols. $SO_4^=$ is about 60 percent removed by the scrubber, and so is probably associated with the larger particulates.

Of the 22 major trace elements analyzed in the flue gas stream, 11 exceeded their MATE values at the scrubber inlet while only 5 exceeded MATE values at the scrubber outlet. These 5 elements are arsenic, cadmium, chromium, nickel and vanadium. With the exception of chromium, elements exceeding their MATE values at the scrubber outlet were removed from the flue gas stream with efficiencies lower than the overall average removal efficiency of

87 percent.

Beryllium emissions were 0.001 mg/m^3 after scrubbing; this corresponds to ahlf the MATE value for this element. At this emission concentration, the National Standard for Hazardous Air Pollutants limitation of 10 grams beryllium per day would only be exceeded by boilers of 100 MW capacity or greater.

Mass balance closure for 10 of the 20 trace elements analyzed is between 50 and 136 percent. Poorer mass balance closure was obtained for the remainder of the trace elements due to the extremely low concentrations and/or contamination of the scrubber recycle solution by coal firing components.

Organics

Organic emissions determined by FID analysis were generally less than 5 ng/J (0.01 lb/MM Btu) and appear to be composed primarily of C_1 to C_6 hydrocarbons and organics heavier than C_{16}. However, gas chromatograph and gravimetric data indicate that FID values may be low by a factor of 2 to 3. Approximately 88 and 83 percent of the C_7 to C_{16} and higher than C_{16} organics, respectively, were removed by the scrubber

The organic compounds identified in the gas samples were generally not representative of combustion-generated organic materials, but were compounds associated with materials used in the sampling equipment and in various analytical procedures. This again confirms the low level of organic emissions.

Polycyclic organic material (POM) was not found in the scrubber inlet or outlet streams at detection limits of 0.3 μg/m^3. MATE values for most POM's are greater than this detection limit. However, since the MATE values for at least two POM compounds - benzo(a)pyrene and dibenz(a,h)anthracene - are less than 0.3 μg/m^3, additional GC/MS analysis at higher sensitivity would be required to conclusively preclude the presence of all POM's at MATE levels.

Liquid Effluents

The combined wastewater stream from the boiler operation may not pose an environmental hazard in terms of organic materials since the discharge concentrations of organics are all well below their MATE values. A similar conclusion may be drawn with respect to inorganic materials since inorganics, with the exception of nickel and copper, did not exceed their MATE values for liquid streams. Owing to uncertainty associated with SSMS analysis, nickel and copper may exceed their MATE values although this is not necessarily the case.

Solid Waste

With the exceptions of antimony, boron, molybdenum and zinc, trace element concentrations in the scrubber cake exceed their MATE values. Because the trace elements may leach from the disposed scrubber cake, these solid wastes must be disposed of in specially designed landfills.

SECTION 5

COMPARATIVE ASSESSMENTS

The comprehensive assessments were used to develop a comparative emissions and environmental assessment.

COMPARATIVE EMISSIONS ASSESSMENT

Criteria Pollutants

Uncontrolled emissions of criteria pollutants produced during coal firing correspond well with emission factors from AP-42. This observation does not generally hold true for oil fired emissions. Full load NO_x emissions from oil firing were 19 percent lower than the AP-42 emission factor, although they appear to be within the normal range for similar industrial units. CO emissions from oil firing were nearly 63 percent lower than the AP-42 emission factor. Oil-fired SO_2 and total hydrocarbons correspond well with their respective AP-42 emission factors. Particulate emissions from oil firing, in the absence of coal ash contamination, are approximately twice the value tabulated in AP-42.

NO_x emissions increased with increasing load for both coal and oil firing, as expected. Available data indicate that for boiler loadings between 90 and 100 percent, NO_x emissions from coal firing are approximately three times greater than from oil firing.

Observed reductions of NO_x emissions for coal firing and early oil firing tests appear to be due, at least in part, to air leakage into the scrubber outlet sampling line. Data from later oil firing tests, not known to be subject to leakage problems, indicate that NO_x removal across the scrubber is on the order of 2 percent.

Uncontrolled CO emissions from coal firing were 15.9 ng/J (0.04 lb/MM Btu) while those from oil firing were 5.47 ng/J (0.01 lb/MM Btu). This factor of three difference is at variance with AP-42 data indicating that CO emissions from oil firing are 23 percent lower than those from coal firing. Apparent reductions in CO emissions across the scrubber are not considered significant due to air leakage in the sampling train and the low sensitivity of analysis at the measured CO concentrations.

Uncontrolled SO_2 emission rates during coal and oil firing were 1112 ng/J (2.59 lb/MM Btu) and 993 ng/J (2.31 lb/MM Btu), respectively. Removal data indicate an average scrubber removal efficiency of 97 percent during both coal and oil firing. Controlled SO_2 emissions for coal and oil firing were 36.3 ng/J (0.08 lb/MM Btu) and 26.8 ng/J (0.06 lb/MM Btu), respectively, which are lower than either existing or proposed NSPS limitations.

Particulate loadings prior to scrubbing were 2951 ng/J (6.86 lb/MM Btu) during coal firing and 59.0 ng/J (0.14 lb/MM Btu) during oil firing, in the absence of coal ash contamination. Scrubbing removed 99 percent of the coal-fired particulates and 75 percent of the oil-fired particulates. The lower removal efficiency obtained during oil firing is attributed to the increased fraction of particles smaller than 3 μm; at least 21 percent of the uncontrolled oil-fired particulates are less than 3 μm in diameter while substantially less than 1 percent of uncontrolled coal-fired particulates are under 3 μm.

There appeared to be a net increase in emission rates across the scrubber for coal-fired particulates less than 3 μm in size. This net increase can be attributed to the poor removal efficiency of the scrubber for fine particulates, and to the sodium bisulfate ($NaHSO_4$) and calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2\ H_2O$) particulates generated by the scrubber. Both $NaHSO_4$ and $CaSO_3 \cdot 1/2\ H_2O$ have been identified at the scrubber outlet but not at the inlet. Although a very slight increase in oil-fired particulates in the 1-3 μm range was observed, a net decrease in particulates less than 3 μm was observed during oil firing. Based on the results of coal firing tests, it appears reasonable that scrubber generated particulates were present in the scrubber outlet stream during oil firing but that the high fine particulate loading associated with oil firing masked detection of these materials.

Inorganics

Of the 22 major trace elements analyzed in the flue gas stream during coal firing, 18 exceed their MATE values at the scrubber inlet and four at the scrubber outlet. Similarly, for oil firing, 11 exceeded their MATE values at the scrubber inlet while five exceeded their MATE values at the scrubber outlet. Elements exceeding their MATE values at the scrubber outlet and which are common to both fuels are arsenic, chromium and nickel. Additionally, iron exceeded its MATE value at the scrubber outlet during coal firing as did cadmium and vanadium during oil firing. The overall removal of trace elements across the scrubber is 99 percent for coal firing and 87 percent for oil firing.

Beryllium emissions after scrubbing were less than or equal to the beryllium MATE value during coal and oil firing. At the measured emission concentrations, the National Standard for Hazardous Air Pollutants limitation of 10 grams beryllium per day would only be exceeded by boilers of 50 MW capacity for coal firing and 100 MW capacity for oil firing.

The fraction of fuel sulfur converted to SO_3 during oil firing was 50 to 75 percent higher than during coal firing. In contrast, the fraction of fuel sulfur converted to sulfates during coal firing was twice that during oil firing.

Sulfates are more efficiently removed than SO_3 (60 percent removal for oil firing and 88 percent for coal firing). This indicates that $SO_4^=$ is probably associated with the larger particulates, which are more efficiently removed than smaller particulates. The higher sulfate removal from the coal flue gases is explained by the higher particulate loading during coal firing.

Uncontrolled chloride and fluoride loadings were higher during coal firing (5 and 0.2 ng/J, respectively) than during oil firing (0.2 and 0.02 ng/J, respectively. This was attributed, in the case of chlorides, to a higher fuel chlorine content for coal than for oil. Chlorides were removed with better than 99 percent efficiency from coal flue gases and with about 51 percent efficiency from oil flue gases. This difference was attributed to the higher particulate removal efficiency for coal particulates. Fluorides were removed with greater than 86 percent and about 87 percent efficiency for coal and oil firing, respectively. Uncontrolled nitrate emissions were 0.08 ng/J during oil firing, and nitrates were removed from oil flue gases with 57 percent efficiency.

Organics

Polycyclic organic material (POM) was not found in the scrubber inlet or outlet at detection limits of 0.3 $\mu g/m^3$ for either coal or oil firing. MATE values for most POM's are greater than this detection limit. However, since the MATE values for at least two POM compounds - benzo(a)pyrene and dibenz(a,h)anthracene - are less than 0.3 $\mu g/m^3$, additional GC/MS analyses at higher sensitivity would be required to conclusively preclude the presence of all POM's at MATE levels.

Organic emissions for coal and oil firing were very similar. Total organic emissions were less than 9 ng/J (0.02 lb/MM Btu) for both tests, and these emissions appear to be primarily C_1 to C_6 hydrocarbons and organics heavier than C_{16}. While uncontrolled emission rates for both coal and oil firing are low, emissions of these organics were further reduced by about 75 to 85 percent in the scrubber unit.

The organic compounds identified in the gas samples from both coal and oil firing were generally not representative of combustion-generated organic materials, but were compounds associated with materials used in the sampling equipment and in various analytical procedures. This again confirms the low level of organic emissions.

Liquid Waste

The combined waste water stream from the boiler operation may not pose an environmental hazard in terms of organic materials since the discharge concentrations of organics are well below their MATE values for both coal and oil firing. The same conclusion may be drawn for inorganic compounds with the exception of cobalt, nickel, copper and cadmium for coar firing and nickel and copper for oil firing since these metals may exceed their MATE values.

Solid Waste

The scrubber cake produced when either fuel is burned contains concentrations of trace elements high enough to exceed most MATE values. Because of these high concentrations the scrubber cake must be disposed of in specially designed landfills.

COMPARATIVE ENVIRONMENTAL ASSESSMENT

The difference in environmental insult expected to result between coal and oil combustion emissions from a single controlled 10 MW industrial boiler is insignificant. This is because: 1) there are only slight differences in the emissions levels of the pollutants, or 2) the absolute impact of either fuel use is insignificant. The environmental impacts of emissions from a cluster of controlled 10 MW industrial boilers are potentially significant. The impacts include health effects, material damages, and ecological effects from high levels of SO_2, NO_x and suspended particulate matter; health effects and ecological damage due to trace metal accumulation in soils and plants; and aesthetic degradation from visibility reduction and waste disposal sites.

The risk of environmental damage from emissions of controlled industrial boilers, whether oil or coal-fired, is considerably less than the risk posed by emissions from uncontrolled industrial boilers. It should be noted that this finding is based on an exceptional facility. The reference facility is very well run and maintained, and emissions are low.

The environmental acceptability of a cluster of controlled industrial boilers is more dependent on site specific factors (e.g., background pollution levels, location and number of other sources) than type of fuel utilized. Careful control of the site specific factors can avert potential environmental damages and generally compensate for any differential effects arising between the use of coal or oil.

With the possible exception of ambient levels of NO_x, the risk of violating the National Ambient Air Quality Standards (NAAQS) due to the operation of clusters of controlled industrial boilers is essentially the same whether the fuel combusted is coal or oil. Based on tests of the reference 10 MW boiler (which was not controlled for NO_x emissions), localized NO_x concentrations produced by coal firing are estimated to be twice the level of that resulting from oil firing, and greater than the levels permitted by the NAAQS for 24-hour and one-year averaging periods.

Short term (3-hour and 24-hour averaging times) maximum ambient concentrations present the most significant air pollution problem resulting from operation of controlled industrial boilers. Restrictions imposed by the NAAQS for short term ambient levels would be most constraining to boiler operation in areas where air quality is already only marginally acceptable. Expected long term concentrations arising from boiler emissions would not appear to pose a risk for violation of the NAAQS.

Coal firing appears to produce a greater enrichment of trace elements in the flue gas desulfurization cake than oil firing produces. However, the scrubber cake resulting from either coal or oil firing contains sufficient amounts of heavy metals and toxic substances to pose difficult waste disposal problems.

The impact categories considered include public health, ecology, societal, economic, and energy. The specific findings with respect to the various impact categories are summarized briefly below.

Health Effects

Based on the Lundy/Grahn Model for health effects associated with suspended sulfate levels, regional emissions levels from controlled oil or coal-fired industrial boilers would not be expected to cause a significant impact on regional health. Emissions from uncontrolled boilers would result in substantially greater levels of regional suspended sulfate levels, and the associated health effects would be an order of magnitude greater.

Emissions from clusters of controlled industrial boilers are expected to cause significant adverse health effects in a localized area near the plant cluster. Oil firing would be expected to result in localized health effects about one third less severe than those resulting from coal firing. The increase in mortality attributable to either controlled coal or oil firing is appreciably less than that associated with uncontrolled industrial boilers emitting higher levels of particulates and SO_x.

The impact of solid waste generation on health is essentially the same for controlled coal firing and oil firing, provided suitable land disposal techniques are employed to assure minimal leaching rates and migration of trace elements to groundwater and the terrestrial environment.

Addition of cadmium to a localized environment in the quantities produced by clustered controlled industrial boilers may result in cadmium concentrations in living plants approaching levels injurious to man. Because cigarettes contain significant cadmium levels, smokers are more apt to achieve thresholds of observable symptoms for cadmium exposure when consuming additional cadmium via the food chain.

The concentration of metals in runoff waters due to controlled oil firing is predicted to be slightly less than that occurring from controlled coal firing; in either case, hazard to human health by drinking water is remote.

Trace element emissions from clusters of controlled industrial boilers may significantly increase local background levels in drinking water, plant tissue, soil, and the atmosphere; however, the expected increases in the levels of such elements are generally several orders of magnitude less than allowable exposure levels. Oil firing is estimated to cause cadmium burdens in plants approaching levels injurious to man, and coal firing may produce plant concentrations of molybdenum which are injurious to cattle.

Ecology

The potential for crop damage from either controlled coal firing or oil firing depends greatly on ambient levels of NO_x, SO_2, or trace element soil concentrations. If such levels are presently high, localized plant damage would be expected to occur within a 1 to 2 km range from a controlled boiler cluster. Leaf destruction from SO_2 exposure would be expected to be slightly more severe in the vicinity of a cluster of controlled boilers which are coal-fired as opposed to oil-fired. For boilers uncontrolled for NO_x emissions, plant damage would be expected to be significantly greater in the vicinity of the coal-fired cluster, owing to higher levels of ambient NO_x produced. The likelihood of damage occurring in plants due to emissions of trace elements from either controlled oil or coal firing is remote, with the possible exception of injury due to elevated levels of molybdenum and cadmium in plant tissue resulting from coal firing and oil firing, respectively.

The effect of emissions from industrial boilers on trace element burdens in plants would be greater via soil uptake than by foliar interception. This is because soil concentrations are the result of accumulative long term exposure to boiler emissions whereas foliar exposure is determined by the immediate deposition rate of emissions on the plant surface and the lifetime of the leaf.

The impact of fossil fuel combustion in controlled oil or coal-fired boilers on plant damage via acid precipitation would be insignificant. The levels of supended sulfate (the origin of acid rain) would be essentially the same whether the controlled boilers are coal or oil fired.

Measurement and analyses of leaching rates at experimental waste disposal sites indicate that landfills of untreated flue gas desulfurization system scrubber cake can be constructed such that significant adverse impacts will not occur.

Societal

The impact of boiler emissions on corrosion in the local area near a cluster of controlled industrial boilers would be significant. The corrosion rate would be slightly greater when the boilers are coal-fired. However, the extent of this overall impact (oil or coal) is minor compared to that which occurs when industrial boilers are uncontrolled.

The increase in annual TSP and soiling damages in the vicinity of a cluster of controlled industrial boilers would result in additional cleaning and maintenance costs about 10 to 15 percent greater than that already experienced in a typical urban area. The cleaning costs may be slightly greater when the boilers are coal-fired.

Emissions of particulate matter from controlled industrial boilers would result in visibility reduction. This aesthetic degradation would occur in a localized area near the boiler cluster, and would occur to essentially the same extent whether the boilers are oil or coal-fired.

Total land disposal requirements for scrubber cake waste generated by controlled coal firing are three times greater than those for controlled oil firing. Waste disposal of the scrubber wastes may result in significant depreciation of property value and aesthetic degradation in the area of the disposal site. These impacts would be more severe if boilers use coal rather than oil.

Economic

The differential direct economic impact between emissions from coal firing and oil firing is generally insignificant with the possible exception of some differences occurring in a limited localized area near clusters of boilers. The extent of the incremental direct economic impacts is proportional to the extent of the incremental environmental damages.

Differential second order economic impacts, such as changes in hospital employment, alteration of taxes, or changes in income, are expected to be insignificant between emissions from controlled oil and coal-fired industrial boilers.

Energy

At the present time, the comparative assessment of the effects of emissions from controlled oil and coal-fired industrial boilers tends to support the national energy plan for intensified utilization of coal. The fuel choice of oil or coal is a relatively minor issue concerning the environmental acceptability of controlled industrial boilers; other site specific and plant design factors exert a greater effect on environmental damages. While it was shown that fuel choice caused significant differences in impacts to occur when the boiler is uncontrolled for NO_x emissions, these differences may be mitigated by the addition of NO_x control technologies with minimal overall cost impact.

As concern for environmental protection increases, the issue may not be whether coal or oil use is more environmentally acceptable, but whether the increasing use of fossil fuels can be continued at the present levels of control technology without potential long term damages. If it is found that long term effects of pollution (e.g., trace metals accumulation, lake acidity from acid rains) from fossil fuel combustion and other sources are environmentally unacceptable, it is clear that energy use may be affected. Energy cost will increase with increasing control requirements, possibly to the level where other cleaner forms of energy become more competitive.

TABLE 1. SUMMARY OF BOILER PARAMETERS

Boiler type:	Oil/pulverized coal; face fired; integral furnace; dry bottom
Manufacturer:	Babcock and Wilcox, Type P-22 EL
Type of burner:	Circular conical
Number of burners:	3
Burner arrangement:	Triangular, one face
Air preheater:	Yes
Fuel:	Number of 6 fuel oil; High volatile bituminous coal, Class II, Group 2, of ASTM D388
Design steam rate:	45,000 kg/hr (100,000 lb/hr);
Use:	Process steam

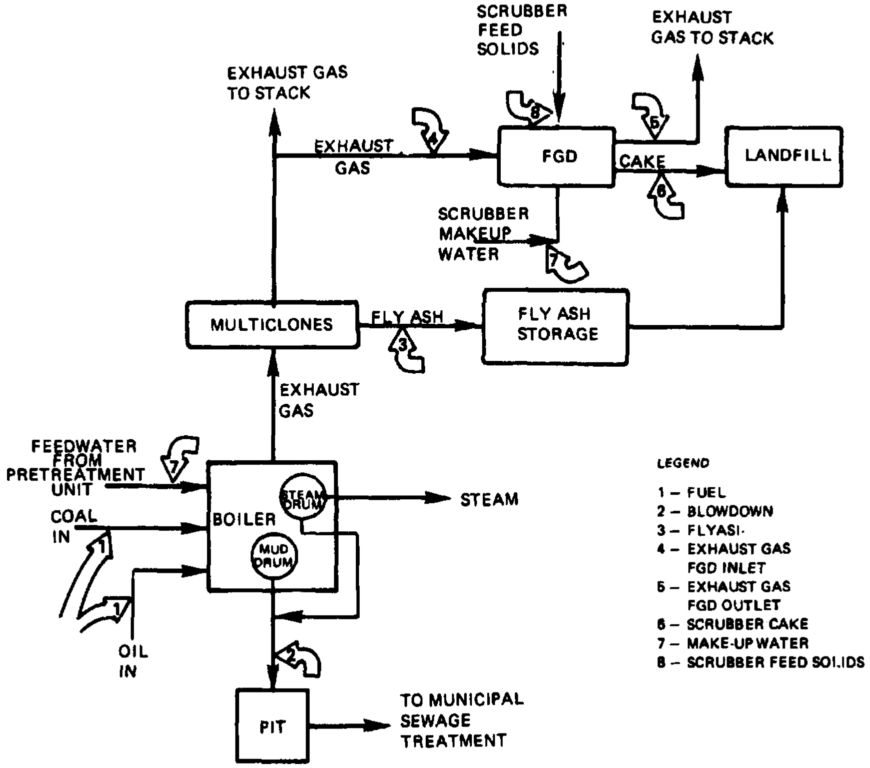

Figure 1. Diagram of boiler and flue gas desulfurization system showing sampling locations.

TABLE 2. ANNUAL EMISSIONS

Pollutant		kg/year					
		Scrubber Inlet			Scrubber Outlet		
		Coal Firing	Oil Firing	Coal/Oil	Coal Firing	Oil Firing	Coal/Oil
Gaseous	NOx (as NO_2)	500,810	164,230	3.05	442,520	157,390	2.81
	SO_2	1,127,300	906,202	1.24	36,800	24,453	1.51
	SO_3	6,184	7,249	0.85	4,157	5,183	0.80
	$SO_4^=$	67,214	20,894	3.22	8,110	8,303	0.98
	CO	16,119	4,991	3.23	14,497	4,845	2.99
	Organics (as CH_4)	5,870	2,272	2.58	6,377	2,500	2.55
	C_1 - C_6[†]	<5,606	<4,164	--	<5,606	<4,164	--
	C_7 - C_{16}	345	155	2.22	274	18	15.2
	C_{16}+	2,311	2,381	0.97	335	392	0.85
	Total Particulates	2,991,700	53,832	55.6	18,856	13,686	1.38
	<1μ	--	--	--	11,691	11,359	1.03
	1 - 3μ	--	--	--	5,657	1,642	3.45
	3 - 10μ	--	--	--	1,320	634	1.93
	>10μ	--	--	--	188	0[±]	--
		m³/year					
Liquid	Blowdown/Waste Water	~76,000	~ 76,000	~ 1	~ 76,000	~76,000	~ 1
	Cooling Water	~86,000	~ 86,000	~ 1	86,000	~86,000	~ 1
Solid	Bottom Ash	~ 778,600	~ 7,600	~ 103	~ 778,600	~ 7,600	~103
	Fly Ash	~1,800,000	~ 15,000	~ 120	~1,800,000	~15,000	~120
	Scrubber Cake	0	0	--	8,054,100	3,011,000	2.67

[*] Assuming 100% load, 45 weeks per year (7,560 hrs/year).

[†] These values represent the detection limit of the instrument used.

[±] These values represent oil firing particulate with a minimum of coal ash contamination.

ENVIRONMENTAL ASSESSMENT OF STATIONARY SOURCE NO_x CONTROL TECHNOLOGIES

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ABSTRACT

The "Environmental Assessment of NO_x Control Technologies" (NO_x EA) was initiated in 1976 with the primary objectives to: a) identify potential multimedia environmental hazards from stationary combustion sources under both uncontrolled and controlled (for NO_x) operation; b) develop control application guidelines on the economic, energy, and operational impacts of meeting prescribed emission levels, and c) identify the most cost effective and environmentally acceptable NO_x control techniques to achieve and maintain air quality standards. To address these goals efforts have been focused toward ranking stationary combustion sources according to potentially hazardous pollutant emissions, field testing to fill emissions data gaps, impact analysis to estimate both the incremental impact of NO_x control application and the overall environmental hazard presented by stationary combustion sources, and air quality analysis to provide a quantitative basis for identifying future NO_x control needs.

This paper discusses results obtained to date in each of these areas. The results of a multimedia emissions inventory for stationary sources is presented and emissions projections to the year 2000 for various energy use scenarios are discussed. Multimedia emissions data from a field test of a 180 MW tangential coal fired utility boiler are discussed. Analysis of these data using a source analysis model suggest that the use of staged combustion to reduce NO_x emissions results in an overall decrease in potential source hazard. Estimated source population impact rankings for stationary combustion sources are presented and discussed. Finally, results of air quality analysis studies are presented in light of preferred controls to meet current and projected NO_2 ambient air quality standards.

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SECTION 1

INTRODUCTION

In 1975, the Environmental Protection Agency increased its emphasis on identifying and controlling potentially hazardous waste-stream discharges from energy systems and industrial processes. This increased emphasis resulted from recognition that a large number of multimedia (air, land, and water) pollutants may be causing unacceptable environmental impacts. Also, the energy supply shortage reenforced the need for coordinated energy system development and environmental control development. In response, the Industrial Environmental Research Laboratories of EPA started a major Environmental Assessment (EA) program to guide environmental control development and support standards setting and regulatory policy.

The "Environmental Assessment of Stationary Source NO_x Control Technologies" (NO_x EA) was started in 1976 as one of over 20 EA's sponsored by the Industrial Environmental Research Laboratories. The need for an EA of NO_x control technology was based on the increasing use of controls for which the side effects are uncertain, and on the recognition that new advanced controls will be needed to meet future emission standards and air quality standards. The three primary objectives of the NO_x EA are to:

- Identify potential multimedia environmental hazards from stationary combustion sources
    - under baseline operation without NO_x controls
    - under low NO_x operation
- Develop control application guidelines on the economic, energy and operational impacts of meeting prescribed emission levels
- Identify the most cost effective and environmentally acceptable NO_x control techniques to achieve and maintain air quality considering

- current and anticipated air quality standards
- alternate equipment use and fuel use scenarios to the year 2000.

The principal products of the NO_x EA are: rankings of potentially hazardous pollutants for various source/control combinations; estimates of costs and process impacts for existing and emerging control techniques for each major stationary source; and rankings of NO_x control techniques according to their importance in air quality maintenance now and in the future. The pollutant rankings are intended for use by EPA to identify control development needs and as a data base for standards setting groups. The source/control cost and process data are intended for control users and regulatory groups concerned with selecting the best control for a specific application. The NO_x control rankings are used by EPA to set control development priorities so that controls will be available when needed in the regulatory program.

Figure 1 shows the major NO_x EA components (indicated by boxes) and major products (indicated by ovals). The figure also notes the sections of the paper where results are discussed. Results of the process engineering effort are presented in another paper in this symposium proceedings (Reference 1).

The program approach shown in Figure 1 is iterative. Initially, the major program components were activated to help set program priorities and to evaluate the need to develop assessment methodology. Subsequently, more detailed effort has focused on generating new results and evaluating results of other assessment activities. The chronological sequence of the program is shown on Figure 2. Results from the early studies on source/control priorities, emission characterization and impact models are documented in References 2 through 5. These results are currently being refined and updated. Interim results on process studies and the test program are documented in Reference 6. The major reports for each source type on control application guidelines and pollutant rankings from the test program are in the draft stage. The first, for utility boilers will be published in Spring 1979 (Reference 7).

SECTION 2

EMISSION CHARACTERIZATION

Emission characterization serves to rank emission sources and provide key data base for impact analysis and air quality analysis. An emission inventory was generated with the following features (Reference 3):

- gaseous, liquid and solid effluents
- 42 equipment classes
- 17 fuel types
- NO_x, SO_x, CO, particulate, trace metals, and polycyclic organics
- nationwide and regional
- controlled and uncontrolled for NO_x, SO_2, and particulate
- 1974, 1985, 2000

The approach is summarized below, and is shown as Figure 3.

NO_x EMISSION INVENTORY

The emission factors, fuel consumption, and nationwide emissions for the year 1974 are listed in Table I for the 120 equipment/fuel combinations having significant NO_x emissions. The emission factors were taken from field test data and are revised as recent results become available. The fuel consumption data are from Federal regulatory agencies and manufacturer trade groups. These data are currently being updated to 1978.

NO_x emission rates summed by major equipment type and fuel type are listed on Table II. The total annual nationwide emissions from all stationary sources sums to 12.0 Tg. This comprises 52 percent of total NO_x emissions, with mobile sources accounting for 9.6 Tg/yr. In Table II, the "utility boilers" class includes all field erected watertube boilers with a heat input greater than 75 MW (250 MBtu/hr), while package boilers include all industrial, commercial and residential boilers and hot water systems with heat input below 75 MW (250 MBtu/hr). Conventional fossil fuel combustion accounts for 94 percent of stationary emissions and utility boilers account for 48.3 percent. In 1974, controls implemented for utility boilers gave only a 3 percent NO_x reduction nationwide relative to the uncontrolled utility boiler estimate. The effect of controls is increasing, however, as sources equipped to meet the 1971 New Source Performance Standard, 301 ng/J (0.7 lb $NO_2/10^6$ Btu), are brought on line. Although some controls were installed for gas turbines and nitric acid plants, the effect on nationwide emissions was negligible.

A ranking of discrete equipment type/fuel type combinations by nationwide emission loadings is shown in Table III for the 15 highest emitters. Here, the relative ranking is due both to the emission rates per source and to the total installed capacity. Tangential coal fired utility boilers rank first due to their high installed capacity - 11.3 percent of stationary conventional fossil fuel consumption. Large spark ignition IC engines rank high due to their high emission rate: 10.5 percent of total emission vs 1.8 percent of fuel consumption. Similarly, coal fired cyclone utility boilers rank fourth with 7 percent of stationary emissions while accounting for only 3.5 percent of stationary fuel consumption.

The nationwide emission rates and source rankings for pollutants other than NO_x are documented in Reference 3.

EMISSION PROJECTIONS

Emission projections to the year 2000 are highly uncertain due to the uncertainty in fuels allocation by source and national energy policy. To get upper and lower bounds on future NO_x emissions, a high energy growth scenario--based on continuation of future trends--and a low growth scenario --based on the National Energy Plan--were used. The emission projections for the two scenarios are shown on Figures 4 and 5. Two emission standards scenarios are shown. The first assumes that no additional new source performance standards would be set. The second, moderate scenario assumes standards will be set based on projections of emission levels achievable wit technology currently under development.

Under the high growth scenario with no additional standards total emissions more than double by 2000 and stationary emissions more than triple. The moderate NSPS scenario partially offsets the growth but stationary emissions are projected to approximately double by 2000. Projected mobile source emissions actually decline in the mid-1980's as current standards affect a larger proportion of the auto population. Continued growth counterbalances this in the 1990's however.

Under the low growth scenario with no additional controls projected, total NO_x emissions increase by 50 percent in the year 2000, with stationary source emissions increasing by 70 percent. Stationary emissions growth is suppressed to about 40 percent with moderate standards based on a continuation of current R&D.

SECTION 3

TEST PROGRAM

During compilation of the baseline emissions inventory discussed in Section 2 and in a preliminary impact analysis of the incremental effects of NO_x controls on pollutant emissions other than NO_x (Reference 2), numerous data gaps became apparent. Data on the effects of NO_x combustion controls on emission levels of noncriteria flue gas pollutants and liquid and solid effluents were virtually nonexistent. To address these data needs a field test sampling and analysis program was conducted.

Based on the results of the preliminary source impact ranking performed in the first year of the NO_x EA (Reference 2) a series of 19 candidate field tests were identified. From the 19 potential tests, seven were selected and tested. A summary of these seven tests is given in Table IV. Where possible, the NO_x EA tests were done as an augmentation to planned or ongoing tests.

For each test the following environmental assessment sampling protocol was followed:

- Continuous monitoring of flue gas NO_x, SO_2, CO, CO_2, and O_2
- Flue gas Source Assessment Sampling System (SASS), EPA Method 5 particulate load, and EPA Method 8 (or equivalent) sulfur species sampling; both upstream and downstream of the particulate collector, if applicable
- Flue gas grab sampling and onsite gas chromatographic analysis for C_1-C_6 hydrocarbons; both upstream and downstream of the particulate collector, if applicable
- Bottom ash slurry sampling
- Particulate collector hopper ash (slurry) sampling

- Fuel and fuel additive, if applicable, sample collection
- Operating data collection

As noted in Table IV, the test program was conducted, as a minimum, for at least two conditions of source operation: baseline (uncontrolled) and low NO_x operation. In several instances, operation at intermediate levels of NO_x control was tested. In addition, replicate testing was performed in selected cases.

A key part of the test program involved close monitoring of source operating data. This was done not only to ensure that test conditions remained constant and representative of acceptable source operation over the duration of sample collection, but also to provide the necessary input to further process analysis efforts.

Subsequent laboratory chemical analyses of samples collected generally followed IERL-RTP Level 1 environmental assessment procedures (Reference 8). Atomic absorption spectroscopy was employed to determine the concentration of the 23 commonly occurring elements listed in Table V. The organic analyses were extended, when feasible, to the determination of the 11 polycyclic organic compounds (POM) listed in Table VI.

Following the EA analysis procedures, the following data could be obtained for each test point:

- Continuous flue gas NO_x, SO_2, CO, CO_2, and O_2
- Flue gas SO_2, SO_3, and speciated C_1-C_6 hydrocarbon
- Flue gas particulate load and size distribution
- Flue gas vapor phase trace element composition for the 23 elements listed in Table V
- Flue gas $>C_7$ organic composition in terms of seven compound polarity fractions and flue gas POM composition for the 11 POM species listed in Table VI
- Particulate composition for the 23 elements listed in Table V and the six ionic species listed in Table VII, as a function of particulate size
- Particulate organic composition for seven polarity fractions, and for the 11 POM species listed in Table VI, as a function of particulate size
- Liquid/solid stream (bottom, hopper ash) composition for the 23 elements listed in Table V and the six ionic species listed in Table VII

- Liquid/solid stream (bottom, hopper ash) organic composition for seven polarity fractions and for the 11 POM species listed in Table VI
- Particulate and ash C and H content
- Fuel proximate and ultimate analysis (heating value, and water, C, H, O, N, and S content)
- Fuel trace element content for the 23 elements listed in Table V

In addition to the chemical analysis program, bioassay testing in accordance with IERL-RTP Level 1 guidelines (Reference 9) were performed on samples collected during the gas turbine, oil-fired utility boiler, second coal-fired utility boiler, and second coal-fired industrial stoker tests. The general bioassay protocol followed is indicated in Table VIII.

The field test program was completed in September 1978, and chemical and biological analyses are nearing completion. As the analyses are completed, they are combined with the process engineering results to give the composite environmental, energy, efficiency, and operational impacts of NO_x combustion modification controls.

The analysis results for the flue gas stream of a 180 MW tangentially fired utility boiler are summarized on Table IX. Two levels of NO_x reduction were tested. Retrofit bias firing gave a 32 percent NO_x reduction, and operation with the upper row of nozzles on air only gave a 38 percent NO_x reduction. The furnace efficiency either remained constant or increased slightly (due to lower excess air) under low NO_x operation. There was no appreciable increase in carbon-in-flyash with NO_x controls. It should be mentioned that these tests were for short periods, so the long term operability under these low NO_x conditions was not necessarily validated.

For the majority of elements listed in Table IX, the changes in emission rates between baseline operation and low NO_x firing were within the accuracy of the analysis and are not judged to be significant. Notable exceptions are the leachable nitrates and ammonium compounds. Here, it is possible that local fuel rich conditions under low NO_x operation suppresses reduced nitrogen compound oxidation normal to baseline operation.

The organics analyses yielded only general conclusions. Following the prescribed environmental assessment sampling and analysis protocol, there was not a sufficient amount of organic material in any of the samples to warrant fractionation by liquid chromatography. The mass spectral analyses of the fractions resulting from the liquid chromatography were, thus, not performed.

The general results of the organic analyses show that organic emissions were slightly higher in the low NO_x, burners out of service, test. The organic material concentrations in the bottom ash, mechanical collector ash, electrostatic precipitator ash, and the flue gas outlet (vapor phase) were higher for low NO_x firing. The flue gas outlet particulate organic content was slightly higher in the normal firing test. Although organic emissions were low in these tests, there is a need to conduct more quantitative organic analyses due to the relative hazards posed by certain organic compounds.

SECTION 4

IMPACT ANALYSIS

Two pollutant impact models have been developed and applied. The first is a single source analysis model (Reference 5) used to screen emissions data and highlight those pollutant species emitted in sufficient quantity to be potentially hazardous. The second model is a population exposure model which approximates the hazard from all sources of a given type nationwide. This model is used to rank sources on the basis of potential environmental impact.

SINGLE SOURCE SCREENING MODEL

For purposes of screening pollutant emissions data to identify species requiring further study, a Potential Degree of Hazard (PDOH) is defined as follows:

$$\mathrm{PDOH}_i = \frac{\text{concentration of pollutant } i \text{ in effluent stream}}{\text{"allowable" effluent concentration}}$$

The "allowable" effluent concentration is, in general, the defined Threshold Limit Value for the pollutant, which is the maximum pollutant concentration considered safe for occupational exposure. When PDOH exceeds unity, more refined chemical analysis may be required to quantify specific compounds present.

To compare waste stream potential hazards, a Potential Toxic Unit Discharge Rate is defined as follows:

$$\mathrm{PTUDR} = \left(\sum_i \mathrm{PDOH}_i\right) \times \text{Mass Flow rate},$$

where the potential degree of hazard is summed over all species analyzed. The PTUDR is an indicator of throughput of hazardous pollutants and can be used to rank the needs for controls for waste streams.

This model was applied to the analysis results for the 180 MW tangential coal fired utility boiler discussed in Section 3. Table X lists the PDOH values for those inorganic species or compounds where PDOH $\geq$ 1 for one of the three tests. It is evident that the gaseous pollutants, particularly SO_2 and NO_x dominate the potential toxicity of the flue gas stream. Of the trace metals, arsenic shows the highest PDOH, but none of the metals showed any large change under low NO_x conditions. As may be expected, SO_3 decreased under low NO_x operation and reduced N compounds increased.

The potential toxic unit discharge rate for the inorganic component of four waste streams of the boiler are compared in Table XI. It is evident that the flue gas stream dominates the PTUDR. Here, the PTUDR reduction with biased firing and BOOS is primarily due to the decrease in NO_x concentration in the flue gas. The PTUDR's for the other waste streams either decreased, or were constant when going to low NO_x firing. As mentioned in Section 3, more data are needed for waste stream organic composition before the degree of hazard, relative to inorganics, can be estimated.

POPULATION IMPACT MODEL

To estimate population exposed to potentially hazardous pollutant levels from stationary combustion sources, a population impact model was developed. The impact model includes the following factors:

- Multipollutant emission estimates for each source type (NO_x, SO_x, CO, HC, particulates, trace metals, polycyclic organics).
- Emission dispersion accounting for stack height and multiple area sources.
- Population density in the source proximity.
- Estimates of permissible ambient concentrations.
- Ambient background concentrations.

An impact factor was defined as:

$$\int P \frac{\chi + \chi_b}{\chi_m} dA, \qquad (1)$$

where, P = population density,

χ = ground level pollutant concentration,

χ_b = ambient background pollutant concentration from other sources,
χ_m = maximum permissible concentration, and
A = affected area as defined by the dispersion approximation.

Equation (1) was computed for a single source of each equipment/fuel type and for each pollutant species. The impact factor was then summed over all sources of a given type nationwide, and over all pollutant species from each source.

Emission dispersion was approximated by a Gaussian plume model for large point sources (Reference 10), and by a multi-source mixing model for area sources (Reference 11). The spatial variations in population density and ambient background were approximated by defining urban and rural regions based on data from the US Bureau of Census and the National Emissions Data System (NEDS). Equation (1) was calculated separately for each equipment/fuel type in a rural area and in an urban area. The nationwide impact factor was computed from estimates of the total capacity of each equipment type which were in predominantly urban areas and in predominantly rural areas.

The nationwide NO_x impact rankings, normalized to the highest ranking source, are listed in Table XII for the top 17 sources. By comparison to the emissions ranking in Table III, it is evident that several sources, notably IC engines, rank lower in impact than in emission loadings. This is largely because these sources are located in rural areas where both population density and ambient background concentrations are low. By contrast, in an urban area where the background concentration is a significant percentage of the permissible limit, the presence of a large point source can cause the limit to be exceeded over an extensive area.

The multispecies impact ranking, which includes species in addition to NO_x and is shown in Table XIII, shows utility boilers with a much lower overall ranking compared to the NO_x impacts (Table XII). This is primarily because the total multispecies impact is dominated by trace metals in the particulate, and utility boilers are efficiently controlled for particulate emissions. Package boilers, however, are less efficiently controlled and thus rank higher in estimated impact. As expected, coal and heavy oil are responsible for the highest multispecies impacts.

SECTION 5

AIR QUALITY ANALYSIS

The purpose of the air quality analysis is to provide a quantitative basis for identifying the future needs (when, where, how much, and what kind) for NO_x controls to satisfy the requirements of the Clean Air Act. This information can then be used to recommend R&D directions and schedules for developing necessary controls. In the air quality analysis, uncontrolled emissions projections, controls cost and effectiveness data, fuel costs, and ambient air quality goals are combined to evaluate the control needs for a particular Air Quality Control Region (AQCR).

Currently the only NO_x related ambient goals are the 100 $\mu g/m^3$ annual average for NO_2 and a 160 $\mu g/m^3$ 1-hour standard for oxidant. In addition, the Clean Air Act amendments of 1977 require EPA to determine the need for a short term NO_2 standard. To date, no short term standard has been proposed; although, EPA is known to be considering a 1-hour standard for NO_2 between 200 and 1000 $\mu g/m^3$. Although we have considered both the oxidant and potential NO_2 short term standards in our analysis, the primary focus for the present discussion is the NO_2 annual average standard (Reference 6).

To allow us to examine a large number of growth/control scenarios for a variety of AQCR's we selected a modified form of rollback for an air quality model. (The applicability of rollback for this type of analysis was somewhat justified by two different analyses using the photochemical models LIRAQ and DIFKIN (Reference 6)). This reduced the amount of emission data needed, minimized computational costs, and provided maximum flexibility in the analysis. Furthermore, only the NO_x/NO_2 relationship was considered; thus, HC emissions data collection was not required. The primary sources of emissions and fuel use data were the National Emissions Data System and the Federal Energy Regulatory Commission (Federal Power Commission) annual reports.

In the rollback formulation employed it was possible to specify the relative importance of each source type by using a source weighting factor. Each choice of weighting factors is equivalent to choosing a different air quality model for the AQCR. The utility of the model was further increased by testing the sensitivity of the results to the input values. Control strategies were developed for numerous combinations of stationary and mobile source growth, base year calibration, and source weighting factors for each AQCR. (These are briefly described on Tables XIV and XV.) This ensured that the predicted control requirements would be responsive to the majority of NO_x critical situations that might develop.

Over 20 different emissions growth/source weighting combinations for eight AQCRs, listed in Table XVI, were considered. The eight AQCRs were selected to represent a variety of source category, fuel use, and mobile/stationary source mixes.

The variety of emissions source growth scenarios, mobile control schedules, and AQCRs, resulted in predicted uncontrolled (no stationary source controls beyond current NSPS) NO_x emissions changes relative to 1973 emissions of -6 percent to +3 percent in 1985 and of +5 percent to +50 percent in 2000. The relatively small spread in 1985 emissions reflects the relatively small impact of different mobile source control possibilities between now and 1985. The very large spread in 2000 reflects the different projected impacts from low stationary source growth with very strict mobile control and high stationary source growth (~3 percent per year) with nominal mobile growth and control compounded over 28 years.

Changes in ambient concentration corresponding to the above emissions changes, ranged between -12 and +3 percent for 1985 and zero to +43 percent in the year 2000. (The zero percent lower limit applies only to heavily mobile dominated AQCRs with an extremely effective mobile control program.) Since these results are from a variety of AQCRs, they are representative of the range of expected change in ambient concentration for all AQCRs. These calculated changes in ambient concentration do not exactly follow the percent changes in emissions since the use of the source weighting factors in the air quality model can reduce or increase the impact of emissions growth of selected sources.

The level of NO_x control required to offset the increase in ambient concentration depends on the initial value (1973) of the annual average NO_2 concentration, the relative impact assigned to each source, and the mobile/stationary mix. Based on results for all the AQCRs considered, a conservative estimate is that at least four AQCRs will need significant application of combustion modification NO_x controls to attain the annual average NO_2 standard by 1985. By the year 2000 this number will conservatively increase to 15, of which one-half would also need implementation of advanced controls such as ammonia injection and possibly flue gas treatment. A 25 percent increase in annual average NO_2 level by the year 2000 is most representative of expected changes; therefore, any AQCR with a 1973 annual average greater than 80 $\mu g/m^3$ would exceed 100 $\mu g/m^3$ by 2000.

Specific results from the matrix of control needs calculations for two AQCRs are shown in Tables XIV and XV. The growth scenarios, source weighting factors, and base year calibration for each case are shown in the Tables. Control requirements to meet 100 $\mu g/m^3$ or ambient levels, if less than 100 $\mu g/m^3$, are shown for 1985 and 2000 for each case. The required NO_x control levels, indicated by 0, 1, 2, 3 and V, are described in Table XVII. Controls are applied in the most cost-effective manner, and new controls are introduced, if required, at the time (year) they are assumed to be developed.

The San Francisco AQCR is representative of those AQCRs which are not currently nonattainment areas for NO_2 but which could become so in the future. Emissions of NO_x in the region are heavily dominated by mobile sources (~70 percent). The results shown in Table XIV are representative of mobile source dominated AQCRs with 1973 concentrations in the range of 75 to 100 $\mu g/m^3$. The dominance of mobile sources is clearly indicated by the significant reduction in 1985 concentrations in all cases and by the results for the low mobile cases in both 1985 and 2000. The results for the high base year concentration (BYR = 101 $\mu g/m^3$) show that a mobile dominated AQCR that is near nonattainment now will need the maximum amount of combustion modification NO_x control by the year 2000. Furthermore, if powerplants are not a significant contributor to the annual average (powerplant weighting factor of 0.2), then even more NO_x control will be required.

St. Louis is representative of an industrialized region dominated by stationary sources (75 percent) with coal firing as a significant source of NO_x (72 percent of stationary source NO_x is from coal-fired sources). Results for St. Louis are shown in Table XV. The relatively minor impact of different mobile source growth and control scenarios is illustrated by comparing the nominal growth and low mobile cases. Similarly, high stationary growth begins to have significant impact by the year 2000, even for the low base year concentration (76 $\mu g/m^3$). The difference in control requirements between mobile and stationary source dominated AQCRs is further illustrated by comparison of the low base year cases for St. Louis and San Francisco. The base year concentration is the same, but the ambient levels or control requirements in the year 2000 are much different.

A significant feature of these results, which are typical of stationary source dominated AQCRs, is that although no NO_x controls are needed in 1985, considerable NO_x control is required by the year 2000, even though the present ambient level is well below the annual average standard.

It should be emphasized that these conservative estimates are used to compensate for the extreme uncertainty in the monitoring data and the inherent errors in the assumptions of the model. It should also be noted that conservative growth rates and a successful mobile control program are "built-in" to the estimates. All of this is to say that the above should be considered an optimistic view of future NO_x control needs to meet the present annual average standard.

In addition to our investigation of NO_x control requirements to meet the annual average standard, we have also considered the impact of a one-hour NO_2 standard (Reference 6). Recent studies performed by EPA have shown that high short term NO_2 concentrations come about through any one of several paths:

- Area source emissions (both mobile and dispersed stationary sources)

- Isolated point sources with multiple combustors impacting on a single site
- Multiple point sources impacting on the same receptor
- Both area and point sources with all sources contributing to high concentrations
- Terrain impaction by a plume from a large point source

The relative importance of these paths is highly dependent on both the level which is established as the short term standard and the relative contribution of each source type to the short term NO_2 levels. Moreover, the NO_x control requirements may be significantly different for each path.

Point source impacts were analyzed by modeling a series of prototypic combustion plants ranging in size and operating parameters corresponding to various source categories (e.g., utility boilers, industrial boilers, and furnaces). The plants were analyzed individually, using a simple Gaussian dispersion model and meteorological conditions associated with ground level maximum NO_2, to assess the air quality impacts of all respective NO_x sources in the NEDS file. Conversion of NO to NO_2 was approximated from consideration of the time to maximum ground level impact and the background NO_2 level, which was determined from NO_2 monitoring information within individual AQCRs.

Area sources were analyzed by considering the available monitoring data (Reference 12). All those AQCRs estimated to have current one-hour NO_2 levels above 200 $\mu g/m^3$ were included in the analysis.

Based on these two analyses, conservative estimates of the number of AQCRs that would currently be in violation of various levels of a one-hour NO_2 standard are: 1000 $\mu g/m^3$ - 6, 500 $\mu g/m^3$ - 30, and 250 $\mu g/m^3$ - 120. By 1982 the estimated number of violators could slightly decrease, depending on source growth and control. Beyond 1982 estimates are heavily dependent on growth and control assumptions. Control requirements for attainment in case of the above standards range from combustion modifications to FGT and are very site specific.

Another aspect of the air quality analysis has considered the interaction of NO_x and HC controls on both NO_2 and ozone. Photochemical modeling results indicate that control of NO_x only does not provide as much reduction in the NO_2 peak as simultaneous control of NO_x and HC. Furthermore, control of NO_x only aggravates the ozone problem for conditions like those in many nonattainment areas for ozone. Any control strategy for NO_x must also consider HC control and the resultant impact on both short and long term NO_2 levels, as well as the ozone levels.

SECTION 6

SUMMARY

The preceding sections have discussed results obtained to date in several related tasks of the NO_2 Control Technology Environmental Assessment Program. In summary it can be concluded that:

- Based on a 1974 emissions inventory, stationary sources accounted for 52 percent of nationwide NO_x emissions. Utility boilers contributed 48.3 percent of the stationary source emissions and represented seven of the ten most significant emitter categories.
- Projections to the year 2000 indicate that, under a high energy growth scenario with no emissions standards beyond the 1971 NSPS, nationwide NO_x emissions more than double and stationary source emissions more than triple. Under a low energy growth scenario with moderate promulgation of new standards stationary emission growth is held to about 40 percent.
- Multimedia field test data on a 180 MW tangential coal fired utility boiler indicate that applying staged combustion through removing burners from service has neglibible effects on emission of most pollutant species other than NO_x. However, $SO_3/SO_4^=$ emissions decreased and reduced nitrogen compound (NH_4^+) emission increased with low NO_x operation.
- Application of a source analysis model to the utility boiler field test data indicate that total potential source environmental impact decreases under low NO_x operation. Though not discussed above, analysis data obtained in tests of an industrial stoker fired boiler substantiate this conclusion.
- Results of an impact ranking taking into account installed capacity, pollutant dispersion, and population density indicate that specific utility boiler equipment categories represent the nine most potentially hazardous stationary sources with respect to NO_x emissions alone. When trace metals, particulate, SO_x, CO, HC, and polycyclic organic species are incorporated into the analysis stoker fired packaged boilers displace utility boilers as three of the top ten most potentially hazardous source categories.

- Air quality analyses suggest that the number of NO_2 nonattainment regions will steadily increase, even with a highly successful mobile control program. By 2000 at least 15 AQCR's will require extensive application of combustion modification NO_x controls and several will require ammonia injection or FGT. Furthermore, a short term NO_2 standard much less than 1000 $\mu g/m^3$ would significantly increase the requirements for NO_x control.
- The air quality analysis results also indicate that the impact of any NO_x control strategy on both NO_2 and ozone levels must be carefully considered for each specific application.

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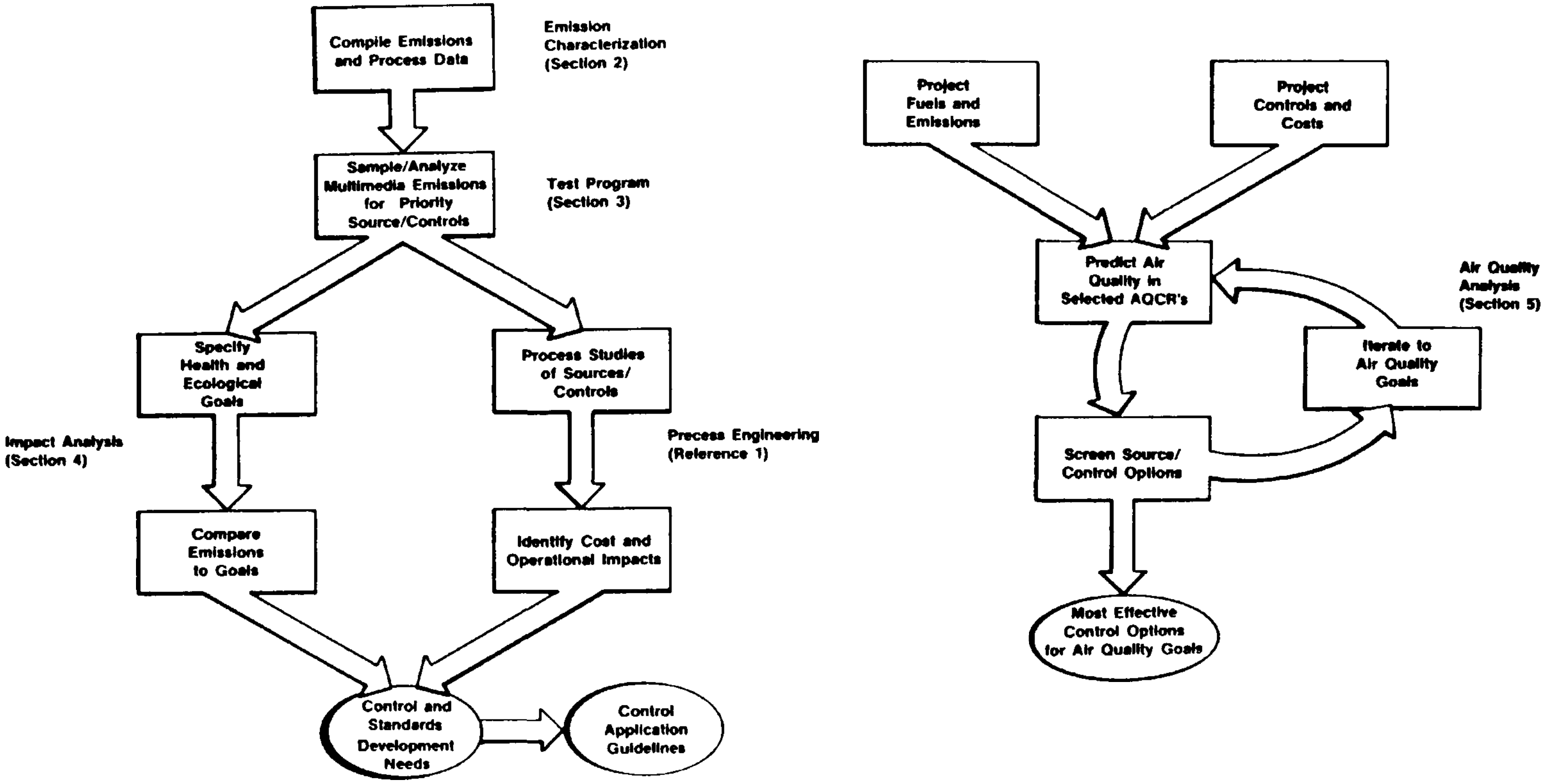

Figure 1. NO_x EA program elements.

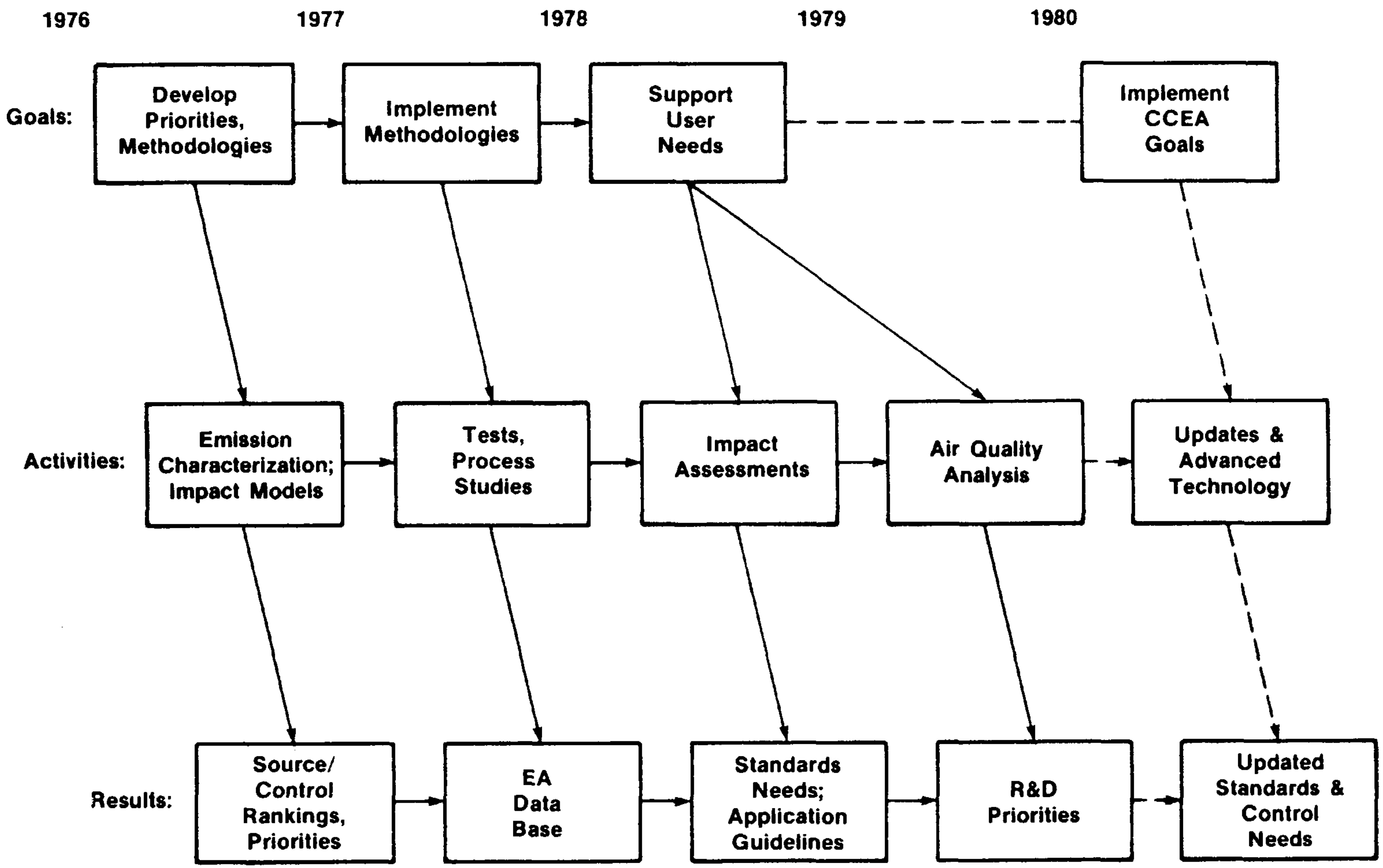

Figure 2. NO_x EA chronological sequence.

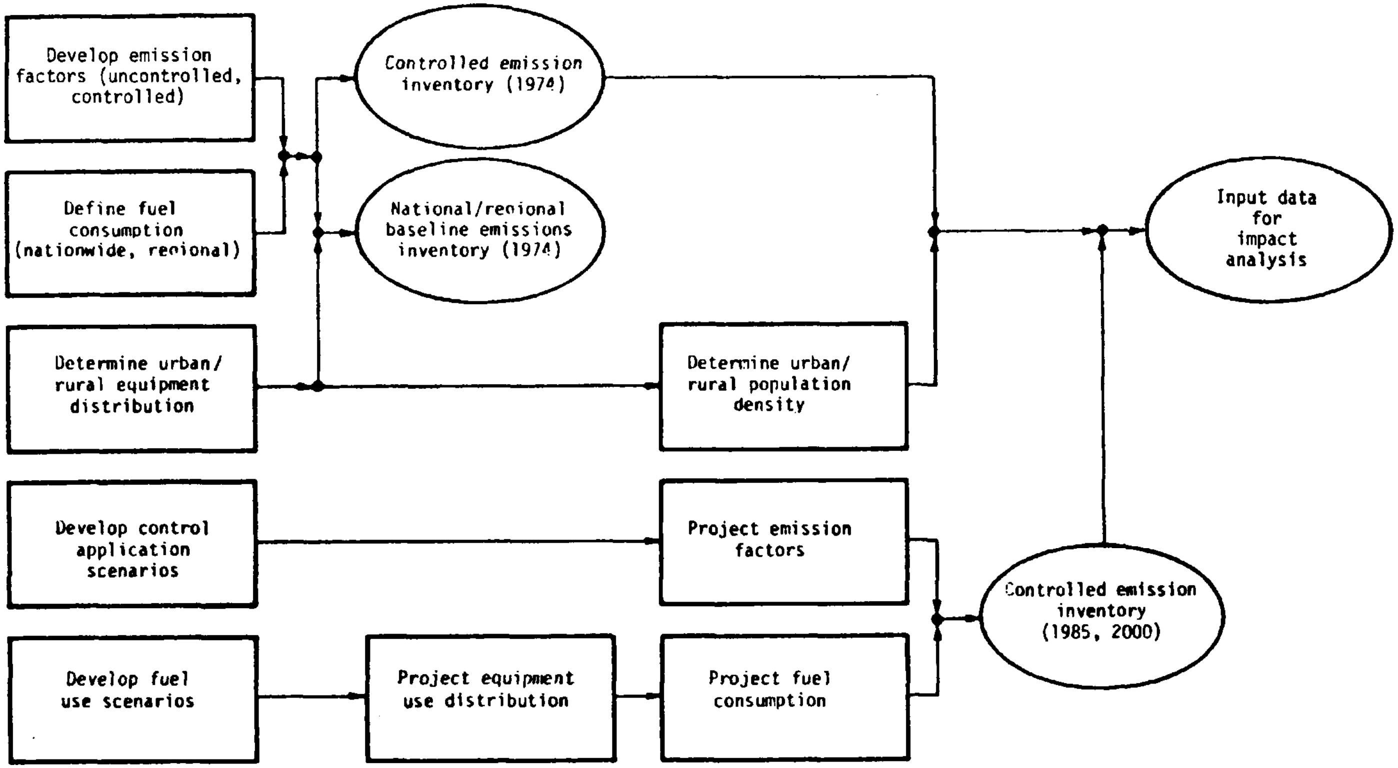

Figure 3. Emission characterization.

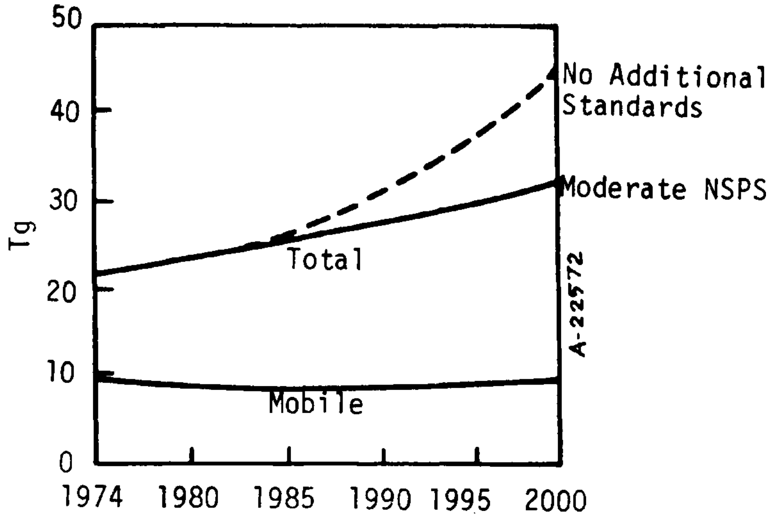

Figure 4. NO_x emission projections - high growth scenario.

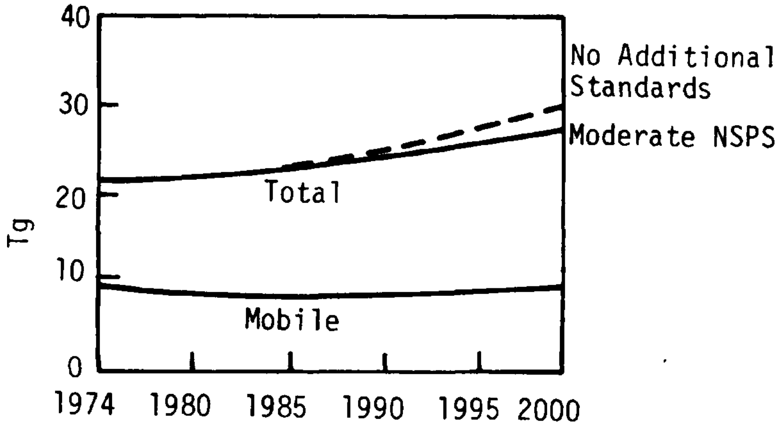

Figure 5. NO_x emission projections - low growth scenario.

TABLE I. STATIONARY SOURCE FUEL CONSUMPTION AND NO$_x$ EMISSIONS - 1974

Equipment Type	Firing Type	Fuel Type	Fuel Usage (PJ)	Baseline Emission Factors (ng NO$_2$/J)	Total NO$_x$ Emissions (Gg NO$_2$)
Utility Boilers	Tangential Boilers	Eastern Bitumin.	2624.0	275.0	721.6
		Central Bitumin.	1584.0	275.0	435.6
		Western Bitumin.	869.0	275.0	239.0
		Lignite	53.0	245.0	13.0
		High S Res. Oil	196.0	153.0	29.6
		Med S Res. Oil	492.0	153.0	74.2
		Low S Res. Oil	636.0	153.0	95.9
		Distillate Oil	36.0	153.0	5.4
		Natural Gas	1134.0	129.0	137.9
	Wall Fired Boilers, Dry	Eastern Bitumin.	1051.0	322.0	337.9
		Central Bitumin.	635.0	322.0	204.2
		Western Bitumin.	348.0	322.0	111.9
		Lignite	5.0	353.0	1.8
		High S Res. Oil	196.0	322.0	60.1
		Med S Res. Oil	493.0	322.0	151.1
		Low S Res. Oil	637.0	322.0	195.3
		Distillate Oil	169.0	322.0	51.8
		Natural Gas	2453.0	301.0	646.8
	Wall Fired Boilers, Wet	Eastern Bitumin.	461.0	537.0	247.6
		Central Bitumin.	279.0	537.0	149.8
		Western Bitumin.	153.0	537.0	82.2
		Lignite	6.0	378.0	2.3
	Opposed Wall Boilers, Dry	Eastern Bitumin.	293.0	322.0	94.0
		Central Bitumin.	176.0	322.0	56.6
		Western Bitumin.	97.0	322.0	31.2
		Lignite	9.0	353.0	3.2
		High S Res. Oil	79.0	322.0	24.2
		Med S Res. Oil	199.0	322.0	61.0
		Low S Res. Oil	258.0	322.0	79.1
		Distillate Oil	15.0	322.0	4.6
		Natural Gas	1258.0	301.0	352.2
	Opposed Wall Boilers, Wet	Eastern Bitumin.	130.0	537.0	69.8
		Central Bitumin.	78.0	537.0	41.9
		Western Bitumin.	43.0	537.0	23.1
		Lignite	12.0	378.0	4.5
	Cyclone Boilers	Eastern Bitumin.	158.0	559.0	86.9
		Central Bitumin.	1292.0	559.0	710.2
		Lignite	137.0	374.0	51.2
		High S Res. Oil	12.0	219.0	2.5
		Med S Res. Oil	28.0	219.0	5.9
		Low S Res. Oil	37.0	219.0	7.8
		Natural Gas	61.0	241.0	14.7
	Vertical & Stoker Boilers	Anthracite	109.0	269.0	29.3
		Eastern Bitumin.	110.0	269.0	29.6
		Central Bitumin.	110.0	269.0	29.6
Packaged Boilers	Wall Fired W-Tube > 29.3 MW^a	Distillate Oil	85.0	322.0	27.4
		Natural Gas	928.0	301.0	279.3
		Process Gas	130.0	301.0	39.1
		Bit/Lig Coal	510.0	322.0	164.2
		Residual Oil	637.0	322.0	205.1
	Stoker W-Tube > 29.3 MW^a	Bit/Lig Coal	466.0	269.0	125.4
	Single Burner W-T < 29.3 MW^a	Distillate Oil	103.0	67.5	7.0
		Natural Gas	1690.0	98.9	167.1
		Process Gas	130.0	98.9	12.9
		Bit/Lig Coal	317.0	322.0	102.1
		Residual Oil	595.0	184.0	109.5

T-957

[a] Heat input

[b] Shaft output

[c] CI = compression ignition; SI = spark ignition

TABLE I. Continued

Equipment Type	Firing Type	Fuel Type	Fuel Usage (PJ)	Baseline Emission Factors (ng NO_2/J)	Total NO_x Emissions (Gg NO_2)
Packaged Boilers (Continued)	Scotch Firetube <29.3 MW[a]	Distillate Oil	446.0	67.5	30.1
		Natural Gas	972.0	98.9	96.1
		Process Gas	19.0	98.0	1.9
		Residual Oil	945.0	184.0	173.9
	Firebox Firetube <29.3 MW[a]	Distillate Oil	403.0	67.5	27.2
		Natural Gas	899.0	98.9	88.9
		Process Gas	19.0	98.9	1.9
		Residual Oil	609.0	184.0	112.1
	Stoker Fired W-T <29.3 MW[a]	Anthracite	21.0	179.0	3.8
		Bit/Lig Coal	1533.0	179.0	274.4
	Cast Iron	Distillate Oil	181.0	67.5	12.2
		Natural Gas	264.0	51.6	13.6
		Residual Oil	195.0	184.0	35.9
	Stoker F-T <29.3 MW[a]	Anthracite	42.0	179.0	7.5
		Bit/Lig Coal	556.0	179.0	99.5
	HRT <29.3 MW[a]	Distillate Oil	263.0	67.5	17.8
		Natural Gas	535.0	98.9	52.9
		Residual Oil	370.0	184.5	68.3
	Res/Comm Steam & Hot Water	Anthracite	14.0	179.3	2.5
		Distillate Oil	880.0	55.0	48.4
		Natural Gas	737.0	34.4	25.4
		Bit/Lig Coal	11.0	179.3	2.0
		Residual Oil	69.0	162.0	11.2
Warm Air Furnaces	Warm Air Central Furnace	Natural Gas	3091.0	34.4	106.3
		Oil	1405.0	61.0	85.7
	Warm Air Space Heater	Natural Gas	1451.0	34.4	49.9
		Oil	727.0	61.0	44.3
	Miscellaneous Combustion	Natural Gas	1000.0	34.4	34.4
Gas Turbines	Simple Cycle >15 MW[b]	Distillate Oil	264.0	365.0	96.4
		Natural Gas	212.0	195.0	41.3
	Simple Cycle 4.0 to 15 MW[b]	Distillate Oil	579.0	365.0	211.3
		Natural Gas	468.0	194.0	90.8
	Simple Cycle <4.0 MW[b]	Distillate Oil	1.0	365.0	.4
		Natural Gas	1.0	194.0	.2
Reciprocating IC Engine	C.I. >75 kW/cyl[b]	Distillate Oil	54.0	1741.0	94.0
		Dual (oil & gas)	70.0	1023.0	71.6
	S.I. >75 kW/cyl[b]	Natural Gas	813.0	1552.0	1261.8
	C.I. 75 kW to 75 kW/cyl[b]	Distillate Oil	129.0	1741.0	224.6
	S.I. 75 kW to 75 kW/cyl[b]	Natural Gas	43.0	1552.0	66.7
		Gasoline	84.0	1195.0	100.4
	S.I. <75 kW[b]	Gasoline	49.0	774.0	37.9

T957

[a] Heat input

[b] Shaft output

[c] CI = compression ignition; SI = spark ignition

TABLE I. (Concluded)

Equipment Type	Firing Type	Fuel Type	Production (Tg)	Baseline Emission Factors g/kg product	Total NO_x Emissions (Gg NO_2)
Ind. Process Combustion	Cement Kilns	Processed Mat'l	76.96	1.3	100.0
	Glass Melting Furnaces	Processed Mat'l	15.42	3.68	56.7
	Glass Annealing Lehrs	Processed Mat'l	15.42	0.69	10.6
	Coke Oven Underfire	Processed Mat'l	57.01	0.07	4.0
	Steel Sintering Machines	Processed Mat'l	48.51	0.52	25.2
	Open Hearth Furnace (oil)	Processed Mat'l	32.27	0.62	20.0
	Brick & Ceramic Kilns	Processed Mat'l	31.58	0.25	7.9
	Cat Cracking (FCCU)	Processed Mat'l	2294.0[a]	.2[b]	45.9
	Refinery Flares	Processed Mat'l	7.8[c]	1.0[d]	7.8
	Iron & Steel Flares	Processed Mat'l	.3[c]	1.0[d]	0.3
	Ref. HTR. Nat. Draft,	Gas	1119.0[e]	70.1[f]	78.4
	Ref. HTR. Nat. Draft,	Oil	256.5[e]	154.8[f]	39.7
	Ref. HTR. For. Draft,	Gas	128.2[e]	110.5[f]	14.2
	Ref. HTR. For. Draft,	Oil	80.6[e]	184.5[f]	14.9

T-957

[a] 10^8 ℓ feed

[b] g/ℓ feed

[c] Gg NO_2/yr

[d] production is not quantifiable, estimate of NO_x is made in fuel consumption column

[e] PJ

[f] ng/J

TABLE II. SUMMARY OF 1974 STATIONARY SOURCE NO_x[a] EMISSIONS BY FUEL TYPE

Sector	NO_x Production Gg/yr (% of total)			Total by Sector	Cumulative (%)
	Coal	Oil	Gas	(% of total)	
Utility Boilers	3810 (31.7)	848 (7.0)	1156 (9.6)	5810 (48.3)	48.3
Packaged Boilers[b]	781 (6.5)	886 (7.4)	779 (6.5)	2446 (20.3)	68.6
Warm Air Furnaces	--	130 (1.1)	190 (1.6)	320 (2.7)	71.3
Gas Turbines	--	308 (2.6)	132 (1.1)	440 (3.7)	75.0
Reciprocating IC Engines	--	456[c] (3.8)	1400[d] (11.6)	1856 (15.4)	90.4
Industrial Process Heating	--	--	--	426 (3.5)	93.9
Noncombustion	--	--	--	193 (1.6)	95.5
Incineration	--	--	--	40 (0.3)	95.8
Fugitive	--	--	--	498 (4.2)	100.0
Total	4591 (38.2)	2628 (21.8)	3653 (30.4)	12,029 (100.0)	

[a] NO_2 basis

[b] Includes steam and hot water commercial and residential heating units

[c] Includes gasoline

[d] Includes dual fuels (oil and gas)

TABLE III. NO_x[a] MASS EMISSION RANKING OF STATIONARY COMBUSTION EQUIPMENT FOR 1974

Rank	Sector	Equipment Type	Fuel	Annual NO_x (Mg)	Cumulative (Mg)	Cumulative[e] (percent)
1	Utility Boilers	Tangential	Coal	1,410,000	1,410,000	11.7
2	Reciprocating IC Engines	>75 kW/cyl[c]	Gas	1,262,000	2,672,000	22.2
3	Utility Boilers	Wall Firing	Coal	1,137,000	3,809,000	31.7
4	Utility Boilers	Cyclone Furnace	Coal	848,300	4,657,300	38.7
5	Utility Boilers	Wall Firing	Gas	646,800	5,304,100	44.1
6	Utility Boilers	Wall Firing	Oil	458,300	5,762,400	47.9
7	Utility Boilers	Horizontally Opposed	Gas	352,200	6,114,600	50.8
8	Reciprocating IC Engines	75 kW to 75 kW/cyl[c]	Oil[d]	325,000	6,439,600	53.5
9	Utility Boilers	Horizontally Opposed	Coal	324,500	6,764,100	56.2
10	Packaged Boilers	Watertube >29 MW[b]	Gas	318,500	7,082,600	58.9
11	Packaged Boilers	Watertube Stoker <29 MW[b]	Coal	278,170	7,360,770	61.2
12	Packaged Boilers	Watertube >29 MW[b]	Oil	232,480	7,593,250	63.1
13	Utility Boilers	Tangential	Oil	205,100	7,798,350	64.8
14	Packaged Boilers	Firetube Scotch	Oil	203,900	8,002,250	66.5
15	Packaged Boilers	Watertube <29 MW[b]	Gas	180,000	8,182,250	68.0

T-958

[a] NO_2 basis

[b] Heat input

[c] Power output

[d] Includes both distillate oil and gasoline

[e] Based on percent of total stationary source NO_x emissions

TABLE IV. NO_x EA FIELD TEST PROGRAM

Source Category	Description	Test Points (Unit Operation)	Sampling Protocol	Test Collaborator
Coal-fired Utility Boiler	180 MW tangential; twin furnace, 12 burners/ furnace, three elevations; cyclone, two ESP's for particulate control	Baseline Biased Firing (2) BOOS (2)	Continuous NO_x, SO_2, CO, CO_2, O_2 Inlet to first ESP: -- SASS -- Method 5 -- Method 8 -- Gas grab (C_1-C_6 HC) Outlet of first ESP: -- SASS -- Method 5 -- Method 8 Bottom ash Hopper ash (first ESP, cyclone) Fuel Operating data	TVA
Coal-fired Utility Boiler	500 MW opposed wall fired; 24 burners, three elevations; ESP for particulate control	Baseline BOOS (2)	Continuous NO_x, SO_2, CO, CO_2, O_2 ESP inlet -- SASS -- Method 5 -- Method 8 -- Gas grab (C_1-C_6 HC) ESP outlet -- SASS -- Method 5 -- Method 8 -- Gas grab (C_1-C_6 HC) Bottom ash ESP hopper ash Fuel Operating data Bioassay	Exxon
Oil-fired Utility Boiler	740 MW opposed wall fired; 48 burners, six elevations	Baseline FGR FGR + OFA	Continuous NO_x, SO_2, CO, CO_2, O_2 SASS Method 5 Method 8 Gas grab (C_1-C_6 HC) Fuel Operating data Bioassay	New test start

TABLE IV. Concluded

Source Category	Description	Test Points (Unit Operation)	Sampling Protocol	Test Collaborator
Coal-fired Industrial Boiler	Traveling grate spreader stoker, 44 kg/s (350,000 lb/hr); ESP for particulate control; wet scrubber for SO_x control	Baseline LEA + high OFA	Continuous NO_x, SO_2, CO, CO_2, O_2 Boiler exit: -- SASS -- Method 5 -- Shell-Emeryville -- Gas grab (C_1-C_6 HC) ESP outlet -- SASS -- Method 5 -- Shell-Emeryville -- Gas grab (C_1-C_6 HC) Bottom ash Cyclone hopper ash Fuel Operating data	KVB
Coal-fired Industrial Boiler	Traveling grate spreader stoker, 32 kg/s (250,000 lb/hr) ESP for particulate control	Baseline LEA + High OFA	Continuous NO_x, SO_2, CO, CO_2, O_2 Boiler exit: -- SASS -- Method 5 -- Shell-Emeryville -- Gas grab (C_1-C_6 HC) ESP Outlet -- SASS -- Method 5 -- Shell-Emeryville -- Gas grab (C_1-C_6 HC) Bottom ash ESP hopper ash Fuel Operating data Bioassay	KVB
Oil-fired Gas Turbine	60 MW GE MS 7001 C machine	Baseline Maximum water injection	Continuous NO_x, SO_2, CO, CO_2, O_2 SASS Method 5 Method 8 Fuel Water Operating data Bioassay	General Electric
Oil-fired Residential Heating Unit	Blue Ray low NO_x furnace, Medford, New York	Continuous Cycling	Continuous NO_x, SO_2, CO, CO_2, O_2 SASS Method 5 Method 8 Fuel	New test start with IERL/RTP

TABLE V. ELEMENTAL ANALYSIS: SPECIES DETERMINED

Antimony (Sb)
Arsenic (As)
Barium (Ba)
Beryllium (Be)
Bismuth (Bi)
Boron (B)
Cadmium (Cd)
Chromium (Cr)
Cobalt (Co)
Copper (Cu)
Iron (Fe)
Lead (Pb)
Manganese (Mn)
Mercury (Hg)
Molybdenum (Mo)
Nickel (Ni)
Selenium (Se)
Tellurium (Te)
Thallium (Ti)
Tin (Sn)
Titanium (Ti)
Vanadium (V)
Zinc (Zn)

TABLE VI. POM ANALYSIS: SPECIES DETERMINED

Anthracene
Anthanthrene
Benz(a)anthracene
Benzo(g,h,i)perylene
Benzo(a)pyrene
Benzo(e)pyrene
Coronene
Fluoranthene
Phenanthrene
Perylene
Pyrene

TABLE VII. ANION ANALYSIS: SPECIES DETERMINED

Chloride (Cl^-)
Fluoride (F^-)
Nitrate (NO_3^-)
Cyanide (CN^-)
Sulfate (SO_4^{2-})
Ammonium (NH_4^+)

TABLE VIII. BIOASSAY ANALYSIS PROTOCOL

Sample Type	Bioassay Test Protocol	Sample Size Requirements
SASS cyclones, 10μ + 3μ	Microbial Mutagenesis Cytotoxicity, WI-38	1.0g 0.5g
SASS cyclones, 1μ + filter	Microbial Mutagenesis Cytotoxicity, WI-38	1.0g 0.5g
XAD-2 extract	Microbial Mutagenesis Cytotoxicity, RAM	50 mℓ 50
Bottom ash	Microbial Mutagenesis Cytotoxicity, WI-38 Rodent Acute Toxicity Freshwater Algal Bioassay Freshwater Static Bioassay	1.0g 0.5g 100g 50 kg (200 ℓ if sluiced)
ESP Hopper ash	Microbial Mutagenesis Cytotoxicity, WI-38 Rodent Acute Toxicity Freshwater Algal Bioassay Freshwater Static Bioassay	1.0g 0.5g 100g 50 kg

TABLE IX. ANALYSIS RESULTS FOR A TANGENTIALLY COAL-FIRED UTILITY BOILER: FLUE GAS, INORGANICS

Test	BASELINE	BIAS (test 1)	BOOS (test 2)
Heat Input (% of baseline)	100	100.9	92.4
Emissions $\frac{\mu g}{m^3}$ dry			
NO$_x$(ppm @ 3% O$_2$ dry)	$1.16\text{x}10^{6}$(490)	$7.35\text{x}10^{5}$ (336)	$6.54\text{x}10^{5}$(304)
SO$_2$(ppm @ 3% O$_2$ dry)	$4.18\text{x}10^{6}$(1668)	$3.5\text{x}10^{6}$ (1354)	$4.21\text{x}10^{6}$(1591)
SO$_3$(ppm @ 3% O$_2$ dry)	$1.45\text{x}10^{4}$(3)	$1.32\text{x}10^{4}$(3)	9580 (3)
CO (ppm @ 3% O$_2$ dry)	$3.07\text{x}10^{4}$(28.6)	$4.58\text{x}10^{4}$(35.0)	$3.19\text{x}10^{4}$(21.7)
CO$_2$(%)	$2.72\text{x}10^{8}$(13.9)	$2.82\text{x}10^{8}$(14.4)	$2.86\text{x}10^{8}$(14.6)
O$_2$ (%)	(5.2)	(4.7)	(4.4)
Particulate	$6.3\text{x}10^{5}$	$6.7\text{x}10^{5}$	$4.3\text{x}10^{5}$
Antimony	3.9	<2.6	<2.6
Arsenic	95	77	81
Barium	$2.25\text{x}10^{3}$	$1.7\text{x}10^{3}$	$1.5\text{x}10^{3}$
Beryllium	9.0	11	7.2
Bismuth	<44	<55	$2.3\text{x}10^{2}$
Boron	-	-	$8.7\text{x}10^{2}$
Cadmium	<1.8	<2.4	<2.1
Chromium	$1.69\text{x}10^{3}$	$4.7\text{x}10^{2}$	$2.4\text{x}10^{3}$
Cobalt	66	75	89
Copper	$2.8\text{x}10^{2}$	$3.3\text{x}10^{2}$	$3.2\text{x}10^{2}$
Iron	$4.5\text{x}10^{4}$	$3.3\text{x}10^{4}$	$3.3\text{x}10^{4}$
Lead	74	86	61
Manganese	$2.4\text{x}10^{2}$	$1.3\text{x}10^{2}$	$1.9\text{x}10^{2}$
Mercury	1.8 <3.1	<0.06	3.5< 5.5
Molybdenum	$1.5\text{x}10^{2}$	< 55	$8.7\text{x}10^{2}$
Nickel	$8.0\text{x}10^{2}$	$2.6\text{x}10^{2}$	$1.5\text{x}10^{3}$
Selenium	9.9	3.0	< 2.1
Tellurium	< 4.1	< 4.0	< 3.7

TABLE X. FLUE GAS POTENTIAL DEGREE OF HAZARD - INORGANICS; 180 MW TANGENTIAL COAL-FIRED UTILITY BOILER

	BASELINE	BIAS	BOOS
NO_x	129	84	73
SO_2	322	269	324
SO_3	15	13	9.6
CO	0.77	1.1	0.80
CO_2	30	31	32
Be	4.5	5.5	3.6
Ba	4.5	3.4	3.0
As	48	39	41
Ti	1	0.95	0.60
N (Mainly NH_4)	0.07	0.22	6.1
SO_4	6.5	3.9	2.1
Chlorides	0.68	1	2.1

TABLE XI. POTENTIAL TOXIC UNIT DISCHARGE RATES (g/s) - 180 MW TANGENTIAL COAL-FIRED UTILITY BOILERS - INORGANICS

	BASELINE	BIAS	BOSS
Flue Gas	$4.3x10^7$	$3.5x10^7$	$3.7x10^7$
Cyclone Ash	$1.9x10^4$	$1.6x10^4$	$1.6x10^4$
ESP Ash	$6.1x10^3$	$6.1x10^3$	$5.1x10^3$
Bottom Ash Slurry	$5.7x10^4$	$5.3x10^4$	$4.2x10^4$

TABLE XIII

TABLE XIII. MULTISPECIES IMPACT RANKING FOR STATIONARY SOURCES

Rank	Sector	Equipment Type	Fuel	Normalized Impact Factor
1	Packaged Boilers	Stoker Firing WT[c] < 29 MW[a]	Coal	1.00
2	Packaged Boilers	Stoker Firing FT[d] < 29 MW[a]	Coal	0.83
3	Utility Boilers	Tangential	Coal	0.21
4	Utility Boilers	Wall Firing	Coal	0.16
5	Packaged Boilers	Wall Firing WT[c] > 29 MW[a]	Coal	0.12
6	Packaged Boilers	Stoker Firing WT[c] > 29 MW[a]	Coal	0.11
7	Utility Boilers	Vertical and Stoker	Coal	0.085
8	Utility Boilers	Cyclone	Coal	0.061
9	Utility Boilers	Horizontally Opposed	Coal	0.031
10	Utility Boilers	Tangential	Oil	0.0039
11	Utility Boilers	Wall Firing	Oil	0.0033
12	Utility Boilers	Horizontally Opposed	Oil	0.0017
13	Packaged Boilers	Wall Firing WT[c] > 29 MW[a]	Oil	0.0010
14	Packaged Boilers	Scotch FT[d] < 29 MW[a]	Oil	0.0008
15	Packaged Boilers	Firebox FT[d] < 29 MW[a]	Oil	0.0005
16	Utility Boilers	Tangential	Gas	0.0005
17	Packaged Boilers	Scotch FT[d]	Gas	0.0004

T-1524

[a] Heat input
[b] Heat output
[c] Watertube
[d] Firetube

TABLE XIV. SUMMARY OF CONTROL LEVELS REQUIRED TO MEET THE ANNUAL AVERAGE NO_2 STANDARD IN SAN FRANCISCO, AQCR (030)

Case	BYR[a] = 76 $\mu g/m^3$			BYR = 101 $\mu g/m^3$		
	PP[b] = 1.0 MS[c] = 1.0	PP = 0.5 MS = 1.2	PP = 0.2 MS = 1.0	PP = 1.0 MS = 1.0	PP = 0.5 MS = 1.2	PP = 0.2 MS = 1.0
Nominal Growth[e]	0(67)[d] / 0(83)	0(64) / 0(80)	0(65) / 0(81)	0(88) / 3	0(85) / 3	0(86) / V
Low Mobile[f]	0(60) / 0(66)	0(56) / 0(62)	0(57) / 0(64)	0(79) / 0(88)	0(74) / 0(81)	0(75) / 0(84)
High Stationary[g]	0(75) / 0(85)	0(69) / 0(81)	0(68) / 0(82)	0(100) / 3	0(91) / 3	0(90) / V

1985 / 2000

T-1293

TABLE XV. SUMMARY OF CONTROL LEVELS REQUIRED TO MEET THE ANNUAL AVERAGE NO_2 STANDARD IN ST. LOUIS, AQCR (070)

Case	BYR[a] = 76 $\mu g/m^3$			BYR = 85 $\mu g/m^3$		
	PP[b] = 1.0 MS[c] = 1.0	PP = 0.5 MS = 1.2	PP - 0.2 MS = 1.0	PP = 1.0 MS = 1.0	PP = 0.5 MS = 1.2	PP = 0.2 MS = 1.0
Nominal Growth[e]	0(77)[d] / 0(96)	0(75) / 0(98)	0(76) / 1	0(86) / 2	0(84) / 2	0(85) / 3
Low Mobile[f]	0(73) / 0(85)	0(70) / 0(81)	0(70) / 0(84)	0(82) / 0(95)	0(79) / 0(91)	0(78) / 0(94)
High Stationary[g]	0(80) / 2	0(79) / 2	0(80) / 2	0(90) / 3	0(88) / 3	0(92) / V

1985 / 200

T-1292

[a] BYR -- Base year ambient concentration for calibration

[b] PP -- Powerplant weighting factor

[c] MS -- Mobile source weighting factor

[d] Numbers in parentheses indicate annual average concentration in $\mu g/m^3$. If no number given, annual average equals or exceeds 100 $\mu g/m^3$.

[e] Stationary source growth less than historical, mobile sources grow at 3.5%/yr, 0.62 g/km in 1981

[f] Stationary source growth less than historical, mobile sources grow at 1.0%/yr, 0.25 g/km in 1985

[g] Stationary source growth at approximately historical rates, mobile sources grow at 3.5%/yr, 0.62 g/km in 1981

TABLE XVI. AQCR's INVESTIGATED FOR NO_x CONTROL REQUIREMENTS

		Low -- Recorded Annual Average NO_2 ($\mu g/m^3$) 1972 - 1975	High -- Rolling Quarter Average NO_2 ($\mu g/m^3$) 1972 - 1975
Los Angeles	(024)	132	182
Chicago	(067)	96	121
Philadelphia	(045)	83	121
New York City	(043)	99	113
Denver	(036)	88	110
San Francisco	(030)	76	101
Pittsburgh	(197)	62	98
St. Louis	(070)	76	85

TABLE XVII. DEFINITION OF STATIONARY SOURCE NO_x CONTROL LEVELS

Level[a]	
0	• No controls (assumes 1971 NSPS for large boilers is met)
1	• 40 - 80 percent control of new residential and commercial furnaces • 6 - 16 percent control by low excess air for industrial and utility boilers
2	• Staged combustion, flue gas recirculation, low-NO_x burners and other advanced designs for boilers • Operating adjustments and new design for IC engines • Water injection for gas turbines (30% reduction)
3	• Ammonia injection for boilers (50% reduction beyond level 2 controls)
V	• Combustion control limits exceeded, flue gas treatment required

[a] Control levels are ordered by increasing cost of the controls. Within each level controls are applied in order of increasing cost.

AN OVERVIEW OF THE CONVENTIONAL COMBUSTION ENVIRONMENTAL ASSESSMENT PROGRAM

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ABSTRACT

The conventional combustion of fossil fuels for heat and electricity production has been the foundation of today's industrialized society. In fact, over 90 percent of the total U.S. energy needs are still met by fossil fuels. The associated environmental effects of conventional combustion processes, however, are significant and span across the air, water, and land media. These multimedia effects are not separate and distinct, but rather are all interrelated, defining a systemic problem. The scientific and managerial approach to solving such problems has to be by necessity comprehensive and holistic in nature.

The Conventional Combustion Environmental Assessment (CCEA) program, sponsored by the Industrial Environmental Research Laboratory in Research Triangle Park (IERL-RTP), North Carolina, is designed to comprehensively identify and assess the total environmental effects of combusting fossil fuels in all conventional processes. The program integrates ongoing and planned R&D activities into a coherent and unified environmental assessment structure. The overall goals of this program are aimed at providing a base of sound information for use by energy/environmental decision-makers for:

- Standards Development
- Control Technology Development
- Energy/Environmental Policy Formulation
- Allocation of Resources

The program currently consists of a defined set of program goals and objectives, an explicit methodology for conducting a comprehensive environmental assessment, an analytical procedure to identify, evaluate, and integrate the programmatic contents of individual projects, and a management structure to administer the program. The CCEA program currently consists of six projects. The paper will describe the above items and will discuss support given to EPA standard-setting program offices by the CCEA outputs.

SECTION 1

INTRODUCTION AND BACKGROUND

It is not a mere cliché to say that the world of today is quite different from that of yesterday. Whereas most of human history has focused on technological solutions to the problems of the world as we found it, the critical issues of today and tomorrow involve the problems of the world as our technology has made it. In fact, it is the very success of yesterday's technological solutions that has led to the critical problems of today and tomorrow.

A classic example of such a problem is the degradation of the environment resulting from the use of fossil fueled combustion technologies. The development of reliable fossil-fueled combustion technologies has been the foundation of today's industrialized society. In fact, approximately 95 percent (about 70 x 10^{15} Btu) of the total U.S. energy needs are still met by fossil-fueled combustion. Conventional methods of converting fossil fuels to usable energy forms, however, have been a significant source of deleterious environmental impacts. The release of sulfur dioxide from conventional combustion of coal and oil, for example, is a direct cause of increased acidity in rainfall. Carbon dioxide, another major byproduct of conventional combustion, has the potential to seriously affect the world climate by contributing to the so-called "greenhouse" effect. In addition, the introduction of toxic heavy metals such as cadmium and arsenic, and potentially carcinogenic organic compounds such as polycyclic organic matter (POM) into the ground and surface waters as an indirect result of conventional combustion technologies pose serious threats to human health. Control of the environmental impacts from conventional fossil-fueled combustion is one of the major problems facing us today.

The scientific, engineering, and managerial approach to this environmental problem has to be, by necessity, quite different from the traditionally reactive, single objective, viewpoint of past research. The conventional combustion of fossil fuels has multimedia impacts which affect the air, land, and water. Furthermore, these impacts are not separate and distinct; rather, they are all interrelated and involve delicate balances and tradeoffs.

From the scientific point of view, it is essential to identify and understand the environmental relationships that exist between the many orders of indirect impacts. For example, the disposal of fly ash from coal-fired power plants has a direct impact on the land quality of the disposal sites. Leaching of chemical compounds and heavy metals from the disposal sites has an indirect (second-order) impact on the quality of the ground and/or surface water. This in turn may have third-order impacts on the ecology of the area. It is important to identify all direct and indirect impacts. Another major scientific aspect is the multi-pollutant synergistic impacts on human health and the environment of the various pollutants emitted by conventional combustion systems. For example, although polycyclic aromatic hydrocarbons (PAH) are generally toxic, their potency as carcinogens is enhanced by their preferential adsorption on small particles of certain materials such as iron oxide. A similar synergistic intensification may exist between fine particles and sulfur dioxide.

From the engineering point of view, an important concept in dealing with technologically induced environmental problems is the concept of cross-impacts. Since the environment is esentially a closed system, technology to control one pollutant or media has some relative cross-impact on another pollutant or media. For example, flue gas scrubbing to remove SO_2 and particulates significantly increases the amount of solid wastes to be disposed of in an environmentally acceptable manner. The secondary environmental impacts caused by pollutant control technologies themselves are an important engineering problem.

The management of environmental R&D efforts to identify and assess the full health and ecological implications of conventional fossil-fueled combustion must also be approached in a comprehensive and unified manner.

In addition to evaluating the full range of relationships that exist among environmental impacts, communication with environmental control technology development and emission standard setting activities must be closely maintained. The programmatic efforts of these three general areas must be properly coordinated to ensure effective and efficient solutions to the environmental problems.

The Environmental Protection Agency, the lead Federal organization responsible for the identification and control of adverse environmental impacts of pollutant emissions,is aware of the importance of conducting such environmental studies in a holistic, coordinated manner. This awareness has led to the development of major comprehensive assessment programs in such emerging energy technology areas as coal liquefaction, low/medium btu gasification, high btu gasification, and fluidized-bed combustion. Since these technologies are still in the development or demonstration stage, EPA is investigating all potential environmental problems now to ensure that they will have minimal health and ecological impacts when they are fully commercialized.

In the area of conventional, fossil-fueled combustion process, however, existing wide-spread use of the technology precludes a completely proactive environmental assessment prior to commercialization. The majority of the R&D efforts to date have been narrowly defined and reactive in nature, involving such issues as identification of emissions from particular processes, evaluation of the effects of specific compounds, or development of technology to control single pollutants. While data generated by these various efforts provide an important base of information, a full assessment of the environmental effects of conventional fossil-fueled combustion processes is still necessary.

SECTION 2

OVERALL CCEA PROGRAM STRUCTURE

In response to this need, the Environmental Protection Agency's Industrial Environmental Research Laboratory at Research Triangle Park (EPA/IERL-RTP), North Carolina, established the Conventional Combustion · Environmental Assessment (CCEA) program. Initiated in early 1977, the CCEA is chartered to assess comprehensively the environmental, economic, and social impacts of multimedia emissions of pollutants from conventional combustion processes, and to recommend measures for controlling adverse effects within acceptable limits. The program utilizes information generated by past studies and integrates relevant ongoing and planned R&D efforts into an overall environmental assessment structure, coordinates their activities, and serves as a centralized base of information. The CCEA is designed to be both reactive in addressing immediate problems and proactive in undertaking research to identify and recommend solutions to other major environmental problems that may be anticipated in the future.

OBJECTIVES AND SCOPE

The principal objectives of the CCEA program are to identify and assess information from all relevant sources in order to:

(1) determine the extent to which available information can be utilized to assess the total environmental, economic, energy impacts of stationary conventional combustion processes.

(2) identify and acquire additional information needed for such assessment.

(3) define the requirements for modifications or additional development of control technology.

(4) define the requirements for modified or new standards to regulate pollutant emissions.

The results of the CCEA program are aimed at providing a base of sound information for use by energy/environmental decision-makers for:

- Standards Setting
- Control Technology Development
- Policy Formulation
- Resource Allocation

Although the program is comprehensive in its approach and subject matter, there are some major boundaries that shape and focus the efforts of the program. The scope of the CCEA program can be briefly delineated as follows:

- The program is concerned with stationary conventional combustion processes and is focused principally on equipment and combustion processes used in the utility, industrial, commercial/institutional, and residential sectors.
- The program addresses environmental effects that result directly from the operations of the combustion process itself, as well as those that result from the operation of equipment to control the release of pollutants from the combustion process, such as leachate from fly ash impoundment basins.
- The program addresses non-environmental criteria such as social, economic, and political/institutional effects.
- The program also addresses environmental effects from the conventional processing and storage of fuels at the combustion site, such as the crushing of coal at a power plant.
- The program does not address the effects of fuel processing and storage prior to delivery to the combustion site, or during transportation of the fuel.
- The program addresses environmental effects of utilizing synthetic fuels in conventional combustion equipment.
- The program does not address the environmental effects of converting fossil fuels to synthetic fuels, whether performed at the combustion site or elsewhere; thus, it does not include consideration of the impacts of low-btu gasification of coal when the gasification equipment is within the battery limits of the power plant where the gas is burned.
- The program is not directly involved in design or development of combustion processes or pollution control technologies.
- The program is not directly involved in the setting or enforcement of emission standards.

COMPONENTS OF THE PROGRAM

The overall CCEA program structure currently consists of four major interrelated components:

(1) A defined set of long term CCEA program goals and intermediate term objectives.

(2) An explicit methodology to conduct a comprehensive environmental assessment of conventional combustion processes.

(3) An active set of seven major ongoing projects.

(4) A defined management structure to implement the program.

Each of these four CCEA program components are discussed briefly below.

Goals and Objectives

As discussed earlier, the overall aim of the CCEA program is: (1) to assess comprehensively the effects upon human health, the ecology, and the general environment of utilizing fossil fuels in stationary conventional combustion processes, and (2) to recommend measures for controlling adverse effects within acceptable limits.

Consistent with EPA mission, the principal use of environmental assessment information produced by the CCEA program will be to aid managerial decision making relative to environmental standards and pollution control technology development. In terms of this principal use, the program's long-term goals are more explicitly stated as follows:

- To assess the adequacy of existing technology to control the release of pollutants from stationary conventional combustion processes.
- To assess the need for modifications to existing control technology or for the development of new control technology and, if such needs exist, providing guidance and recommending priorities for the technology development effort.
- To assess the adequacy of existing emission or effluent standards designed to limit the release of pollutants to the environment.
- To assess the need for additional standards or modification of existing standards and, if such needs exist, providing guidance and recommending priorities for EPA's standard setting activities.

Supporting each of these goals are several intermediate objectives, most of which correspond to the outputs of various tasks or subtasks of the CCEA program and thus constitute useful products that will be developed during the course of the program.

The key technical and administrative objectives have been identified and categorized as follows:

Combustion Process/Pollutant Characterization Objectives

- Develop a unified, comprehensive base of existing data on combustion pollutants.
- Obtain essential new data from field tests.
- Characterize emissions/effluents from each major type of stationary conventional combustion process.

Health/Ecology/Environmental Impact Assessment Objectives

- Estimate quantities of pollutants released from stationary conventional combustion processes.
- Identify available models and other effects-estimating techniques.
- Develop quantitative estimates of health, ecological, and environmental effects (including associated economic costs) of pollutant emissions.
- Define priority areas for health/ecological/environmental impact studies.

Technology and Information Transfer Objectives

- Determine information needs of current/potential users of environmental assessment information.
- Transfer technical information to appropriate user organizations in a timely manner.

Control Technology Development Objectives

- Develop a comprehensive data base on the capabilities of existing technology to control the release of combustion pollutants to the environment and on the costs of applying such technology.
- Identify specific combustion processes and specific combustion pollutants for which additional control technology capability is needed to meet current standards.

Standards Development Objective

- Identify specific combustion processes and specific combustion pollutants for which modified or new standards are needed to limit pollutant emission/effluents to acceptable levels.

These goals and objectives are discussed in more complete detail in References 1 and 2.

Environmental Assessment Methodology

An environmental assessment (EA) is a special category of holistic investigative study that resulted from the growing awareness of the direct and indirect consequences of modern technology. In particular, an environmental assessment is defined here as an iterative procedure to develop a basis for ranking environmental problems and control needs. The iterative procedure involves:

- Determination of comprehensive environmental effects and control costs associated with various control options for specific sources, processes, or industries; and
- Comparison of the effects with existing standards, estimated environmental goals, and anticipated health impacts.

Within the context of the CCEA program, this definition includes socioeconomic and institutional effects, and cross-media impacts and tradeoffs, in addition to the environmental loading data, control costs, disposal options, bioassay specifications, and other factors included in the above definition. It must be emphasized, however, that environmental assessment activities of the CCEA program do not involve either the development or promotion of the combustion process or the development or promotion of technology to control emissions from the combustion process.

The overall procedure involves the following steps to be performed for each type of combustion process. The interrelations among these steps are shown diagrammatically in Figure 1. (This procedure, presented here in highly condensed form, is expected to be further refined and applied to major stationary conventional combustion processes over a period of about five years.)

Step 1. Characterization of Combustion Process (and Related Pollution Control Equipment) and Its Emission/Effluents.

For each principal type of combustion process the characteristics of fuels, control technology, and measurement/analytical techniques are identified. In particular, it identifies the quantities and characteristics of emissions and effluents.

Step 2. Identification of Health, Ecological, and Environmental Effects of Emissions/Effluents from the Combustion Process.

This step includes the identification of transport and transformation of the specific pollutants in the ambient environment, and anticipated response of the ecology and the exposed population in terms of morbidity/mortality rates, media degradation factors and other appropriate measures. Such factors must take into account background levels of pollutants from noncombustion sources.

Step 3. Development of Environmental Goals and Objectives

In the initial stages of this program, goals will be defined principally in terms of established standards or unofficial permissible media concentrations. In later stages, the set of goals may be expanded to include such factors as the promotion of a specific energy policy or direction of economic development.

Step 4. Comparison of Health/Ecological/Environmental Impacts of Stationary Conventional Combustion Processes Against Environmental Goals and Objectives

This comparison indicates whether established standards are being met, and other defined goals and objectives are being achieved.

This comparison may have three outcomes. (1) If it indicates that standards are, in fact, met and other goals and objectives have been met or can reasonably be expected to be achieved by ongoing R&D activities relating to the combustion process under study, then the EA procedure is completed for this process. (Repetition of the procedure is required for other processes.) (2) If there is some question of whether goals and objectives are being achieved, it may then be necessary to repeat the above three steps, possibly using better data or more precise analyses (see Figure 1). (3) If the comparison indicates that goals and objectives are not being achieved, then the EA procedure is continued as follows:

- Determine the Magnitude of Pollution Impacts from the Combustion Process

  Quantities of pollutants released from continued use of stationary conventional combustion processes at projected levels, ambient levels of such pollutants at appropriate geographic scales, and the degree of hazard (severity indices) associated with continued use of the combustion process are estimated.

- Evaluation of Alternative Control Strategies for Achieving Goals and Objectives

  Strategies that will contribute toward achievement of goals and objectives may include development of more effective pollution control technology or the use of other alternatives such as fuel switching and modification of combustion techniques; alternatively, the strategy may be to modify the existing standards or other goals/objectives.

This last step would indicate alternative approaches for meeting defined goals and objectives (e.g., suggested new technological or non-technological approaches for controlling pollutants from the combustion process under study); hence, it provides new input for iterating the entire EA procedure. Iterations may be required for each viable alternatives identified.

The comprehensive EA methodology is a complex and lengthy procedure which is described above only in general outline. Additional detail for the major steps in the procedure are indicated in Figure 2 and a more detailed description of the entire procedure is presented in Reference 3.

It should be noted that the comprehensive EA methodology described here is based in substantial measure on an EA methodology developed by the Energy Assessment and Control Division (EACD) of IERL-RTP. The EACD methodology has undergone extensive development and has gained widespread acceptance in the technical community. The relationship between the CCEA comprehensive EA methodology and prototype procedure developed at IERL-RTP is discussed in Reference 3.

Current Projects Within Program

The CCEA program currently includes seven major technical projects. Three of these projects were already ongoing when the CCEA program was established. Appropriate parts of these projects have been properly integrated into the program. The other four were initiated later to assist in planning, coordinating, and implementing the CCEA program. Each of these projects is briefly described below. A more detailed discussion, including project results will be given by the other speakers at this session.

- SURVEY OF PROJECTS CONCERNING THE ENVIRONMENTAL ASSESSMENT OF CONVENTIONAL COMBUSTION PROCESSES

  EPA Project Officer: Wade Ponder
  Contractor: Research Triangle Institute
  Term: March 1977 - May 1978 (initial phase only)

This project was initiated at approximately the same time as the initiation of the CCEA program planning effort. The project was undertaken in an effort to identify and evaluate major relevant R&D studies ongoing at that time within EPA, within other Federal organizations, and within non-government organizations. The major objectives of this project are to:

- Summarize information related to the CCEA program on a national basis.
- Determine the significance and utility of the information in meeting CCEA program objectives.
- Organize the survey information in a convenient format for subsequent use in the CCEA program.

The preliminary results of this survey were instrumental in the development of the CCEA program plan.[4]

- DEVELOPMENT OF A PROGRAM FOR THE ENVIRONMENTAL ASSESSMENT OF CONVENTIONAL COMBUSTION PROCESSES

EPA Project Officer: Wade Ponder
Contractor: Metrek Division/The MITRE Corporation
Term: February 1977 - June 1980

This is a major management and program planning project that was initiated to assist in formulation of the overall CCEA program structure. The major objectives of this project are to:

- Develop a coherent, unified methodology for assessing the environmental, economic, and energy impacts of continued and expanded use of stationary conventional combustion processes
- Define long-term goals and short-term objectives for the CCEA Program
- Develop analytical procedures to identify, evaluate and integrate CCEA related activities
- Provide assistance in procuring a CCEA systems contractor

- SYSTEMS ENGINEERING SERVICES FOR THE CCEA PROGRAM

EPA Project Officer: Wade Ponder
Contractor: Not identified at time of printing
Term: February 1979 - February 1981

The systems contractor will be the focal point in implementing the technical aspects of the CCEA program. This project will coordinate with the others to work within the previously established CCEA program plan to achieve stated goals and objectives. The major objectives of this project are to:

- Assess the effects of combustion pollutants on human health, ecology, and the general environment
- Evaluate the adequacy of existing technology to control the release of pollutants from Stationary Conventional Combustion Processes

- Assess the need for modification of additional control technology
- Assess the need for the development of additional control technology
- Evaluate the adequacy of existing emission or effluent standards
- Assess the need for the modification of existing standards
- Assess the need for the development of new standards

- ENVIRONMENTAL ASSESSMENT OF STATIONARY SOURCE NO_x CONTROL TECHNOLOGIES (NO_x EA)

  EPA Project Officers: Joshua S. Bowen, Robert E. Hall
  Contractor: Acurex Corporation
  Term: June 1976 - September 1979

The NO_x EA project was undertaken in response to the critical need to evaluate the environmental, economic, energy, and engineering implications of combustion modification technologies to control NO_x emissions. The overall goals of this project are: (1) to identify the multimedia environmental impacts of stationary combustion sources and NO_x combustion modification controls, and (2) to identify the most cost-effective, environmentally-sound combustion modification NO_x control systems for attaining and maintaining current and projected NO_x air quality standards to the year 2000.

- EMISSIONS CHARACTERIZATION OF CONVENTIONAL COMBUSTION SYSTEMS

  EPA Project Officers: Warren Peters, Wade Ponder
  Contractor: TRW
  Term: October 1976 - June 1980

This is a major CCEA project designed to address the "Combustion Process and Effluent Characterization" step of the environmental assessment methodology. The primary goal of this project is to develop extensive baseline data by identifying and characterizing the gaseous, liquid, and solid pollutants generated by fifty-one specific categories of uncontrolled stationary conventional combustion processes. These categories include the combinations of eight different combustion processes utilizing ten different fuel types in the four major use sectors of utility, industrial, residential, and commercial/institutional. Emissions data are being obtained through the use of the EPA Level 1 and Level 2 comprehensive sampling and analysis protocol. The final output of this project will include estimates of total pollutant emissions by each category of uncontrolled combustion process.

- COMPARATIVE ASSESSMENT OF OIL VS. COAL FIRING IN CONTROLLED INDUSTRIAL AND UTILITY BOILERS

EPA Project Officer: Wade H. Ponder
Contractor: TRW
Term: March 1977 - December 1978

One of the most important types of information needed for technological and policy decision making is the relative environmental impacts of firing coal vs. oil in well-controlled industrial and utility boilers. (Here, "well-controlled" implies the use of appropriate methods of reducing emissions of SO_2 and particulate matter to meet applicable emission standards for these pollutants.) Such information would facilitate the formulation of policy pertaining to fuel use and fuel switching, and would provide technologists with useful data on control technology performance.

This project is an important effort in developing a data base on well-controlled combustion processes. The project was initiated at approximately the same time period as the CCEA program planning effort.

The overall objectives of the project are to:

- conduct a comprehensive multimedia emissions assessment of oil vs. coal firing in both industrial and utility boilers
- evaluate efficiencies and effects of control devices for the boilers tested, and
- assess the environmental, energy, and social impacts on firing coal vs. oil.

These objectives are being met through field tests of selected industrial and utility boilers. The sampling and analysis includes both combined Level 1 and Level 2 sampling and analysis protocol.

- ENVIRONMENTAL ASSESSMENT FOR RESIDUAL OIL UTILIZATION

EPA Project Officer: Sam Rakes
Contractor: Catalytic, Inc.
Term: May 1976 - May 1979

Residual oil from refinery reject streams offers a potentially significant source of fuel for electric utility and industrial applications. This project is a three-year effort to identify and assess the environmental consequences of the production and utilization of residual oil in combustion processes. Control options such as fuel desulfurization and FGD are also included in this study. Although the majority of the funds are currently being spent in the areas of fuel treatment and chemically active fluid bed technology, a significant portion of the technical effort involves gas turbine technology and FGD technology.

The major objectives of the project are to:

- review and analyze the existing environmental, engineering, and cost data;
- identify important pollutants and their projected attainable emission levels;
- identify missing information and design a program(s) to develop such information; and
- design and conduct source sampling, fugitive emission and ambient monitoring programs.

Program Management Structure

The overall CCEA program is currently managed by the Process Technology Branch (PTB) within IERL-RTP's Utility and Industrial Power Division (UIPD). Although some of the projects are sponsored by other divisions within IERL-RTP, the technical and budgetary portions of the environmental assessment activities are managed by UIPD.

The major functional groups in the CCEA management structure are shown in Figure 3. The day-to-day management of the overall program is the responsibility of the CCEA program manager and his staff. The program manager coordinates the activities among the various projects and acts as the key link between the technical and management aspects of the program.

The Steering Committee (SC) will serve as an advisory group to the IERL Director on the overall direction and conduct of the CCEA program. In addition, it will provide oversight guidance to the Technical Working Group (TWG) in the coordination of CCEA activities. Further examples of duties include such things as recommending allocation of resources (CCEA versus other programs) and recommending redirection of program/project emphasis as needed.

Cooperative program solving across organization lines will be the goal of the TWG and the SC. The SC will attempt to resolve, by consensus, problems/issues which result from impasses in the Technical Working Group.

The resolution of such problems/issues will be passed to the TWG for implementation in the program. Problems which the SC cannot resolve in this manner will be elevated to the IERL Director for final resolution. These major responsibilities are outlined on Table 1.

The Technical Working Group will review, coordinate and serve as the forum for the working level activities of the CCEA program and its component projects requiring group coordination. Since the CCEA program components cut across current organizational lines, it is important to establish an accepted functional framework within which the TWG can perform its duties.

The TWG is made up of IERL Branch Chiefs and Project Officers who are directly involved with component projects in the CCEA program. The TWG, chaired by the Chief of the Process Technology Branch, will conduct CCEA activities requiring coordination of program components at the TWG level. It is anticipated that the majority of CCEA issues will be resolved at the TWG level, but it is important to note that TWG members can individually or collectively take unresolved problems directly to the UIPD Director. Further, if his decision is not acceptable to the parties involved, they can seek elevation of the problem to the Steering Committee through their respective Division Directors who are members of the Steering Committee. Major responsibilities of the TWG are outlined in Table I.

The TWG functional framework described above permits continuation of the CCEA program within the existing IERL organizational structure. CCEA projects remain in their respective Divisions and, existing organizational lines of communication remain intact and unchanged. In addition, the UIPD Director has the responsibility to attempt resolution of TWG problems before elevation to the full Steering Committee. The Steering Committee has the responsibility to attempt resolution prior to elevation to the IERL Director.

SECTION III

CCEA SUPPORT TO EPA PROGRAM OFFICES

Consistent with the Environmental Protection Agency's primary role as a regulatory organization, one of the principal purposes of the CCEA is to provide technical support for developing emissions and effluents standards. Specific types of informational support regarding such subject areas as combustion process descriptions, emissions/effluents characterization, transport/transformation/fate of pollutants, health/ecological effects, national and regional effects, control technology performance, and economics are essential in setting priorities and formulating standards and regulations.

Research to develop this information is specifically designed into the EA methodology of the CCEA program. Also designed into the CCEA management structure are channels for communications and information exchange with potential users. An important effort currently (at the time of publication of this paper) being undertaken is the identification of specific data needs of EPA Program Offices and a comparison of projected CCEA outputs with these needs. This comparison will provide useful guidance in focusing, developing, and implementing future activities within CCEA.

A preliminary effort under this "applicability analysis" activity is the comparison of projected CCEA outputs with data requirements to fullfil legislative mandates. Although the effort is not completed (at the time of publication) an example of a partially completed comparison matrix is shown in Tables II and III. Table II is a partial draft showing projected CCEA program support for the development of seven New Source Performance Standards (NSPS). Similarly, Table III shows a partially completed draft of CCEA program support for developing National Ambient Air Quality Standards (NAAQS). It is emphasized that these tables are preliminary and partial and are included here only to exemplify the matrix after it has been completed.

These applicability matrices, along with similar matrices covering other legislative mandates are currently being reviewed with the Office of Air Quality Planning and Standards (OAQPS), Office of Water and Waste Management (OWWM), and the Office of Solid Wastes (OSW) to ensure completeness and accuracy. Future activities under this effort will include the identification and comparison of general data needs of EPA Program Offices, EPA Enforcement Offices, and technology development divisions within the Department of Energy.

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3. Ponder, W. H. and D. C. Kenkeremath, Conventional Combustion Environmental Assessment Program, M78-44 Rev. 1, Mitre Corporation, September 1978.
4. Thompson, W. E. and J. W. Harrison, Survey of Projects Concerning Conventional Combustion Environmental Assessments, EPA-600/7-78-139, July 1978.

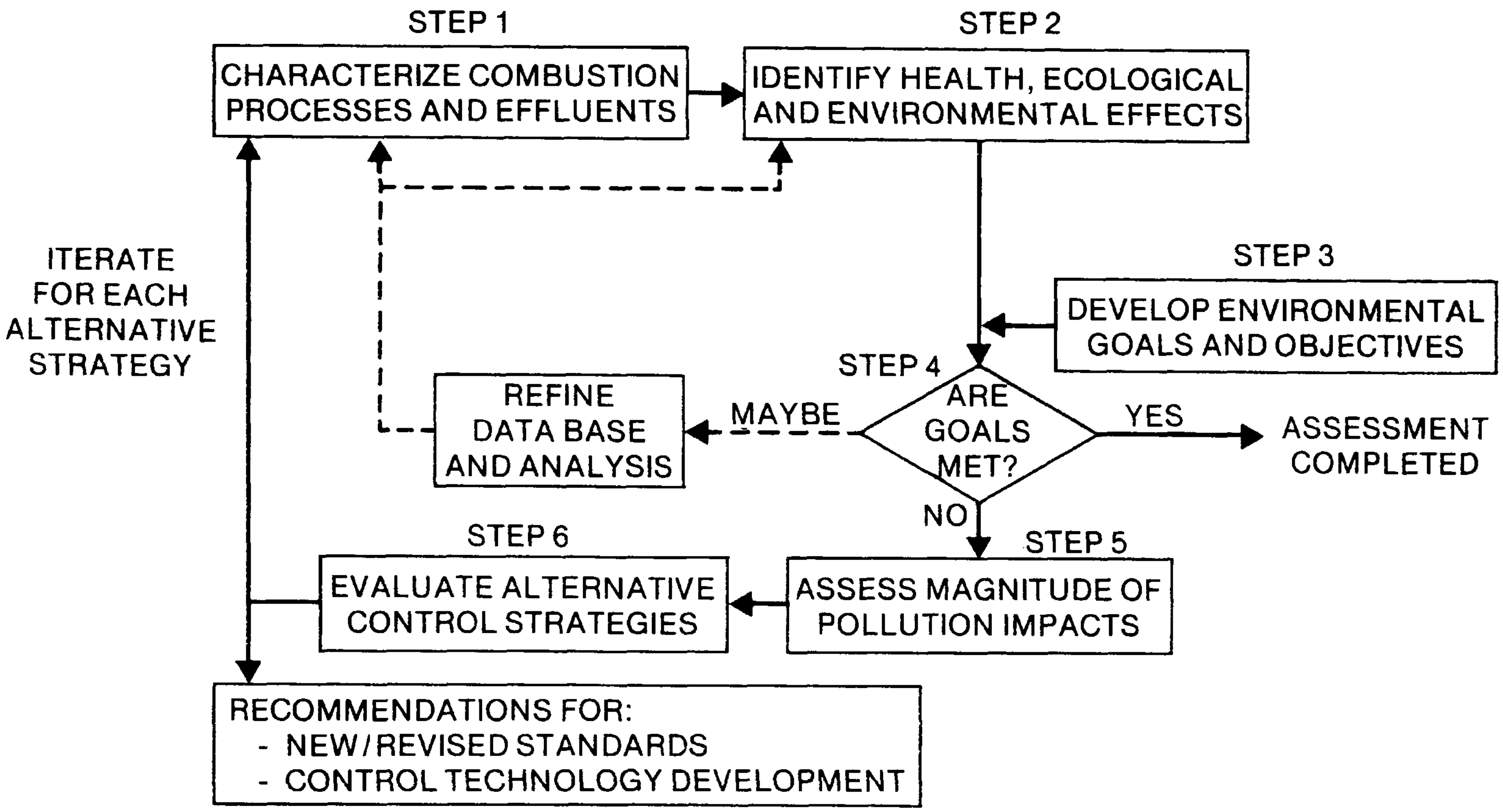

Figure 1 - Comprehensive Environmental Assessment Methodology Principal Steps

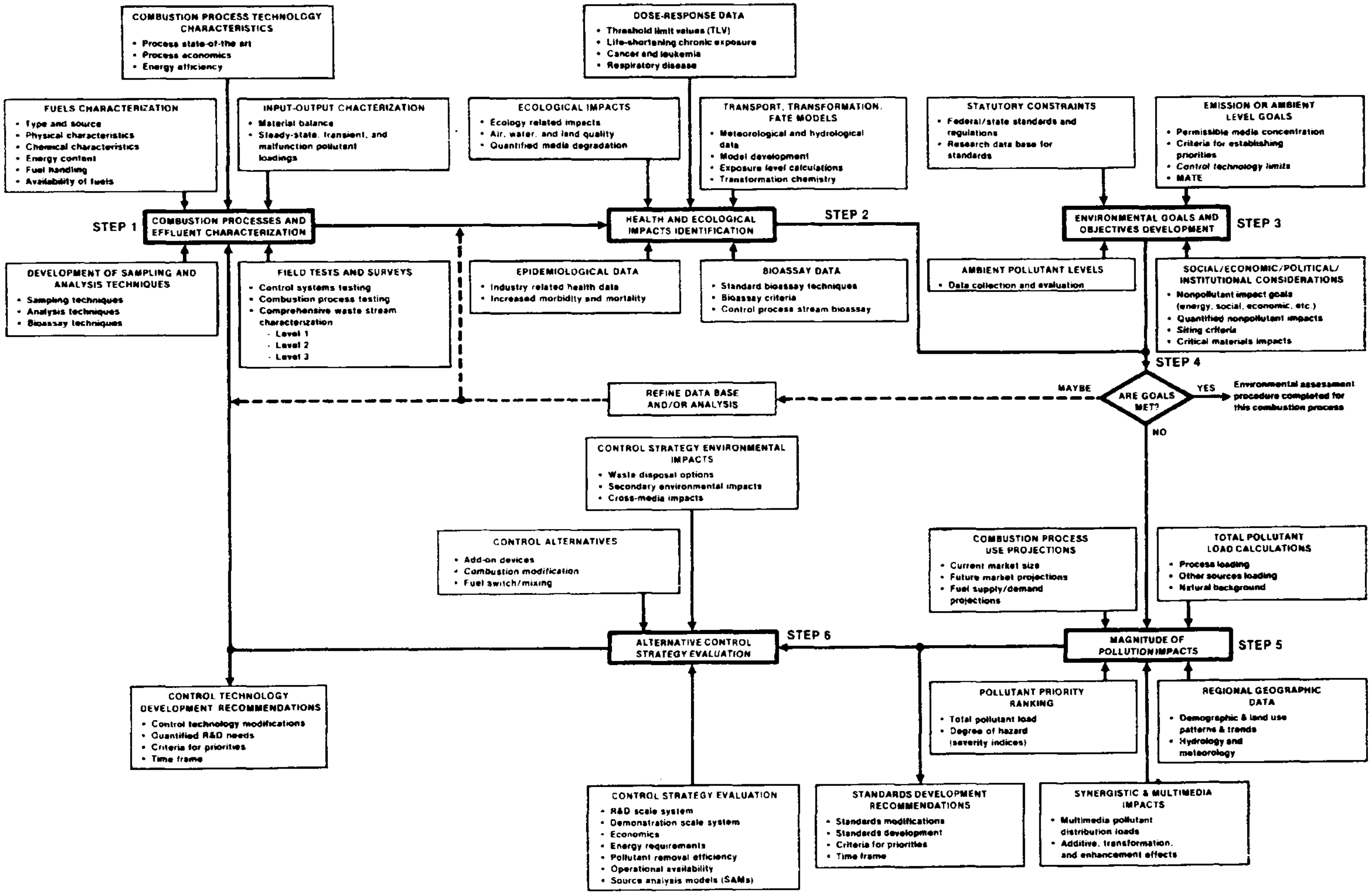

Figure 2 - Comprehensive EA Methodology for CCEA—Detailed Procedure

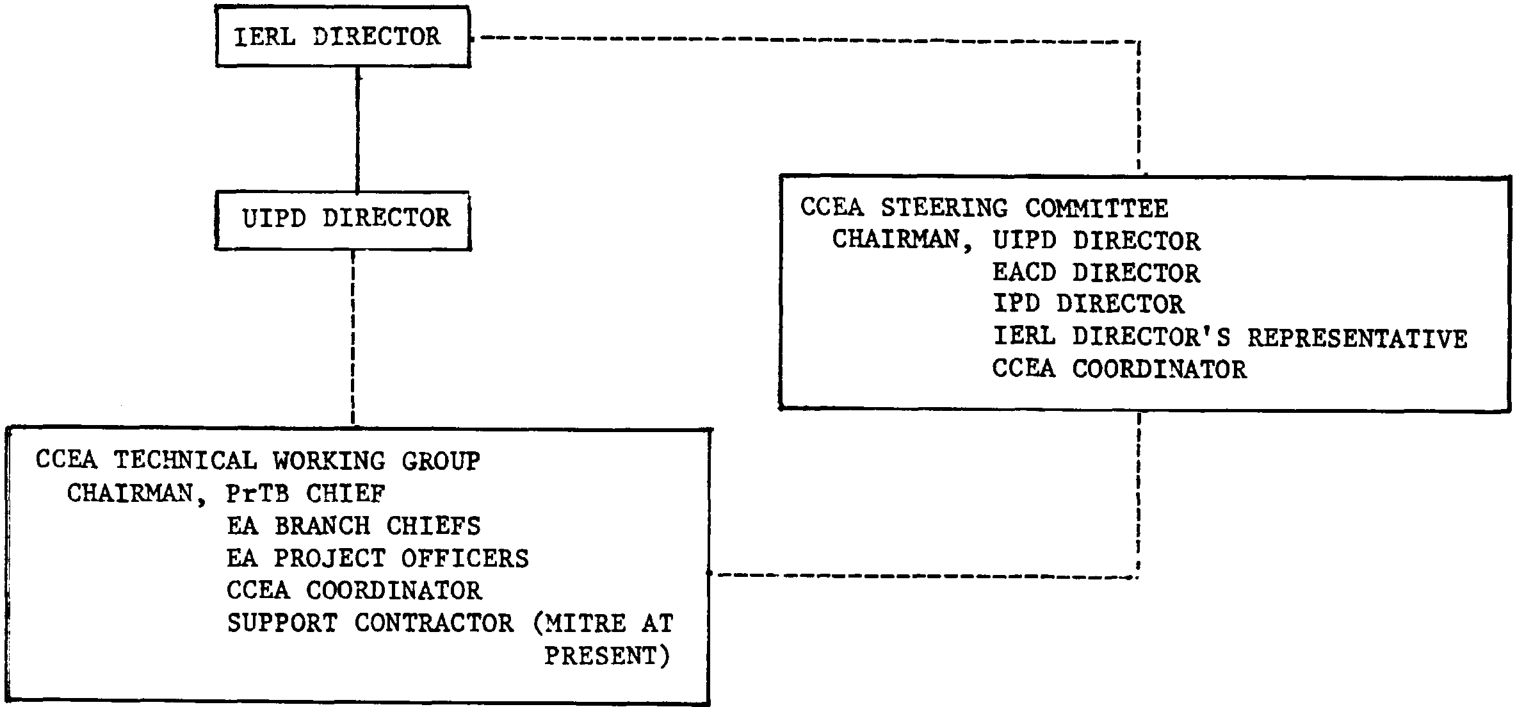

Figure 3 - CCEA Functional Management Structure

TABLE I

CCEA MANAGEMENT RESPONSIBILITIES

TECHNICAL WORKING GROUP

- Develops and recommends CCEA Program scope, funding and schedules for approval of Steering Committee
- Prepares draft accomplishment plans
- Prepares and presents program review materials
- Recommends correction of program/project emphasis as needed to the Steering Committee
- Resolves routine problems/issues
- Elevates other problems/issues to UIPD Director Steering Committee resolution
- Meets quarterly to discharge its responsibilities although special meetings will be called on an ad hoc basis as necessary

STEERING COMMITTEE

- Advises IERL Director concerning CCEA Program
- Reviews annual CCEA Program plans
- Recommends allocation of resources--CCEA versus other programs
- CCEA program reviews
- Reviews and evaluates CCEA Program outputs
- Corrects program/project emphases as needed
- Recommends resolution of problems raised by working group
- Meets at the request of the members--approximately twice per year

TABLE II

Partial Draft Showing CCEA Program Support for NSPS Development

STANDARDS UNDER CONSIDERATION BY OAQPS CCEA TECHNICAL PROJECTS	Internal Combustion Engine Control Technology (CAA-111) P=2/79;F=2/80	Tall Stacks Regulations (CAA-112) P=9/78;F=2/79	Gas Turbines (NO_x Emissions) ;F=2/79	Incinerators	Utility Boilers (Revised) ;F=3/79	Industrial Boilers (Revised) P=10/80;F=8/81	Waste Fuel Boilers
ENVIRONMENTAL ASSESSMENT OF STATIONARY SOURCE NO_x CONTROL TECHNOLOGIES (ACUREX CORPORATION)	Task 5.4 - Control Engineering & Environmental Impact Assessment of IC Engines		Task 5.5 - Control Engineering & Environmental Impact Assessment of Gas Turbines		Task 5.1 - Control Engineering & Environmental Impact Assessment of Utility Boilers		
EMISSIONS CHARACTERIZATION OF CONVENTIONAL COMBUSTION SYSTEMS (TRW)	Task 2 - Multimedia Pollutants assessment of IC Sources for Electric Power Generation & Steam	Task 1 - Multimedia pollutants assessment of stationary conventional combustion processes	Task 2 - Multimedia Pollutants assessment of Internal Combustion Sources for Electric Power Generation and Steam	Task 3 - Multimedia Pollutants assessment of other sources for Electric Power Generation and Steam	Task 3 - Multimedia Pollutants assessment of other sources for Electric Power Generation & Steam	Task 3 - Multimedia Pollutants assessment of other sources for Electric Power Generation & Steam Task 5 - Multimedia Pollutants assessment of Industrial Combustion Sources	
SYSTEMS ENGINEERING SERVICES FOR CCEA (CONTRACT BEING NEGOTIATED)	Task 1.1 - Pollutant characterization (primary & secondary) and control levels Task 2.0 - Characteristics of Pollutant Emissions from Specific Sources Task 2.1 - Identification of types of stationary conventional combustion processes not adequately characterized Task 3.2 - Total National Emissions of Combustion Pollutants by Source Task 4.2 - Capability and costs of Control Technologies to meet existing & Proposed Federal Standards	Task 1.1 - Pollutant characterization (primary & secondary) and control levels Task 3.1 - Techniques for Quantifying Health/Environmental Effects of Combustion Pollutants Task 4.2 - Capability and costs of control technologies to meet existing and proposed Federal standards	Task 1.1 - Pollutant characterization (primary & secondary) and control levels Task 3.2 - Total National Emissions of Combustion Pollutants by Source Task 4.3 - Prioritized listing for Modifying Existing Control Technologies or for New Technology Development	Task 1.1 - Pollutant characterization (primary & secondary) and control levels Task 2.0 - Characteristics of Pollutant Emissions from Specific Sources Task 4.2 - Capability and costs of control technologies to meet existing and proposed Federal standards	Task 1.1 - Pollutant characterization (primary & secondary) and control levels Task 3.2 - Total National Emissions of Combustion Pollutants by Source Task 4.3 - Prioritized listing for Modifying Existing Control Technologies or for New Technology Development	Task 1.1 - Pollutant characterization (primary & secondary) and control levels Task 4.3 - Prioritized listing for Modifying Existing Control Technologies or for New Technology Development	Task 1.1 - Pollutant characterization (primary & secondary) and control levels Task 2.3 - Plan for acquiring missing Data on characteristics of Pollutant Emissions Task 3.2 - Total National Emissions of Combustion Pollutants by Source Task 4.3 - Prioritized listing for Modifying Existing Control Technologies or for New Technology Development

TABLE II

Partial Draft Showing CCEA Program Support for NSPS Development (Continued)

STANDARDS UNDER CONSIDERATION BY OAQPS / CCEA TECHNICAL PROJECTS	Internal Combustion Engine Control Technology (CAA-111) P=2/79;F=2/80	Tall Stacks Regulations (CAA-112) P=9/78;F=2/79	Gas Turbines (NO$_x$ Emissions) ;F=2/79	Incinerators	Utility Boilers (Revised) ;F=3/79	Industrial Boilers (Revised) P=10/80;F=8/81	Waste Fuel Boilers
COMPARATIVE ASSESSMENT OF COAL VS. OIL FIRING IN WELL-CONTROLLED INDUSTRIAL & UTILITY BOILERS (TRW)					Task 1.2 - Multimedia emissions tests for utility boilers Task 2.2 - Environmental assessment of coal & oil firing in Utility Boilers Task 3.2 - Comparative emissions assessment Task 4.2 - Comparative Energy & Social Impacts of Coal vs. Oil for Utility Boilers	Task 1.1 - Multimedia emissions tests for industrial boilers Task 2.1 - Environmental assessment of coal & oil firing in Industrial Boilers Task 3.1 - Comparative emissions assessment of coal vs. oil for Industrial Boilers Task 4.1 - Comparative Energy & Social Impacts of Coal vs. Oil for Industrial Boilers	
ENVIRONMENTAL ASSESSMENT OF RESIDUAL OIL UTILIZATION (CATALYTIC CORPORATION)		Task 4 - Assessment of control technology for Residual Oil Processes Task 5 - Environmental Alternatives assessment (control processes vs. Pollutant Prioritization)			Task 2 - Multimedia Environmental Goals, including TLV's, existing & proposed standards & NSPS Task 6 - Future Research needs (including processes ready for pilot or demonstration plant scale)	Task 2 - Multimedia Environmental Goals, including TLV's, existing & proposed standards & NSPS Task 6 - Future Research needs (including processes ready for pilot or demonstration plant scale)	

TABLE III

Partial Draft Showing CCEA Program Support for NAAQS Development

STANDARDS UNDER CONSIDERATION BY OAQPS CCEA TECHNICAL PROJECTS	Review of Long Term NAAQS for NO_2 (CAA-108) P=1/79;F=6/79	Development of short term NAAQS for NO_2 (CAA-109) P=12/78;F=6/79	Review of NAAQS for photochemical oxidants F=12/78	Review of NAAQS for CO P=4/79;F=7/79	Review of NAAQS for SO_x P=5/80;F=12/80	Review of NAAQS for particulates P=5/80;F=12/80	Listing of radioactive pollutants (how classified) F=8/80
ENVIRONMENTAL ASSESSMENT OF STATIONARY SOURCE NO_x CONTROL TECHNOLOGIES (ACUREX CORPORATION)	Task 6 - Identification of cost effective and environmentally sound NO_x Control System.	Task 2 - Multimedia NO_x Emission Impacts & Adequacy of Data Task 4 - Evaluation of NO_x Sampling Techniques Task 6 - Identification of cost effective and environmentally sound NO_x Control System.	Task 2 - Multimedia NO_x Emission Impacts & Adequacy of Data Task 4 - Evaluation of NO_x Sampling Techniques				
EMISSIONS CHARACTERIZATION OF CONVENTIONAL COMBUSTION SYSTEMS (TRW)	Task 1 - Multimedia Pollutants assessment of Residential Sources Task 2 - Multimedia Pollutants assessments of IC Sources for Electricity Power Generation & Steam Task 3 - Multimedia Pollutants assessment of other combustion sources for Electricity Power Generation & Steam Task 4 - Multimedia Pollutants assessment of Commercial/ Institutional Sources Task 5 - Multimedia Pollutants assessment of Industrial Combustion Sources	Task 1 - Multimedia Pollutants assessment of Residential Sources Task 2 - Multimedia Pollutants assessments of IC Sources for Electricity Power Generation & Steam Task 3 - Multimedia Pollutants assessment of other combustion sources for Electricity Power Generation & Steam Task 4 - Multimedia Pollutants assessment of Commercial/ Institutional Sources Task 5 - Multimedia Pollutants assessment of Industrial Combustion Sources		Task 1 - Multimedia Pollutants assessment of Residential Sources Task 2 - Multimedia Pollutants assessments of IC Sources for Electricity Power Generation & Steam Task 3 - Multimedia Pollutants assessment of other combustion sources for Electricity Power Generation & Steam Task 4 - Multimedia Pollutants assessment of Commercial/ Institutional Sources Task 5 - Multimedia Pollutants assessment of Industrial Combustion Sources	Task 1 - Multimedia Pollutants assessment of Residential Sources Task 2 - Multi media Pollutants assessments of IC Sources for Electricity Power Generation & Steam Task 3 - Multimedia Pollutants assessment of other combustion sources for Electricity Power Generation & Steam Task 4 - Multimedia Pollutants assessment of Commercial/ Institutional Sources Task 5 - Multimedia Pollutants assessment of Industrial Combustion Sources	Task 1 - Multimedia Pollutants assessment of Residential Sources Task 2 - Multimedia Pollutants assessments of IC Sources for Electricity Power Generation & Steam Task 3 - Multimedia Pollutants assessment of other combustion sources for Electricity Power Generation & Steam Task 4 - Multimedia Pollutants assessment of Commercial/ Institutional Sources Task 5 - Multimedia Pollutants assessment of Industrial Combustion Sources	

TABLE III

Partial Draft Showing CCEA Program Support for NAAQS Development (Continued)

STANDARDS UNDER CONSIDERATION BY OAQPS CCEA TECHNICAL PROJECTS	Review of Long Term NAAQS for NO_2 (CAA-108) P=1/79;F=6/79	Development of short term NAAQS for NO_2 (CAA-109) P=12/78;F=6/79	Review of NAAQS for photochemical oxidants F=12/78	Review of NAAQS for CO P=4/79;F=7/79	Review of NAAQS for SO_x P=5/80;F=12/80	Review of NAAQS for particulates P=5/80;F=12/80	Listing of radioactive pollutants (how classified) F=8/80
SYSTEMS ENGINEERING SERVICES FOR CCEA (CONTRACT BEING NEGOTIATED)	Task 1.1 - Pollutant characterization (primary & secondary) and control levels Task 3.1 - Techniques for quantifying Health/Environment Effect of Combustion Pollutants Task 3.2 - Total National Emissions of Combustion Pollutants by Source Task 3.3 - Qualitative & Quantitative Effects of Criteria & Other selected Pollutants Task 4.1 - Evaluation of Existing, Developmental & Proposed Control Technology for Combustion Pollutants on MEG list	Task 1.1 - Pollutant characterization (primary & secondary) and control levels Task 3.1 - Techniques for quantifying Health/Environment Effect of Combustion Pollutants Task 3.2 - Total National Emissions of Combustion Pollutants by Source Task 3.3 - Qualitative & Quantitative Effects of Criteria & Other selected Pollutants Task 4.1 - Evaluation of Existing, Developmental & Proposed Control Technology for Combustion Pollutants on MEG List	Task 1.1 - Pollutant characterization (primary & secondary) and control levels Task 3.1 - Techniques for quantifying Health/Environment Effect of Combustion Pollutants Task 3.2 - Total National Emissions of Combustion Pollutants by Source Task 3.3 - Qualitative & Quantitative Effects of Criteria & Other selected Pollutants Task 4.1 - Evaluation of Existing, Developmental & Proposed Control Technology for Combustion Pollutants on MEG list	Task 1.1 - Pollutant characterization (primary & secondary) and control levels Task 3.1 - Techniques for quantifying Health/Environment Effect of Combustion Pollutants Task 3.2 - Total National Emissions of Combustion Pollutants by Source Task 3.3 - Qualitative & Quantitative Effects of Criteria & Other selected Pollutants Task 4.1 - Evaluation of Existing, Developmental & Proposed Control Technology for Combustion Pollutants on MEG list	Task 1.1 - Pollutant characterization (primary & secondary) and control levels Task 3.1 - Techniques for quantifying Health/Environment Effect of Combustion Pollutants Task 3.2 - Total National Emissions of Combustion Pollutants by Source Task 3.3 - Qualitative & Quantitative Effects of Criteria & Other selected Pollutants Task 4.1 - Evaluation of Existing, Developmental & Proposed Control Technology for Combustion Pollutants on MEG list		Task 2.3 - Plan for acquiring missing data
COMPARATIVE ASSESSMENT OF COAL VS. OIL FIRING IN WELL CONTROLLED INDUSTRIAL & UTILITY BOILERS (TRW)	Task 2.1 - Environmental assessment of Coal & Oil Firing in Industrial Boilers Task 2.2 - Environmental assessment of coal vs. oil Firing in Utility Boilers	Task 2.1 - Environmental assessment of Coal & Oil Firing in Industrial Boilers Task 2.2 - Environmental assessment coal vs. oil Firing in Utility Boilers	Task 2.1 - Environmental assessment of Coal & Oil Firing in Industrial Boilers Task 2.2 - Environmental assessment coal vs. oil Firing in Utility Boilers	Task 2.1 - Environmental assessment of Coal & Oil Firing in Industrial Boilers Task 2.2 - Environmental assessment coal vs. oil Firing in Utility Boilers	Task 2.1 - Environmental assessment of Coal & Oil Firing in Industrial Boilers Task 2.2 - Environmental assessment coal vs. oil Firing in Utility Boilers	Task 2.1 - Environmental assessment of Coal & Oil Firing in Industrial Boilers Task 2.2 - Environmental assessment coal vs. oil Firing in Utility Boilers	
ENVIRONMENTAL ASSESSMENT OF RESIDUAL OIL UTILIZATION				Task 2 - Multimedia Environmental Goals, including Existing & Proposed Standards, NSPS & TLV's.	Task 2 - Multimedia Environmental Goals, including Existing & Proposed Standards, NSPS & TLV's.		

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

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16. ABSTRACT The proceedings document the approximately 50 presentations made during the symposium, March 5-8, 1979, in San Francisco. Sponsored by the Combustion Research Branch of EPA's Industrial Environmental Research Laboratory-RTP, the symposium dealt with subjects relating both to developing improved combustion technology for the reduction of air pollutant emissions from stationary sources, and to improving equipment efficiency. The symposium was in seven parts, and the proceedings are in five volumes: I. Utility, Industrial, Commercial, and Residential Systems; II. Advanced Processes and Special Topics; III. Stationary Engine and Industrial Process Combustion Systems; IV. Fundamental Combustion Research and Environmental Assessment; and V. Addendum. The symposium provided contractor, industrial, and government representatives with the latest information on EPA inhouse and contract combustion research projects relating to pollution control, with emphasis on reducing NOx while controlling other emissions and improving efficiency.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Air Pollution	Gas Turbines	Air Pollution Control	13B	13G
Combustion	Nitrogen Oxides	Stationary Sources	21B	07B
Field Tests	Efficiency	Environmental Assessment	14B	
Assessments	Utilities			
Combustion Control	Industrial Processes	Combustion Modification		
Fossil Fuels		Trace Species	21D	13H
Boilers	Hydrocarbons	Fuel Nitrogen	13A	07C

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