MASTER

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KINETICS OF NO_x FORMATION DURING EARLY STAGES
OF PULVERIZED COAL COMBUSTION

FIRST QUARTERLY REPORT

for the period

26 September 1980 to 28 December 1980

W. V. Krill, E. K. Chu, and H. Tong

January 30, 1981

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Work Performed Under Contract
DE-AC22-80PC-30295

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Prepared for the

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ABSTRACT

The first quarter results under the Department of Energy Contract DE-AC22-80PC-30295 are reported. A stirred reactor technique to simulate the early combustion environment of coal particles has been devised. An existing cold flow model has been modified to develop the operating conditions required for combustion experiments. A test matrix for the cold flow tests has been developed and the system readied for testing. The anticipated analytical measurement approaches to the combustion test phases of the program are also discussed.

An initial reported set of gas phase reactions has been incorporated into the PROF code. Predictions of NO_x formation to date have exhibited good agreement with existing combustion data. Experimental data of thermal NO_x formation in the stirred reactor will be integrated with the kinetic model during the following quarter.

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1. CONTRACT OBJECTIVES

A unique experimental system has been devised to simulate the combustion environment of a coal particle during its early devolatilization. A stirred reactor will be used to characterize the volatilization, evolution of nitrogen containing gas species, and oxidation of the hydrocarbon and intermediate nitrogen species during the early stages of combustion. Reactor tests will obtain data required to develop a kinetic model of these early combustion processes, elucidating the combustion conditions that can be varied to obtain low NO_x emissions in practical combustion systems. The results will be extended to a variety of coal types and compositions.

2. CONTRACT TASKS

During the first quarter of the contract, preparations have been made for the cold flow reactor tests, and the basis of the kinetics model has been formulated. The following discussion describes these activities performed under Tasks 1.1 and 1.4.

2.1 Experimental Design (Task 1.1)

Progress under the Experimental Design task has included formulation of the requirements for cold flow reactor tests, reactor design and setup, development of the cold flow reactor test matrix, and formulation of the analytical measurement techniques for hot flow tests. The cold flow tests have two overall objectives:

1. Verify the anticipated coal particle trajectories through the hot, well-stirred gas region, and
2. Determine the stirred nature of the gas phase

Satisfying the first objective will establish that coal devolatilization is occurring over a known temperature and time, allowing the rate of devolatilization to be determined. The second objective will establish the fluid interactions between the stirred gas phase and the particle volatiles that are important to the kinetic model.

Cold Flow Test Requirements

To achieve the stated objectives, the cold flow reactor must be similar (geometrically and fluid mechanically) to the configuration anticipated for hot flow testing. The experimental reactor is shown conceptually in Figure 1. The reactor configuration and orientation of the 12 air/CH₄ injectors are the same as in a prior program (Reference 1). That study verified the well-stirred nature of the gas phase. Modification of the concept for this program has included addition of the downward projecting coal jet. A plastic cold flow model remained from the previous study and has been modified to include the coal jet. The coal particle trajectories can thus be verified visually. The support equipment for gas phase mixing measurements is described below.

Reactor Design and Setup

The work performed in Reference 1 included similar reactors of two different sizes, having volumes of 7.6 l and 1.7 l. The smaller of the two has been selected for use in this program, based on the coal jet velocities required to achieve the desired 5 to 20 ms time within the reactor. The corresponding particle velocities are 156 and 39 ft/sec, respectively. This range should be simple to achieve at the jet entrance. These velocities are sufficient for transport of coal through feed lines and in excess of coal/air flame speeds (for safety).

Plastic cold flow models are available for both reactor sizes. The smaller chamber dimensions are shown in Figure 2. As described in Reference 1, the model has been rigorously demonstrated to be well stirred in the gas phase. Care was taken (following measurements of the gas stirring) to match jet Reynolds number and residence time between the cold flow and combustion test reactors to maintain similar conditions. The plastic model has been modified to include the vertical coal jet.

The reactor system schematic is shown in Figure 3. The plastic model is currently in place on the test bench, and the metering rotameters, reactant

Figure 1. Reactor configuration.

Figure 2. Reactor chamber dimensions (cm).

Figure 3. Reactor system schematic.

flow lines, and coal manifolding have been installed. Check valves and a burst diaphragm have been included in the gas flow lines to prevent buildup and explosion of a combustible mixture. Addition of the NO dopant instrumentation will occur prior to combustion testing of the cast refractory reactors. The instrumentation is currently set up to meter maximum flows of 5.4 scfm coal carrier gas and 60 scfm combustion air.

To perform reactor stirring measurements, a helium tracer technique was developed in Reference 1 and modified for this program. The model reactor is operated on air through all jets including the centerline coal jet. A small amount of helium (approximately 3 percent of the total flow) is added to each jet level in turn. The baseline helium concentration is recorded (via response of a hot wire anemometer) and turned off to measure the transient decay. If the decay rate is exponential and similar for all of the jets, the model is assumed well stirred.

The associated electronics (shown in Figure 4 in a test configuration) have been set up and checked out. During testing, the reactor body replaces the connecting nozzle and bolt in the figure. The helium flow is established and cut off by an electromagnetic valve with a response time of approximately 3 msec. The He decay is sensed by the hot wire and recorded on an oscilloscope. The trace data are photographed, analyzed, and compared for each of the jets. An exponential decay function indicates well stirred behavior. Prior to actual model tests, the effects of solenoid valve response time and nozzle volume will be evaluated by the setup of Figure 4. This initial test will also serve to debug and calibrate the electronics package. Tests will commence in the first month of the second quarter.

Cold Flow Test Matrix

The first set of tests to be run on the described reactor will address the ability of the pulverized coal particles to traverse the well stirred gas region. Air will be fed through all 12 gas jets, and coal and air will be introduced through the top jet. In earlier tests, the small reactor was shown to be very well mixed with a total gas flow of 20 to 30 scfm through the jets.

Figure 4. Schematic of helium test components.

A range of air flow of 15 to 30 scfm will be investigated in these coal trajectory studies to see if sacrificing some of the mixing ability of the reactor will result in better control of coal trajectories.

The coal flow requirements are set to achieve the desired 5 to 20 ms residence time through the stirred region. Residence times of 5, 10, 15, and 20 ms will be run for mixing air flows of 15, 20, 25, and 30 scfm. This will require a coal flow of approximately 0.7 to 3.0 lbm/hr (to be consistent with analytical instrumentation measuring gaseous emissions during combustion) and coal carrier gas flows of 4.8, 3.6, 2.4, and 1.2 scfm to achieve the respective residence times. Therefore, the four by four matrix of Table 1 will be used to determine acceptable flow conditions. Acceptability will be judged primarily by visual and possibly photographic observation through the clear plastic model, verifying that the majority of the coal particles pass directly through the reactor without collision with reactor walls.

The second objective of the cold flow tests, determining the stirred nature of the gas phase with the addition of the top jet, will be performed with the helium tracer technique described above. The mixing intensity of the reactor will be investigated first to verify that the addition of the centerline jet does not degrade the stirring generated by the 12 gas jets. This requires introduction of the helium tracer into each jet level and comparing the exponential decay of concentration.

A second set of tests will evaluate the degree of coal feed jet breakup and mixing by injection of the helium tracer through the top jet (operating on air only). The results will establish the time scale for volatile combustion, necessary to the kinetic model. All of the stirring measurements will be conducted at the same reactor flowrates and analogous coal jet flowrates to the listed residence times of Table 1. The results will not only indicate the well stirred combination of conditions in the matrix, but also the mixing time scale of the coal jet gas phase for each matrix point. The results of both the coal trajectory and mixing tests will be used to generate an expanded combustion test matrix during the following quarter.

TABLE 1. COAL TRAJECTORY TEST MATRIX

		Coal Residence Time (ms)			
		5	10	15	20
Gas Stirring flowrate (scfm)	15	X	X	X	X
	20	X	X	X	X
	25	X	X		
	30	X			

X -- acceptable coal traversing

Analytical Measurement Techniques

The hot wire anemometer technique for cold flow reactor measurements has been described above. Exhaust gas analysis measurement techniques for combustion tests have also been formulated during the quarter. The applicability and accuracy of available continuous gas analyzers have been verified as consistent with the anticipated coal flows. Assuming partial combustion at equivalence ratios of 1.7 to 2.6, expected concentrations are:

[CO₂] : 1.1 to 1.4 percent

[CO] : 4600 to 9500 ppm

[NO] : 60 to 100 ppm

which are within instrument ranges. Additional instruments will include the wet chemical method for NH₃ and HCN species and the water-quench sample probe for particulate catch of devolatilized coal particles described in Reference 1. Combusted coal catches will be analyzed by proximate and ultimate analyses as required.

2.2 Kinetic Modeling (Task 1.4)

The NO formation process from fuel bound nitrogen in coal has been postulated to occur by various homogeneous and heterogeneous pathways as illustrated in Figure 5. Ideally, one would like to model the process in terms of elementary reactions. Unfortunately, such detailed knowledge is still under development and may require some time before a thorough understanding can be achieved. On the other hand, if a one-step global reaction were assumed, it would be so crude that mechanistic information regarding the formation of NO may not be attained.

Since an analytical design tool for low NO_x burner development is desired, the objective of this program is to develop a quasi-global kinetic model. In this model, the volatilization of coal and secondary reactions of volatilization products are assumed to occur in a small number of global steps while the subsequent sequence of reactions of low molecular weight products are expressed in terms of elementary reactions. A schematic of a possible quasi-global kinetic model is that of Figure 5. Here the assumption is made that, as the coal volatilizes into the hot surroundings, the high molecular weight volatile fractions pyrolyze rapidly to form low molecular weight species. There is evidence to show that pyrolysis reactions are very rapid (References 2 and 3) and as a first approximation, we can neglect intermediate steps and postulate that species such as HCN, NH₃, C₂H₂, C₂H₄, CO and H₂ are formed almost instantaneously from the volatilized compounds. Once the volatile components are cast in this form, elementary reaction sets available for the postulated species can be used as a first order model.

The development of the present kinetic model is comprised of four steps:

- Survey study
- Kinetic model formulation
- Model verification
- Final model correlation

Figure 5. Schematic of fuel-N conversion process.

The survey study is designed to:

- Assess the state of the-art of kinetic modeling, e.g., global reactions versus elementary reactions
- Compile accepted rate data for pertinent reactions
- Compile experimental data which could be used for model verification purposes

Based on the inputs from the survey study, the second step is to formulate the kinetic model. This entails the following activities:

- Define reaction subsets of the kinetic model
- Prioritize the level of importance for each reaction subset
- Determine the level of analytical approach for each reaction subset based on model requirements

To verify the validity of the kinetic model, the third step is to exercise each reaction subset to predict results that are consistent with existing experimental data. The PROF computer code (Reference 4) will be used as the computational tool. Upon the completion of these verification studies, the final test of the model will be to compare its predictions with the stirred reactor and other coal combustion data. Good agreement will insure that proper links between reaction subsets have been modeled properly.

Technical efforts during the first quarter have focused on the survey study. Some work has also been initiated on the kinetic model formulation and model verification. Progress in each of these areas is summarized below.

Literature Survey and Formulation of the Kinetic Model

As mentioned earlier, a quasi-global kinetic model approach is applied to model the fuel nitrogen conversion process. It has the following general form:

This approach has led to the following assumptions:

- The initial degradation of gaseous volatiles via pyrolysis and oxidation is rapid in comparison to other simultaneously ongoing reactions
- The initial decomposition products may be represented by a relatively small set of light hydrocarbon and nitrogenous species
- Hydrocarbons which could react with nitrogenous species are limited to C_1 and, at most, C_2 species

The first two assumptions are easily justified. Based on ignition delay experiments (References 5 to 7), it was found that the ignition delay time for both aliphatic and aromatic hydrocarbons is of the order of microseconds. The devolatilization and the NO destruction reactions, on the other hand, are of the order of milliseconds -- orders of magnitude slower than the volatile

degradation reactions. Thus, the rate step for the volatile degradation reactions may not be of great importance. In addition, some references cited, although inconclusive, indicate that the fuel nitrogen in these devolatilization products appear rapidly and nearly completely as HCN and NH_3 intermediates (Reference 8). The third assumption, however, is uncertain at present because of the complexities involved when higher order hydrocarbons are considered. Furthermore, reaction mechanisms involving C_2 hydrocarbons are still under development. The compilation of rate data for the formulation of the kinetic model will be completed in the second quarter. The current status is summarized in Table 2.

Coal reactions include evolution of products (gases and tar) from rapid particle heating and heterogeneous combustion of coal particles. These two processes typically occur in sequence, but may occur simultaneously or even in reverse order under some conditions (References 9 and 10). In addition, these two processes are dependent on each other. Heterogeneous combustion requires oxidants on the particle surface. Volatiles evolving from the surface not only reduce the mass transfer rate of oxidants to the surface, but also consume the oxidants if gas phase combustion occurs, thereby depleting the availability of oxidant to the surface. Recently, the occurrence of gas phase volatile combustion has been confirmed through direct observations (References 12 and 13). On the other hand, heterogeneous combustion produces heat for the devolatilization process during the early stage. Thus, for the completeness of the model, heterogeneous combustion of coal particles as well as the mutual influences of the two processes must be included. Models to account for these effects are in existence and are described in References 2, 9, and 11.

A recent review on the modeling of devolatilization was given by Anthony (Reference 14). The two most common techniques for predicting devolatilization rates are (1) a method based on a simple rate equation with a distribution of activation energies, and (2) the two-component model:

TABLE 2. FORMULATION OF PRELIMINARY KINETICS MODEL

Class of Reactions	Description of Reactions	Modeling Approach	Existence of Data	Priority of Importance
Coal devolatilization	Coal $\xrightarrow{\text{heat}}$ char + volatiles	One/two step global reaction	Lots	High
Volatile combustion	Volatiles + O ₂ → CO + CO ₂ + H ₂ + HC's + H ₂ O	One step global reaction	Some	High
Coal heterogeneous combustion	Coal + O ₂ → CO + CO ₂ + H ₂ + HC's + H ₂ O	One step global reaction	Some	Uncertain
Simple HC's combustion	Simple HC's + O ₂ → CO + H ₂	One step global reaction (C _n), Elementary reactions (C ₁)	C ₁ -Lots C ₂ , C _n -scarce	High
H ₂ , CO combustion	H ₂ , CO + O ₂ → CO ₂ + H ₂ O	Elementary reactions	Lots	Low
NO formation and destruction	Fuel-N → HCN + ...	One step global reaction	Scarce	High
	HCN → NH _i + ...	Elementary reactions	Some	High
	NH _i + O ₂ → NO + N ₂ + ...	Elementary reactions	Some	High
	NO + CO $\xrightarrow{\text{char}}$ N ₂ + ...	One step global reactions	Some	Low
	NO + HC's → HCN + ...	Elementary reactions	C ₁ -Lots C _n -Scarce	High

where α_1 and α_2 are stoichiometric coefficients, V's are volatiles, S is residue solid, and k_1 and k_2 are reaction rates represented by Arrhenius expressions. The two-component model accounts for the impact of heating rate and final temperature on the rate and extent of devolatilization. This model is generally adequate for pulverized coal combustion at moderate and high temperatures and will be used in the present model.

Regarding the formation of NO, the evolution of fuel nitrogen relative to hydrocarbons from the coal requires special attention. Existing data show that nitrogen evolution is somewhat more temperature sensitive than the liberation of carbon. It evolves more slowly than carbon at low temperatures and more rapidly at high temperatures (References 15 to 17). This behavior is believed to be related to the coal structure. The nitrogen in coal is mostly incorporated in the ring structures (References 18 to 26) with possibly small amounts of nitrogen contained in side chains (References 27 to 29). Based on this coal structure, the following speculative picture for the behavior of coal nitrogen was postulated:

- At low temperatures, pyrolysis of coal is expected to be dominated by the release of nitrogen from side chains, and thus nitrogen is emitted more slowly than carbon
- At moderate or high temperatures, the aromatic rings will decompose and release nitrogen. However, secondary cracking reactions will also occur leading to char formation. Very small or negligible amounts of nitrogen, however, are expected to occur with the char formation process.

Model Verification

As shown in Table 2, elementary reaction sets are available for a reactive system of C_7 hydrocarbons, nitrogen, and oxygen species. In fact, a comprehensive elementary reaction set has been formulated by Energy and Environmental Research Corporation under EPA's funding (Reference 30). The reaction set, shown in Table 3, consists of 136 elementary reactions, and has been applied successfully in predicting NO formation of simple model fuel nitrogen, e.g., NH_3 . To take advantage of this effort, this reaction set is used as our baseline set. The baseline will be expanded to incorporate other reaction mechanisms occurring during gas phase volatiles combustion.

A preliminary evaluation of the baseline reaction set was performed during the quarter by predicting jet-stirred reactor data for methane/air doped with ammonia, nitric oxide, and cyanogen (Reference 31). The comparisons are shown in Figures 6 to 9. Good agreement has been obtained with ammonia and cyanogen as the additive. With NO, however, the agreement was not as good under fuel-rich conditions. The model tends to underpredict NO emissions. Figure 9 shows the comparison of measured and predicted flame temperatures. Again, good agreement was obtained, indicating that the combustion process is properly modeled. As a preliminary evaluation, the results are encouraging. To further improve this reaction set, the following efforts are required:

- Identify the dominant reactions for NO formation and adjust the rate data (if necessary)
- Check the accuracy of the thermochemical data
- Introduce additional reactions (if needed)

This work will be completed during the second quarter.

3. WORK PLANNED

The experimental design efforts of the first quarter will lead to completion of cold flow reactor tests in February. Definition of the

TABLE 3. KINETIC REACTION DATA (REFERENCE 30)

NUMBER OF REACTIONS=136

M	REACTION				PRE EXP FACTOR (MOLE-CM-S)	TEMP EXP	ACTIVATION (KCAL/MOLE)	INDIVIDUAL THIRD BODY EFFIC.			
								NAME1	LTB1	NAME2	ETB2
1	CH4 +	+M	---	CH3 +H	.1000+18+ 0.	.000	88.4000	.000		.000	.000
2	CH3O+	+M	---	CH2O+H	.4000+01+40.	-7.500	22.6000	.000		.000	.000
3	CH2O+	+M	---	CHO +H	.3160+18+ 0.	.000	87.0000	.000		.000	.000
4	CHO +	+M	---	CO +H	.2500+21+ 0.	-1.500	16.8000	.000		.000	.000
5	CO2 +	+M	---	CO +O	.1000+16+ 0.	.000	100.0000	.000		.000	.000
6	H +O	+M	---	OH +	.1000+19+ 0.	-1.000	.0000	.000		.000	.000
7	H +O2	+M	---	HO2 +	.3000+16+ 0.	.000	-1.0000	.000		.000	.000
8	OH +O	+M	---	HO2 +	.1600+21+ 0.	-1.500	.0000	.000		.000	.000
9	H2 +	+M	---	H +H	.2080+16+ 0.	.070	103.8300	.000		.000	.000
10	H2O +	+M	---	OH +H	.2300+25+ 0.	-2.000	122.6000	.000		.000	.000
11	NO +O	+M	---	NO2 +	.1380+22+ 0.	-1.820	.0000	.000		.000	.000
12	N2 +	+M	---	N +N	.4000+22+ 0.	-1.600	225.0000	.000		.000	.000
13	O +O	+M	---	O2 +	.1000+19+ 0.	-1.000	.0000	.000		.000	.000
14	CH4 +CH2	+	---	CH3 +CH3	.1260+13+ 0.	.700	20.0000	.000		.000	.000
15	CH4 +H	+	---	CH3 +H2	.5000+11+ 0.	1.000	10.0000	.000		.000	.000
16	CH4 +OH	+	---	CH3 +H2O	.3000+14+ 0.	.000	5.0000	.000		.000	.000
17	CH4 +O	+	---	CH3 +OH	.1900+15+ 0.	.000	11.7000	.000		.000	.000
18	CH3 +CH2O+	+	---	CH4 +CHO	.2000+12+ 0.	.000	6.5000	.000		.000	.000
19	CH3 +OH	+	---	CH2 +H2O	.2600+12+ 0.	.700	2.0000	.000		.000	.000
20	CH3 +OH	+	---	CH3O+H	.6310+12+ 0.	.000	.0000	.000		.000	.000
21	CH3 +HO2	+	---	CH4 +O2	.1000+12+ 0.	.500	6.0000	.000		.000	.000
22	CH3 +O	+	---	CH2O+H	.2600+15+ 0.	.000	2.0000	.000		.000	.000
23	CH3 +O2	+	---	CH2 +HO2	.3160+13+ 0.	.000	69.5000	.000		.000	.000
24	CH3 +O2	+	---	CH2O+OH	.9000+12+ 0.	.000	12.0000	.000		.000	.000
25	CH3 +O2	+	---	CH3O+O	.3500+14+ 0.	.000	28.8000	.000		.000	.000
26	CH2 +CH2O+	+	---	CH3 +CHO	.2000+12+ 0.	.000	6.5000	.000		.000	.000
27	CH2 +H	+	---	CH +H2	.3160+12+ 0.	.700	5.0000	.000		.000	.000
28	CH2 +OH	+	---	CH +H2O	.5000+12+ 0.	.500	6.0000	.000		.000	.000
29	CH2 +OH	+	---	CH3 +O	.5000+12+ 0.	.500	6.0000	.000		.000	.000
30	CH2 +OH	+	---	CH2O+H	.1000+14+ 0.	.000	5.0000	.000		.000	.000
31	CH2 +H2	+	---	CH3 +H	.3000+13+ 0.	.000	7.0000	.000		.000	.000
32	CH2 +NO	+	---	CH2O+N	.1600+13+ 0.	.000	7.0000	.000		.000	.000
33	CH2 +O	+	---	CHO +H	.5000+12+ 0.	.500	4.0000	.000		.000	.000
34	CH2 +O2	+	---	CH2O+O	.5000+12+ 0.	.500	7.0000	.000		.000	.000
35	CH +CH4	+	---	CH2 +CH3	.1000+13+ 0.	.000	17.1000	.000		.000	.000
36	CH +CO2	+	---	CHO +CO	.1000+11+ 0.	.500	6.0000	.000		.000	.000
37	CH +OH	+	---	CHO +H	.5000+12+ 0.	.500	10.0000	.000		.000	.000
38	CH +HO2	+	---	CH2 +O2	.1000+11+ 0.	.500	15.0000	.000		.000	.000
39	CH +O	+	---	CO +H	.5000+12+ 0.	.500	.0000	.000		.000	.000
40	CH +O2	+	---	CHO +O	.5000+12+ 0.	.500	6.0000	.000		.000	.000
41	CH3O+H	+	---	CH2O+H2	.1000+15+ 0.	.000	.0000	.000		.000	.000
42	CH3O+OH	+	---	CH2O+H2O	.3160+14+ 0.	.000	.0000	.000		.000	.000
43	CH3O+O	+	---	CH2O+OH	.1000+15+ 0.	.000	.0000	.000		.000	.000
44	CH3O+O2	+	---	CH2O+HO2	.1000+13+ 0.	.000	6.0000	.000		.000	.000
45	CH2O+H	+	---	CHO +H2	.1260+11+ 0.	1.000	3.2000	.000		.000	.000
46	CH2O+OH	+	---	CHO +H2O	.3160+11+ 0.	1.000	.0000	.000		.000	.000
47	CH2O+O	+	---	CHO +OH	.2900+12+ 0.	1.000	4.4000	.000		.000	.000
48	CHO +CHO	+	---	CH2O+CO	.1600+12+ 0.	.500	.0000	.000		.000	.000
49	CHO +CH2	+	---	CH3 +CO	.3160+11+ 0.	.700	1.0000	.000		.000	.000
50	CHO +CH3	+	---	CH4 +CO	.3160+12+ 0.	.700	.0000	.000		.000	.000

TABLE 3. CONTINUED

51	CHO +H +	---	CO +H2	.3000+11+ 0.	1.000	.0000	.000	.000
52	CHO +OH +	---	CO +H2O	.3000+11+ 0.	1.000	.0000	.000	.000
53	CHO +H02 +	---	CH2O+O2	.1000+15+ 0.	.000	3.0000	.000	.000
54	CHO +N +	---	CH +NO	.1000+15+ 0.	.000	48.6000	.000	.000
55	CHO +O +	---	CO +UH	.6310+12+ 0.	1.000	.5000	.000	.000
56	CHO +O +	---	CO2 +H	.3160+12+ 0.	.000	.0000	.000	.000
57	CO +OH +	---	CO2 +H	.1510+08+ 0.	1.300	-.7650	.000	.000
58	CO +H02 +	---	CHO +O2	.3000+13+ 0.	.000	37.1000	.000	.000
59	CO +O2 +	---	CO2 +O	.3160+13+ 0.	.000	50.0000	.000	.000
60	CO2 +N +	---	CO +NO	.2000+12+ 0.	.500	25.0000	.000	.000
61	H +OH +	---	H2 +O	.2710+18+ 0.	-.940	14.6900	.000	.000
62	H +H02 +	---	OH +OH	.2500+15+ 0.	.000	1.9000	.000	.000
63	H +N02 +	---	OH +NO	.3160+15+ 0.	.000	1.5000	.000	.000
64	OH +H2 +	---	H +H2O	.2500+14+ 0.	.000	5.2000	.000	.000
65	OH +OH +	---	H2O +O	.6000+13+ 0.	.000	1.0000	.000	.000
66	OH +O +	---	H +O2	.6310+12+ 0.	.500	.0000	.000	.000
67	H02 +H +	---	O2 +H2	.2500+14+ 0.	.000	.7000	.000	.000
68	H02 +OH +	---	H2O +O2	.5000+14+ 0.	.000	1.0000	.000	.000
69	H02 +O +	---	OH +O2	.5000+14+ 0.	.000	1.0000	.000	.000
70	N +OH +	---	NO +H	.6310+12+ 0.	.500	.0000	.000	.000
71	N +NO +	---	N2 +O	.3100+14+ 0.	.000	.3340	.000	.000
72	N +N02 +	---	N2 +O2	.1000+13+ 0.	.000	.0000	.000	.000
73	N +N02 +	---	NO +NO	.4000+13+ 0.	.000	.0000	.000	.000
74	N +O2 +	---	NO +O	.6000+10+ 0.	1.000	6.3000	.000	.000
75	NO +OH +	---	H02 +N	.5000+11+ 0.	.500	96.5000	.000	.000
76	NO +H02 +	---	NO2 +OH	.5000+12+ 0.	.500	3.5200	.000	.000
77	NO2 +O +	---	NO +O2	.1000+14+ 0.	.000	1.0000	.000	.000
78	CH +CH3 +	---	CH2 +CH2	.3200+13+ 0.	.000	8.0000	.000	.000
79	H +NO +M	---	HNO +	.2000+17+ 0.	.000	.0000	.000	.000
80	N2O + +M	---	N2 +O	.4000+15+ 0.	.000	51.4000	.000	.000
81	CH4 +CN +	---	HCN +CH3	.3160+12+ 0.	.700	5.0000	.000	.000
82	CH3 +CN +	---	HCN +CH2	.1000+12+ 0.	.700	3.0000	.000	.000
83	CH3 +HNO +	---	CH4 +NO	.5000+12+ 0.	.500	.0000	.000	.000
84	CH2 +CN +	---	CH +HCN	.3160+13+ 0.	.000	5.0000	.000	.000
85	CH2 +N2 +	---	HCN +NH	.1000+15+ 0.	.000	60.0000	.000	.000
86	CH3O+N +	---	CH2O+NH	.1000+15+ 0.	.000	.0000	.000	.000
87	CH3O+NO +	---	HNO +CH2O	.5000+12+ 0.	.500	4.2300	.000	.000
88	CHO +HNO +	---	CH2O+NO	.3160+12+ 0.	.500	.0000	.000	.000
89	CHO +N +	---	HCN +O	.1000+15+ 0.	.000	.0000	.000	.000
90	CHO +N +	---	CO +NH	.2000+12+ 0.	.500	2.0000	.000	.000
91	CHO +NO +	---	CO +HNO	.2000+12+ 0.	.500	2.0000	.000	.000
92	HCN +OH +	---	CN +H2O	.2000+12+ 0.	.600	5.0000	.000	.000
93	HCN +N +	---	CH +N2	.2500+12+ 0.	.000	16.0000	.000	.000
94	HCN +O +	---	CH +NO	.1000+15+ 0.	.000	72.0000	.000	.000
95	CN +CO2 +	---	NCO +CO	.3720+13+ 0.	.000	.0000	.000	.000
96	CN +OH +	---	HCN +O	.3160+13+ 0.	.000	3.0000	.000	.000
97	CN +OH +	---	NCO +H	.6200+14+ 0.	.000	.0000	.000	.000
98	CN +H2 +	---	HCN +H	.6200+13+ 0.	.000	5.3000	.000	.000
99	CN +NH +	---	CH +N2	.1000+15+ 0.	.000	40.0000	.000	.000
100	CN +NO +	---	CO +N2	.3000+12+ 0.	.000	.0000	.000	.000
101	CN +O +	---	CO +N	.6310+12+ 0.	.500	.0000	.000	.000
102	CN +O2 +	---	CO +NO	.3000+12+ 0.	.000	.0000	.000	.000
103	NCO +H +	---	NH +CO	.5000+12+ 0.	.500	6.8700	.000	.000
104	CO +HNO +	---	CO2 +NH	.1000+12+ 0.	.500	7.0000	.000	.000
105	H +HNO +	---	H2 +NO	.1000+14+ 0.	.000	2.5000	.000	.000
106	H +HNO +	---	NH +OH	.2000+12+ 0.	.500	23.0000	.000	.000
107	H +N2O +	---	OH +N2	.4000+14+ 0.	.000	15.0000	.000	.000

TABLE 3. CONCLUDED

108	H	+N2O	+	--	NH	+NO	.1000+12+	0.	.500	30.0000	.000	.000
109	HNO	+HNO	+	--	N2O	+H2O	.1000+11+	0.	.500	41.5500	.000	.000
110	HNO	+OH	+	--	H2O	+NO	.1000+13+	0.	.000	1.0000	.000	.000
111	HNO	+NO	+	--	OH	+N2O	.2000+13+	0.	.000	26.0000	.000	.000
112	HNO	+O	+	--	OH	+NO	.5000+12+	0.	.500	.0000	.000	.000
113	HNO	+O	+	--	NH	+O2	.1000+12+	0.	.500	7.0000	.000	.000
114	OH	+N2O	+	--	H2O	+N2	.3160+14+	0.	.000	15.0000	.000	.000
115	NH	+H	+	--	N	+H2	.6310+12+	0.	.500	8.0000	.000	.000
116	NH	+OH	+	--	H2O	+N	.5000+12+	0.	.500	2.0000	.000	.000
117	NH	+OH	+	--	NO	+H2	.5000+12+	0.	.500	2.0000	.000	.000
118	NH	+O	+	--	N	+OH	.1700+11+	0.	.700	.1000	.000	.000
119	NH	+O	+	--	NO	+H	.6310+12+	0.	.500	.0000	.000	.000
120	NH	+N	+	--	H	+N2	.6000+12+	0.	.500	.0000	.000	.000
121	NH	+NH	+	--	N2	+H2	.3600+12+	0.	.550	1.9000	.000	.000
122	NH	+NO	+	--	N2	+OH	.2400+13+	0.	.000	.0000	.000	.000
123	NH2	+H	+	--	NH	+H2	.1400+12+	0.	.670	4.3000	.000	.000
124	NH2	+OH	+	--	NH	+H2O	.3000+11+	0.	.680	1.3000	.000	.000
125	NH2	+O	+	--	NH	+OH	.9200+12+	0.	.500	.0000	.000	.000
126	NH2	+O2	+	--	NH	+H2O	.1000+14+	0.	.000	50.5000	.000	.000
127	NH2	+NH2	+	--	NH3	+NH	.1700+12+	0.	.630	3.6000	.000	.000
128	NH2	+NO	+	--	N2	+H2O	.5000+13+	0.	.000	.0000	.000	.000
129	NH3	+OH	+	--	NH2	+H2O	.1260+11+	0.	.680	1.1000	.000	.000
130	NH3	+H	+	--	NH2	+H2	.1900+12+	0.	.670	3.4000	.000	.000
131	NH3	+O	+	--	NH2	+OH	.1500+13+	0.	.000	6.0000	.000	.000
132	NH3	+O2	+	--	NH2	+H2O	.5000+12+	0.	.500	56.0000	.000	.000
133	N2O	+O	+	--	N2	+O2	.1000+15+	0.	.000	28.0000	.000	.000
134	N2O	+O	+	--	NO	+NO	.1000+15+	0.	.000	28.0000	.000	.000
135	NO	+N2O	+	--	NO2	+N2	.2000+15+	0.	.000	50.0000	.000	.000
136	NO	+NO2	+	--	N2O	+O2	.1000+13+	0.	.000	60.0000	.000	.000

Figure 6. Conversion of NH_3 to NO_x .

Figure 7. Conversion of $(\text{CN})_2$ to NO_x .

Figure 8. Retention of added NO.

Figure 9. Temperature versus mixture ratio in jet-stirred combustor.

combustion baseline test plans, fabrication of the refractory reactors, testing of CH₄/air mixtures to determine thermal NO_x formation will also occur in the second quarter.

To complete the gas phase volatile combustion reaction set of the kinetic model, the need for additional hydrocarbon and NO_x reactions will be investigated. The compilation of all required reaction rate data will be completed during the following quarter. The model will be further verified and refined by prediction of thermal NO_x formed in the initial combustion tests of the stirred reactor (Task 1.2).

4. SUMMARY

During the first quarter of the program, fabrication and setup of the cold flow reactor has been completed. Tests of this reactor will establish the operating conditions for subsequent natural gas baseline, char, and coal combustion tests to obtain early NO_x formation kinetic data. The cold flow test matrix has been established and testing will commence early in the following quarter. Initial runs of the kinetic model gas phase reaction set have been completed. Comparison of NO_x formation predictions to existing combustion data appear good. Gas phase mechanisms will be further required, and solid phase/gas interactions will be computed in the following months.

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