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Report No. DOE-PC30295-2

KINETICS OF NO_x FORMATION DURING EARLY STAGES
OF PULVERIZED-COAL COMBUSTION

SECOND QUARTERLY REPORT

for the period

29 December 1980 to 3 April 1981

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April 30, 1981

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

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ABSTRACT

Program results for the Department of Energy Contract DE-AC22-80PC-30295 are reported. The program uses a stirred reactor technique to simulate the mixed gas combustion environment of a coal particle during devolatilization. A cold flow model of the reactor is in use to develop the operating conditions required for combustion experiments. Coal particle trajectories and the effects of the particle on the gas stirring are currently being evaluated. A kinetics computer model for particle devolatilization and combustion is being developed based on the experimental data of the program. A preliminary set of gas phase reactions has been used with good comparison to existing stirred reactor data. Initial combustion tests will be performed in the following quarter.

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TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
Abstract	iii
1 CONTRACT OBJECTIVES	1
2 CONTRACT TASKS	1
2.1 Experimental design (Task 1.1)	1
2.2 Kinetics Modeling (Task 1.4)	3
3 WORK PLANNED	7
4 SUMMARY	7

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 were made for the cold flow reactor tests, and the basis of the kinetics model was formulated. In the second quarter, preliminary tests were conducted on the cold flow model, and refinement of the preliminary kinetics model was completed. These activities were performed under Tasks 1.1 and 1.4 as described below.

2.1 Experimental Design (Task 1.1)

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.

Tests were conducted during the second quarter to observe the coal trajectories over a range of residence times within the reactor of 5 to 20 msec.

These tests were conducted by flowing coal and stirring air through the plastic cold flow model. Although the coal jet could be seen passing into the stirred region, widening of the jet occurred and made it difficult to determine whether a significant portion of the jet achieved the desired trajectory, straight through the reactor. The difficulty in seeing the trajectory near the reactor outlet was apparently due to insufficient scattering of the diffuse light source by the particles as the jet spread. The experiments suggest that better visualization near the jet outlet could be achieved if a more intense light source could be used locally to define the jet boundaries. At the current time, a laser light source is being obtained. Setup and use of the laser should complete definition of the combustion test matrix early in the following quarter.

To perform reactor stirring measurements, a helium tracer technique was developed 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 considered well stirred.

Initial tests with the helium decay apparatus were conducted in the second quarter. The recorded response at the reactor outlet is currently being refined (by electronic adjustments) to provide more quantitative flow information. The reactor mixing will be investigated 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.

Initial tests have also been conducted to evaluate the degree of coal jet carrier gas breakup and mixing by injection of the helium tracer through

the top jet (operating on air only). It appears that a very sharp cutoff of the helium occurs, indicating near-plug flow through the reactor. The final evaluation of this behavior, however, will require development of greater amplification in the hot wire signal. The final results will establish the time scale for volatile combustion, required for the kinetic model.

The hardware for casting the combustion reactors has been assembled. Casting of the new reactors with coal jet and mixing ports will be done during cold flow testing to minimize further program delays between test periods. The cold flow and gas phase combustion tests will be completed during the following quarter.

2.2 Kinetics Modeling (Task 1.4)

The formulated elementary reaction set (adapted from that of Energy and Environmental Research Corporation) for reactive hydrocarbon and nitrogen species has been refined during the program second quarter. Initial computations of nitrogen species production showed some discrepancies in comparison to selected experimental stirred reactor data. Differences in the EER and Acurex thermochemical data (taken from JANAF curve fits) were noted for the heat of formation at 298K and specific heat values for a few species. All the species compared are listed in Table 1. The percentage differences relative to the data used by EER are tabulated for the temperature range of interest ($\approx 1000\text{K}$ to 2500K) for the species whose discrepancies are greater than 1 percent.

The sensitivity of the computational scheme to the curvefit values has been evaluated by eliminating the discrepancies of Table 1 and rerunning of sample data comparisons. Two of the comparisons are shown in Figures 1 and 2. Although the discrepancies were found to be small (less than 10 percent), the effects on NO predictions are significant -- especially on the fuel-lean side. With the updated thermochemical set, higher NO conversion was predicted than that of the old thermochemical set under fuel-lean conditions,

TABLE 1. COMPARISON OF EER AND JANAF THERMOCHEMICAL DATA

Species	Heat of Formation at 298K			Specific Heat %
	EER (Kcal/mole)	JANAF Curve Fit (Kcal/mole)	%	
CO	-26.4165	-26.417		5.
CO ₂	-94.054	-94.054		
CH ₄	-17.895	-17.895		
H ₂ O	-57.7979	-57.798		
O ₂	0	0		
N ₂	0	0.79×10^{-3}	X	
H ₂	0	0.2×10^{-3}	X	
H	52.10	52.1		
O	59.559	59.559		
N	113.0	112.96		
NO	21.58	21.58		
HO	9.492	9.432	1.	
HO ₂	5.0	5.0		
CH ₃	34.82	34.82		
CH ₂ O	-25.95	-27.70	7.	
CHO	9.0	-2.9	132.	2.
NO ₂	7.91	7.91		
N ₂ O	19.61	19.61		
CH ₂	92.35	92.07		5.
CH	142.0	142.0		
HNO	24.5	23.8	3.	
H ₂ N	40.07	40.07		7.
H ₃ N	-10.97	-10.97		
HN	90.0	81.0	10.	
CN	104.0	104.0		
CHN	32.3	32.3

Figure 1. Conversion of NH_3 to NO_x -- 1300 ppm addition NH_3 .

Figure 2. Retention of added NO -- NO addition.

resulting in overpredicting the experimental data. Under fuel-rich conditions, the same trend was observed except that satisfactory agreement with the experimental data was retained. The overprediction of NO was found to be particularly sensitive to the heat of formation of CHO. Since varying the heat of formation of any species can result in variations in the equilibrium constant and, therefore, the reverse reaction rate, adjustments to the rate constants of all reactions containing CHO may be required to further improve the comparisons. This level of refinement is not considered to be warranted at this time, however. Although some discrepancies remain, the new set of thermochemical data is an improvement since it results in closer comparisons under fuel-rich conditions for the retention of added NO case (Figure 2).

3. WORK PLANNED

The completion of cold flow tests has been delayed into the third quarter. Following completion, the baseline gas phase thermal NO_x tests will be conducted in fabricated cast refractory reactors. Initial char tests under Task 1.2 are also expected to be complete in the following quarter.

The basis for the kinetic computational scheme has been developed and calculations are showing good comparison to existing data. The reaction set will be finalized in the next quarter. Preliminary computations will be made to include coal devolatilization and other solid/gas phase interaction models. The code will then be used to predict thermal NO_x formation for comparison to the present reactor data and NO_x destruction as observed in the following char tests of Task 1.2.

4. SUMMARY

During the second quarter of the program, initial coal trajectory and gas mixing cold flow tests were conducted. The data from both test types require refinement to adequately characterize the reactor flows. A laser

light source will be used to better define coal particle paths. Electronic modifications to the helium tracer apparatus are being completed. Refinement of the kinetic model thermochemical data has been completed, providing satisfactory agreement between calculated predictions and selected experimental data. Coal devolatilization mechanisms will now be added to the set of gas phase reactions.