HIGH PRESSURE COAL COMBUSTION KINETICS PROJECT

COOPERATIVE AGREEMENT NO DE-FC26-01NT40777

QUARTERLY REPORT FOR OCTOBER-DECEMBER, 2002

FOR

***NETL AAD Document Control Bldg. 921
U.S. Department of Energy
National Energy Technology Laboratory
P.O. Box 10940
626 Cocharans Mill Road
Pittsburgh, PA 15236-0940***

BY

Chris Guenther, Ph.D.
Fluent Inc.
Primary Recipient
10 Cavendish Court, Lebanon, NH 03766
Point of Contact: Kristi C. Fenner (Business and Financial)
Point of Contact: Dr. Chris Guenther (Technical)

***Foster Wheeler Development Corporation
12 Peach Tree Hill Rd., Livingston, NJ 07039***

***SRI International
333 Ravenswood Ave., Menlo Park, CA 94025***

***American Air Liquide
5230 S. East Ave., Countryside, IL 60525***

University of Connecticut

Department of Chemical Engineering, University of Connecticut, 191 Auditorium Rd.,
Unit 3222, Storrs, CT 06269-3222

Brown University

Division of Engineering, Box D, 182 Hope St., Brown University, Providence RI 02912

Niksa Energy Associates

Niksa Energy Associates, 1745 Terrace Dr., Belmont, CA 94002

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

TABLE OF CONTENTS

1.	Technical Accomplishments	4
2.	Issues and Resolutions	13
3.	Progress Forecast for the Next Quarter	13
4.	Personnel and Affiliation, List of Abbreviations	14
Appendix A: Project Milestone Chart (Update 12-26-01)		15

Executive Summary

SRI has completed the NBFZ test program, made modification to the experimental furnace for the HPBO test. The NBFZ datasets provide the information NEA needs to simulate the combustion and fuel-N conversion with detailed chemical reaction mechanisms. BU has determined a linear swell of 1.55 corresponding to a volumetric increase of a factor of 3.7 (!) and a decrease in char density by the same factor. These results are highly significant, and indicate significantly faster burnout at elevated pressure due to the low char density and large diameter.

1. Technical Accomplishments

Task 0 Planning

Completed

Task 1.0 Submodels for Pollutant Formation

Task 1.2 NBFZ Tests

- The modified "long furnace" SRT-RCFR facility was used to perform 3 additional tests on Pittsburgh No. 8 coal at 30 atm. All tests were performed using a coal suspension loading of 1.33%. In conjunction with the 9 tests reported last month, these tests completed the series at 30 atm. The tests covered an oxygen/coal ratio from 9% to 249%.
- As in the 10 and 20 atm tests, the aerosol product in these tests appears to be almost exclusively soot as opposed to tar. Char and soot samples were submitted to Huffman Laboratories for analysis.
- Tests of Illinois No. 6 coal were begun. Nine tests were conducted at 10 atm, of which 7 were of sufficient quality to complete the series. Again, we began with a high oxygen loading and worked toward lower values, covering a range of oxygen/coal ratios from 5% to 237%. The coal suspension loading was 4.5%. Char and soot samples were submitted to Huffman Laboratories for analysis.
- Tests of Illinois No. 6 coal at 20 atm were begun, with 5 tests completed during the period. The coal suspension loading in these tests was 2.25%.
- All tests with Illinois No. 6 coal have been conducted using mullite flow tubes, but the maximum furnace temperatures in the tests have been restricted to approximately 1580°C. This modest reduction in temperature from the previous values of up to 1610°C, together with use of relatively low coal suspension loadings, has thus far eliminated the flowtube failures experienced in earlier tests.
- Elemental analyses of the char and soot samples from the 20 atm Pitt coal tests were received from Huffman Laboratories. The results were incorporated into the analyses of this dataset, and the completed dataset was forwarded to NEA for their use.

- A complete set of char samples from all the tests of Pittsburgh No. 8 coal at 10, 20, and 30 atm, were sent to Bob Hurt at Brown University for his analysis.
- The modified "long furnace" SRT-RCFR facility was used to perform 6 additional tests on Illinois No. 6 coal at 20 atm. All tests were performed using a coal suspension loading of 2.25%. In conjunction with the 5 tests reported last month, these tests completed the series at 20 atm. The tests covered an oxygen/coal ratio from 50% to 284 %. Tests at lower oxygen concentrations could not be achieved because of severe clogging of the upper and lower centripeter nozzles. Char and soot samples were submitted to Huffman Laboratories for analysis.
- One test of Illinois No. 6 coal at 2 atm was performed with a coal suspension loading of 16.4% and an oxygen/coal ratio of 160%. The primary purpose of this test was to obtain a char sample at low pressure for comparison with the char samples produced at 10 and 20 atm. It also served as a "test case" for HPBO tests that are scheduled to be performed at 1 and 20 atm. Although the oxygen/coal ratio in this test was lower than the 1.15xS.R. planned for the HPBO series, we did find that the centripeter nozzle clogged in a 3 minute run, and water condensed on the cooled centripeter nozzle. These observations may limit the coal suspension loading or the run time in future low pressure tests.
- The modified "long furnace" SRT-RCFR facility was used to perform 7 tests of PRB coal at 10 atm. This series is a repeat of the first series of NBFZ tests performed, but now using the long furnace configuration. The coal suspension loading was 4.5%, and the oxygen/coal ratio ranged from 83% to 243%.
- Elemental analyses of the char and soot samples from the 30 atm Pitt coal tests were received from Huffman Laboratories. The results were incorporated into the analyses of this dataset, and the completed dataset was forwarded to NEA for their use.
- Samples of soot filters from all the test series to date were sent to Joe Helble at UCONN for his analysis. The samples were from the test at maximum oxygen/coal ratio in each series, thus representing maximum burnout. Joe will study these filter samples to determine how much particle size and chemistry information can be determined from them.
- Information was exchanged with Joe Helble on details of implementing the low pressure impactor diagnostic on the HPBO experiments, and a plan of action was developed.
- The modified "long furnace" SRT-RCFR facility was used to perform 3 additional tests of PRB coal at 10 atm. This completed the repeat of the first series of NBFZ tests performed, but now using the long furnace configuration. The coal suspension loading was 4.5%, and the oxygen/coal ratio ranged from 6% to 243%. This repeat test series completed the NBFZ test program.
- Char and soot samples from the PRB test series were forwarded to Huffman Laboratories for analysis.
- Elemental analyses of the char and soot samples from the 10 and 20 atm Illinois coal tests were received from Huffman Laboratories. The results were incorporated into the analyses of these datasets, but incorporation of corrections to calibration data remains to be completed before the results are forwarded to NEA.
- The first stages of hardware changes required to perform HPBO tests were carried out. The tests with minimum residence time for this series will be conducted using only the existing rf furnace operating at 1570°C, but with the insulation modified to create a 15.5 cm long furnace compared to the 12.7-cm long furnace used in the "long furnace" NBFZ tests. Use of a carrier gas velocity of 30 cm/sec gives a

nominal residence time of 0.52 sec. Longer residence times are achieved by adding 33.5-cm long furnace sections heated by Kanthal MoSi_2 heaters operating at 1400°C. Three such sections are available, but we hope to meet the maximum residence times required using just two sections.

- The program plan calls for HPBO experiments to be carried out at oxygen/fuel stoichiometric ratios of 1.15 and oxygen concentrations of 21% and 50%. To meet these specifications at 20 atm, it would be necessary to feed coal (for the case of PRB coal) at rates of 7.4 g/min and 17 g/min, respectively. Our previous experience in the NBFZ tests showed that coal feed rates as low as 1.4 g/minute raised the mullite flowtube temperature above its melting point. This is not surprising, given that a PRB coal feed rate of only 2.1 g/min corresponds to a heat release of 1 kW. Since it is necessary to heat the mullite flowtube to near its maximum temperature rating (1700°C) in order to heat the coal particles to their ignition point, it is easily understood that the addition of kilowatt levels of heat over a short portion of the tube can raise the tube temperature beyond its capability.

Given these constraints on coal feed rate, SRI can satisfy the stoichiometry ratio requirement in the high pressure tests by operating at a lower oxygen level, or we can maintain the specified oxygen levels but operate with a much leaner flame. At low pressure, the feed rate required to achieve a S.R. = 1.15 and an oxygen concentration of 21% can be achieved. We will also attempt to maintain the required stoichiometric ratio at 50% oxygen.

- The program plan also called for each coal to be tested at 1 atm to provide a baseline for comparison of the high pressure effects. However, the analytical instruments we use to characterize the gaseous combustion products, particularly the NDIR instrument we use to measure CO , CO_2 , and O_2 , operate at atmospheric pressure, and require at least 5 psi inlet pressure to provide an adequate flow rate. In order to meet this requirement, and to keep the analytical process consistent with the NBFZ experiments, we have chosen to perform the low pressure tests at 2 atm rather than 1 atm.
- SRI used the basic furnace section to test PRB coal at 20 atm and a nominal residence time of 0.52 seconds, coal feed rate of 1.5 g/min and an oxygen concentration of 4.8% to give the required SR = 1.15. We then added one Kanthal section and used inlet velocities of 47 cm/s and 30 cm/s to achieve nominal residence times of 1.19 and 1.87 sec at the same SR and oxygen concentrations. We used the same configuration to test PRB coal at 2 atm with a nominal residence time of 1.87 s. In this test, a coal feed rate of 0.63 g/min and an oxygen concentration of 21% provided the desired SR = 1.15. Char yields (actually char plus ash particles captured in the centripeter) were 12.4% to 26.1% for the three 20 atm tests, and were 5.4% for the 2 atm test, which is near the ash content limit of 5.0% for this coal.

Task 1.4 Fuel-N Conversion Mechanism Development

NEA reviewed two datasets for Pit. #8 at 10 and 20 atm taken with the longer radiant furnace section at SRI, and noted marked improvements and remarkably good closures on the mass and elemental balances. The tabulated datasets are attached below. There are two columns under each run number. The left column reports the measured values of

the complete product distribution, and the right column shows any adjustments made to improve the closure of any of the mass or elemental balances. For example, in the second and third columns in the 10 atm dataset, the H₂ yield was adjusted from its measured value of 2.4 daf wt. % to 3.8 % to close the H-balance. The closures on the balances for total mass, C, H, and O appear below the block of product yields. The mass balance is based on the daf coal mass plus the amount of oxygen that was actually incorporated into gaseous products, which is typically 70 to 80 % of the O₂ fed into the furnace. The percentage O₂ utilization was assigned from the measured values of residual O₂ in the exhaust. The burnout percentages assigned to gaseous fuels, soot, and char appear below the block of balance closures.

Two adjustments were made uniformly to both datasets: (1) Estimates for the volatile S-species and (2) Corrected H₂O yields at high moisture levels. Since the Pit. #8 contains 6.9 daf. wt. % sulfur, volatile S-species are not negligible. But they were not monitored in the tests either. We arbitrarily expressed the volatile-S species as H₂S under conditions that were sufficiently reducing to retain gaseous fuel compounds, and as SO₂ under conditions where essentially all the gaseous fuel compounds had burned. This procedure would be expected to overestimate the volatile-S species under the most reducing conditions, because we have no evidence that all the coal-S had actually been released into the gas phase under the relatively moderate temperatures in these tests. The procedure probably overestimates the amount of SO₂ as well, because we have not yet considered the equilibrium product distributions for the test conditions. When the equilibrium analysis has been completed, the estimated volatile-S species will be refined.

Don Eckstrom (SRI) believes that all water levels over 27 to 30 daf wt. % were affected by condensation in the transfer lines to the detectors. Corrected values were estimated by adding a sufficient amount of H₂O to close the H-balances. This procedure is probably as accurate as a direct determination because H₂O is the only significant repository for hydrogen whenever moisture condensed in the transfer lines.

The only other adjustments made to the 10 atm dataset were for the secondary pyrolysis case (50B) without O₂, in which the decomposition products plugged the reactor flow tube and the aerosol particle separator. In addition to the upward adjustment to the H₂ yield, the soot yield was increased to the value predicted by PC Coal Lab[®] for the thermal histories imposed in this test, then the char yield was increased to close the mass balance. Note that all four balances were closed to within 2 % by these adjustments. Whereas no additional adjustments were made for any of the other test results, the balances on carbon, and hydrogen generally close to within ± 5 %. Breaches in the mass balances are only slightly higher. The O₂ balances are oversubscribed by over 10 %, and by more than one-third in 56B. However, the O-balances for the three most oxidizing tests (53B, 52B, and 51B) are subject to uncertainties associated with the SO₂ estimates, which make respective contributions to the O-balances of 0.060, 0.047, and 0.040. These cases may be much closer to the target closure of ± 5 %, pending refinements to the S-species. Hence, in this dataset, the closures are fine except for the O-balances on runs 56B and 55B. Only one of these runs (55B) was affected by plugging, and all the fed O₂ was utilized in both of them, which is highly unusual.

The assigned extents of burnout for the gaseous fuel compounds exhibit the expected tendency to increase monotonically for progressively more oxidizing conditions. But

only the final three extents of soot burnout are as systematic. The other three non-zero values are much more erratic. The initial extents of char burnout are may also seem peculiar, in that they immediately increase to 24 %, then stay the same while the gases and soot burn away. However, particles are very rapidly dispersed into the sheath in this turbulent flow, and these particles may be responsible for the immediate increase in burnout. It remains to be seen if the operating conditions assigned from the CFD simulations corroborate this interpretation.

Additional adjustments to the 20 atm dataset were made for the two most reducing cases and the two most oxidizing cases. In both of the most reducing tests, the soot yields were increased to 25.1 %, consistent with the PC Coal Lab[®] prediction. Following these adjustments, all four balances closed to within the target tolerance except for the H-balance on 64B. No adjustments whatsoever were made to the results of 62B, 61B, and 60B, yet nearly all the associated balances close to within ± 5 %. In the two most oxidizing runs, the char yields were adjusted downward to close the C-balances. These adjustments are large, and subject to revision based on the CFD simulations now underway. But it is hard to understand how the extent of char burnout could remain the same after substantial additions of O₂, as indicated by the data. In addition, data collected in runs 65B and 66B were completely rejected, due to very poor closures on the C-, H-, and O-balances. Both these cases imposed similar conditions to 63B, so no information was lost by their omission.

It is gratifying to see the expected tendencies in the extents of burnout for gases, soot, and char in the 20 atm dataset. Gases burn faster than soot which, in turn, burns faster than char. And each burnout profile develops with little or no scatter in the assigned values.

Both these datasets provide the information we need from the NBFZ tests to simulate the combustion and fuel-N conversion with detailed chemical reaction mechanisms. The CFD simulations to specify the conditions for the simulations with detailed chemistry were also completed during this month, and the chemistry simulations should be complete by the end of next month.

Pit. #8, 10 Atm Datasets, with Corrected Values, in daf wt. %.

	50B		56B		55B		54B		53B		52B		51B	
	M	C	M	C	M	C	M	C	M	C	M	C	M	C
CO2	0.4		29.4		52.2		70.9		94.3		142.6		197.7	
H2O	1.2		14.2		22.0		23.7		29.3	33.4	29.2	42.5	28.4	45.8
CO	7.8		35.9		45.1		43.3		41.3		20.1		15.5	
CH4	1.0		0.7		0.5		0.3		0.1		0.0		0.0	
C2	1.4		0.5		0.4		0.2		0.0		0.0		0.0	
C3	0.1		0.1		0.1		0.0		0.0		0.0		0.0	
Oils	0.3		0.3		0.1		0.0		0.0		0.0		0.0	
H2	2.4	3.8	2.5		2.7		2.2		1.3		0.43		0.17	
HCN	1.04		0.89		0.54		0.29		0.06		0.00		0.00	
NH3	0.03		0.06		0.05		0.03		0.02		0.00		0.00	
NO	0		0.01		0.01		0.00		0.01		0.02		0.19	
Tar	0		0		0		0		0		0		0	
H2S	Nm	7.4	Nm	7.4	Nm	7.4	Nm	7.4	Nm		Nm		Nm	
SO2	Nm		Nm		Nm		Nm		Nm	13.8	Nm	13.8	Nm	13.8

Soot	21.1	29.1	19.5	8.0	9.6	13.9	7.6	2.0
Char	40.3	48.5	36.9	38.4	35.7	35.6	26.1	20.4
ΣMass		1.020	1.095	1.063	1.042	1.081	1.027	1.076
ΣC		1.018	0.994	0.991	1.027	1.091	0.999	1.021
ΣH		1.008	0.966	1.135	1.062	0.999	1.000	1.004
ΣO		1.011	1.363	1.243	1.132	1.111	1.092	1.147
Xgas		0	39.5	53.1	68.5	87.4	100.0	100.0
Xsoot		0	32.7	72.5	67.0	52.7	74.2	93.2
Xchar		0	23.9	20.8	26.4	27.6	46.2	57.9

Pit. #8, 20 Atm Datasets, with Corrected Values, in daf wt. %.

	64B		63B		62B		61B		60B		59B		58B	
	M	C	M	C	M	C	M	C	M	C	M	C	M	C
CO2	1.6		4.4		36.4		46.7		119.0		142.0		179.3	
H2O	1.5		6.9		15.3		18.7		27.7	34.9	27.1	39.0	30.7	41.7
CO	12.0		21.8		30.1		33.3		35.5		29.9		22.0	
CH4	2.7		2.1		1.0		0.7		0.3		0.2		0.1	
C2	1.9		1.4		0.6		0.4		0.2		0.1		0.1	
C3	0.3		0.3		0.1		0.1		0.0		0.0		0.0	
Oils	0.8		0.6		0.2		0.1		0.0		0.0		0.0	
H2	3.5		3.1		3.0		2.3		1.1		0.7		0.33	
HCN	1.51		1.39		0.95		0.45		0.23		0.02		0.01	
NH3	0.08		0.07		0.08		0.08		0.05		0.03		0.00	
NO	0		0.05		0		0.03		0.01		0.02		0.11	
Tar	0		0		0		0		0		0		0	
H2S	Nm	7.4	Nm	7.4	Nm	7.4	Nm	7.4	Nm		Nm		Nm	
SO2	Nm		Nm		Nm		Nm		Nm	13.8	Nm	13.8	Nm	13.8

Soot	21.2	25.1	15.3	25.1	15.6	9.5	4.4	4.6	3.3		
Char	45.1		43.5		42.4	39.8	32.3	35.5	25.3	37.7	19.8
Σ Mass		0.964		1.008		1.023		0.981		1.006	
Σ C		0.956		1.000		0.992		0.936		1.036	
Σ H		1.101		0.979		1.057		1.024		1.000	
Σ O		0.955		1.034		1.070		1.027		1.045	
Xgas		0.0		21.4		60.8		75.3		90.1	
Xsoot		0.0		0.8		39.8		63.3		83.0	
Xchar		0.0		2.9		6.0		11.8		23.7	

NEA reviewed the dataset for Pit. #8 at 30 atm taken with the longer radiant furnace section at SRI, and noted marked improvements and remarkably good closures on the mass and elemental balances. The tabulated dataset is attached below. There are two columns under each run number. The left column reports the measured values of the complete product distribution, and the right column shows any adjustments made to improve the closure of any of the mass or elemental balances. For example, in the third and fourth columns, the H₂ yield was adjusted from its measured value of 3.36 daf wt. % to 0.36 % to close the H-balance. The closures on the balances for total mass, C, H, and O appear below the block of product yields. The mass balance is based on the daf coal mass plus the amount of oxygen that was actually incorporated into gaseous products, which is typically 60 to 70 % of the O₂ fed into the furnace. The percentage O₂ utilization was assigned from the measured values of residual O₂ in the exhaust, unless noted otherwise. The datasets are arranged in order of greater incorporation of O₂ into products, from left to right. The burnout percentages assigned to gaseous fuels, soot, and char appear below the block of balance closures.

Two adjustments were made uniformly to these datasets: (1) Estimates for the volatile S-species and (2) Corrected H₂O yields at high moisture levels. Since the Pit. #8 contains 6.9 daf. wt. % sulfur, volatile S-species are not negligible. But they were not monitored in the tests either. We arbitrarily expressed the volatile-S species as H₂S under conditions that were sufficiently reducing to retain gaseous fuel compounds, and as SO₂ under conditions where essentially all the gaseous fuel compounds had burned. This procedure would be expected to overestimate the volatile-S species under the most reducing conditions, because we have no evidence that all the coal-S had actually been released into the gas phase under the relatively moderate temperatures in these tests. The procedure probably overestimates the amount of SO₂ as well, because we have not yet considered the equilibrium product distributions for the test conditions. When the equilibrium analysis has been completed, the estimated volatile-S species will be refined.

Don Eckstrom (SRI) believes that all water levels over 27 to 30 daf wt. % were affected by condensation in the transfer lines to the detectors. Corrected values were estimated by adding a sufficient amount of H₂O to close the H-balances. This procedure is probably as

accurate as a direct determination because H_2O is the only significant repository for hydrogen whenever moisture condensed in the transfer lines. Only the data in runs 68, 69, and 79 were corrected on this basis.

These two adjustments, which we believe are not subject to significant uncertainties, were the only ones made to runs 72, 67, 71, 70, and 68. Consequently, it is especially significant that all four balances close to well within the target uncertainty of $\pm 5\%$ in run 71. The situation is essentially the same for run 67, except that the O_2 utilization into products was increased from 42.6 % to 47.5 % to close the O-balance. The uncertainties on the O-balances on runs 72 and 68 slightly exceed the target, and those in the H-balances on runs 70 and 68 have more substantial breaches. In both the latter two runs, the defects must be associated with the determinations of H_2O and H_2 , because the hydrocarbon yields are low and there is too little hydrogen in soot and char.

The O_2 utilization percentages were also increased in runs 77 and 73, although increasing the percentage to 100 % was still insufficient to close the O-balance in run 77. But this is the only flaw in the balances for this dataset. There were two additional adjustments to runs 77, 74, and 73. The H_2 yields were significantly reduced to close H-balances. This adjustment is more arbitrary than the others, because the problems could be in the relatively very high hydrocarbon yields. However, the analytical uncertainties are generally much lower for hydrocarbons, because they are detected with a flame ionization detector versus a thermal conductivity cell for H_2 . The second adjustment is the reduction in char yields, from 50 - 55daf wt. % to 44 - 47 %. The assigned values for runs 74 and 73 were interpolated from the value assigned for run 77 and the measured value for run 72. Finally, the corrected soot yield for run 74 is an interpolated value based on the soot yields measured in runs 77 and 73.

This dataset did not include a case for pure secondary volatiles pyrolysis. The estimated product distribution is largely based on the measured yields of hydrocarbons and N-species for run 77 and the yields of oxygenated gases and soot predicted with PC Coal Lab[®]. Of course, all four balances are essentially closed for the estimated products.

The assigned extents of burnout for the gaseous fuel compounds exhibit the expected tendency to increase monotonically for progressively more oxidizing conditions, except for runs 70 and 69 where burnout is nearly complete. The extents of soot burnout are almost as systematic, except that there is more scatter in the values for the final four runs. The extents of char burnout increase very gradually for progressively higher O_2 utilization, then reach an asymptotic value of 27 to 29 % for runs 68, 69, and 79. Values for runs 71 and 70 were omitted because they are clearly at odds with the tendency for more burnout for higher O_2 utilization.

This dataset provides the information we need from the NBFZ tests to simulate the combustion and fuel-N conversion with detailed chemical reaction mechanisms. The CFD simulations to specify the conditions for the simulations with detailed chemistry were also completed during this month, and the chemistry simulations should be complete by the end of next month.

Pit. #8, 30 Atm Datasets, with Corrected Values, in daf wt. %.

	2 nd Pyro 1	77B		74B		73B		72B		67B		71B		70B		68B	
		M	C	M	C	M	C	M	C	M	C	M	C	M	C	M	C
CO2	0.8	12.5		23.9		58.1		78.8		85.2		86.2		116		141	
H2O	1.6	11.5		15.9		18.8		23.3		24.2		31.5		31.4		27.8	30.4
CO	5.6	20.9		32.8		31.6		32.0		27.9		26.5		29.4		21.6	
CH4	5.0	4.6		3.5		2.3		1.2		0.7		0.7		0.0		0.3	
C2	4.5	2.9		1.8		1.2		0.5		0.3		0.3		0.4		0.1	
C3	1.6	0.4		0.1		0.1		0.1		0.0		-		0.1		0.0	
Oils	-	1.7		0.7		0.3		0.2		0.0		0.0		0.7		0.1	
H2	2.1	3.3	0.3	2.5	0.5	1.8	0.6	1.8		1.8		0.6		0.8		1.1	
HCN	1.5	1.2		0.7		0.6		0.1		0.3		0.4		0.1		0.0	
NH3	0.18	0.1		0.1		0.1		0.0		0.0		0.1		0.1		0.0	
NO	-	-		-		-		-		-		-		-		0.0	
Tar	-	-		-		-		-		-		-		-		-	
H2S	7.4	-	7.4	-	7.4	-	7.4	-	7.4	-	7.4	-	7.4	-	7.4	-	7.4
SO2	-	-		-		-		-		-		-		-		-	
Soot	22.9	16.5		7.4	13.0	9.5		5.3		7.4		3.8		5.2		7.8	
Char	46.8	55.2	46.8	51.3	45.4	53.7	44.0	42.5		38.8		43.9		44.2		33.3	
ΣMass	1.00		0.9		1.0		1.0		1.0		0.9		0.9		1.0		1.0
ΣC	0.98		1.0		1.0		1.0		1.0		1.0		1.0		1.1		1.0
ΣH	1.00		1.0		1.0		1.0		1.0		1.0		0.9		0.9		1.0
ΣO	1.01		1.1		1.0		1.0		1.0		1.0		0.9		1.0		1.0
Xgas	0.0		12.		44.		63.		81.		89.		89.		87.		94.

		5	2	0	5	1	2	0	0
Xsoot	0.0	28.	43.	58.	76.	67.	83.	77.	65
		0	2	5	9	7	4	3	9
Xchar	0.0	0.0	3.0	6.0	9.2	17.	-	-	28
						1			9

Task 2.0 Submodels for Char Oxidation

Task 2.1 HPBO Test Characterization

No work was conducted on this task until all NBFZ experiments are completed.

Task 2.5 Char Oxidation Mechanism

During October the data set on the characterization of SRI high-pressure chars (PRB 10,20,30 bar, Pitt. 8 10 bar) was analyzed. Tap density measurements indicate essentially no swelling for the PRB coal even at 30 bar (linear swelling factor 0.98). SEM morphologies indicate most particles shown little or no fluidity and no systematic effect of pressure is seen. The Pittsburgh 10 bar chars are highly fluid and the sample at lowest O/Coal ratio shows a linear swelling factors of 1.6, which is substantially higher than any U.S. coal in atmospheric testing in flame reactors (maximum linear swelling factor 1.27). SEM morphologies revealed extensive cenosphere formation. This enhanced fluidity and swelling should make these chars much easier to burn out than atmospheric chars provided their intrinsic reactivities are similar (work still pending).

BU will continue the characterization work on Pitt. #8 chars and hope to finish in December. Work on Illinois samples from SRI will begin as soon as samples are received. Selected char samples will also be sent to P.I. Helble in December for work on the inorganic task. Also in December BU plans to submit a selection of our SEM micrographs to the team and to the project website.

During December BU completed measurements of particle density on the full set of Pittsburgh #8 chars supplied by SRI (at 10,20,30 atm), and also the 10 atm. data for the older PRB sample set. The other measurements (intrinsic reactivity, surface area) are still underway. The char density data is very consistent over 3 duplicates, and the data on the new samples is in good agreement with data on the old samples where the two overlap (Pitt, 10 atm data). The results indicate no swelling for PRB at any pressure, and extreme swelling for Pittsburgh (linear swelling factor 1.5-1.6 at 10 atm., dropping to 1.3-1.4 at 30 atm.). For reference, swelling factors for Pitt at atmospheric pressure are known to be 1.1-1.2. There is thus a clear maximum with pressure. A linear swell of 1.55 corresponds to a volumetric increase of a factor of 3.7 (!) and a decrease in char density by the same factor. These results are highly significant, and

indicate significantly faster burnout at elevated pressure due to the low char density and large diameter.

Task 3.0 Submodels for Flyash and Fumes

Task 3.1-3.4

In the last monthly report, UCONN discussed the results of the computer controlled scanning electron microscopy (CCSEM) analysis of the Pittsburgh #8 coal sample. UCONN found a surprisingly high amount of pyrrhotite in this sample (46.3%w), suggesting partial oxidation of the pyrite in this coal. A second surprising finding was the much higher than expected inorganic content of the coal as calculated from the CCSEM analysis. The calculated ash content of this coal from CCSEM was 25.23% versus 9.44% ash (dry basis) reported in the Penn State database. During this past month, the Pittsburgh #8 sample was re-analyzed by CCSEM to determine whether these results were incorrect, but the results were similar to the first analysis. SRI also completed proximate analyses of this sample this past month and reported an ash content of 12.5%. This discrepancy between the two warrants further investigation to determine whether the CCSEM results are erroneous or whether the UConn sub-sample of Pittsburgh #8 has a higher-than- expected ash content. Fluent is therefore exploring the option of having proximate and ASTM ash analysis conducted on this sample of coal.

During the past month, UCONN also received the results from the CCSEM for the other two coals: Illinois #6 and the Wyodak Anderson PRB coal. The data for the Illinois coal sample are shown in Figures 1 and 2 and Tables 1 and 2; and those for the PRB coal sample are shown in Figures 3 and 4 and Tables 3 and 4. Figures 1 and 3 show the mineral composition detected by CCSEM, which constituted 13.91 %w of the coal for Illinois and 3.99%w for PRB. These amounts are in agreement with the proximate analysis sent to us by SRI for PRB (5.01%) and the one in the Penn State database for Illinois (13.39%).

Figures 2 and 4 show the reported mineral size distributions for Illinois and PRB. Tables 1 and 3 show the detailed mineral particle size distribution of the major minerals present in these samples.

Tables 2 and 4 present the oxide form of the minerals that was calculated from the CCSEM data for Illinois and PRB. This information will be compared with the ASTM ash analysis when the latter becomes available.

ILLINOIS

In the Illinois sample, there is an unexpectedly large amount of pyrrhotite (66.9%w of the minerals), which, together with calcite (9.0%w) and quartz (6.1%w) constitute the main components of the sample. A high percentage of pyrrhotite was also reported for

Pittsburgh # 8 in the past monthly report. The pyrrhotite and calcite in the Illinois sample are mainly excluded minerals (79.2% and 87.5% w).

Figure 1. Mineral composition of the Illinois sample.

As shown in Figure 2, there is a high percentage of large minerals (>22 μ m) present in this coal. According to the detailed mineral data shown in Table 1, all size ranges are dominated by pyrrhotite, a mineral that, in addition to calcite is also present as a major component in the larger particles.

Figure 2. Mineral particle size distribution of the Illinois sample.

Table 1. Mineral particle size distribution and composition of the Illinois sample.

	1-2.2 μ m	2.2-4.6 μ m	4.6- 10.0 μ m	10.0- 22.0 μ m	22.0- 46.0 μ m	46.0- 100.0 μ m	Total, %w
Quartz	18.0	31.1	27.9	19.7	0.0	1.6	6.1
Calcite	0.0	0.0	0.0	1.1	33.3	65.6	9.0

Kaolinite	12.5	16.7	16.7	18.8	4.2	31.3	2.4
Montmorillonite	10.0	20.0	10.0	20.0	30.0	10.0	1.0
K Al-silicate	14.7	20.6	17.6	19.1	19.1	8.8	3.4
Fe Al-silicate	0.0	0.0	0.0	50.0	50.0	0.0	0.2
Na-Al-silicate	0.0	0.0	0.0	0.0	0.0	0.0	0.1
Aluminosilicate	0.0	0.0	25.0	25.0	25.0	25.0	0.2
Mixed Al-silicate	0.0	16.7	16.7	16.7	0.0	33.3	0.6
Ca Silicate	0.0	0.0	0.0	0.0	0.0	50.0	0.2
Pyrite	0.0	0.0	0.0	3.6	46.4	50.0	2.8
Pyrrhotite	0.6	1.5	4.9	14.3	43.8	34.8	66.9
Oxidized Pyrrho	0.0	0.0	25.0	56.3	18.8	0.0	0.8
Gypsum	0.0	0.0	0.0	0.0	0.0	0.0	0.1
Apatite	0.0	0.0	0.0	0.0	10.0	90.0	1.0
Si-rich	14.3	42.9	14.3	0.0	14.3	14.3	0.7
Unclassified	16.3	16.3	11.6	16.3	18.6	18.6	4.3

Table 2. Calculated oxide composition obtained from CCSEM analysis of Illinois sample (mass fraction as oxide)

	Illinois
SiO ₂	0.14
Al ₂ O ₃	0.03
Fe ₂ O ₃	0.25
TiO ₂	0.00
P ₂ O ₅	0.00
CaO	0.07
MgO	0.00
Na ₂ O	0.00
K ₂ O	0.01
SO ₃	0.48

PRB- WYODAK ANDERSON

For this coal sample, the major components are quartz (27.1%w), kaolinite (20.5%w), Cal Al-P (12.2%w) and unclassified ones (13.3%w). There is a small amount of pyrrhotite (6.4%w), but mainly as excluded minerals (95%).

The major amount of minerals is concentrated between 4.6 and 46 μ m (see Figure 4). All the size ranges up to 22 μ m are dominated by quartz, kaolinite and CaAlP. In particles larger than 22 μ m, kaolinite, quartz, pyrrhotite, gypsum/aluminosilicates and unclassified minerals are the major components.

Figure 3. Mineral composition of the PRB sample

Figure 4. Mineral particle size distribution of the PRB sample

Table 3. Mineral particle size distribution and composition of the PRB sample

	1-2.2 μm	2.2-4.6 μm	4.6- 10.0μm	10.0- 22.0μm	22.0- 46.0μm	46.0- 100.0μm	Total, %w
Quartz	8.9	15.1	27.3	18.5	16.2	13.7	27.1
Iron oxide	12.5	12.5	12.5	0.0	62.5	0.0	0.8
Rutile	0.0	40.0	40.0	0.0	20.0	0.0	0.5

Dolomite	0.0	0.0	100.0	0.0	0.0	0.0	0.2
Kaolinite	3.4	12.2	18.0	28.8	26.8	9.8	20.5
Montmorillonite	4.5	0.0	4.5	27.3	40.9	22.7	2.2
K Al-silicate	12.5	25.0	0.0	0.0	25.0	37.5	0.8
Ca-Al-silicate	0.0	3.6	14.3	21.4	32.1	28.6	2.8
Aluminosilicate	0.0	0.0	0.0	0.0	37.5	50.0	0.8
Mixed Al-silicate	0.0	0.0	0.0	0.0	0.0	100.0	0.2
Fe Silicate	0.0	83.3	16.7	0.0	0.0	0.0	0.3
Ca Silicate	0.0	0.0	25.0	25.0	40.0	10.0	1.0
Pyrite	0.0	0.0	0.0	0.0	27.3	72.7	1.1
Pyrrhotite	4.7	0.0	4.7	10.9	47.7	32.0	6.4
Oxidized Pyrrho	0.0	0.0	0.0	0.0	100.0	0.0	0.3
Gypsum	0.0	0.0	100.0	0.0	0.0	0.0	0.1
Barite	0.0	100.0	0.0	0.0	0.0	0.0	0.1
Apatite	0.0	0.0	0.0	0.0	0.0	100.0	0.2
Ca Al-P	6.6	9.0	36.1	33.6	9.8	4.9	12.2
Gypsum/Al-Silic	0.0	0.0	24.6	10.8	40.0	24.6	6.5
Si-rich	0.0	0.0	16.7	25.0	25.0	29.2	2.4
Unclassified	2.3	1.5	38.3	15.8	23.3	18.0	13.3

Table 4. Calculated oxide composition obtained from CCSEM analysis of PRB sample (mass fraction as oxide)

	PRB
SiO ₂	0.54
Al ₂ O ₃	0.18
Fe ₂ O ₃	0.04
TiO ₂	0.01
P ₂ O ₅	0.05
CaO	0.07
MgO	0.01
Na ₂ O	0.00
K ₂ O	0.00
SO ₃	0.09

The amounts of excluded minerals in the three samples are similar for the Pittsburgh #8 and Illinois coals (70 and 69% respectively). The amount of excluded minerals in the PRB coal is lower (54%). UCONN is preparing a more detailed analysis of the mineral size distributions and compositions for both excluded and included minerals for each coal, and will present these results in the next monthly report.

In the last monthly report, UCONN presented the preliminary results of computer controlled scanning electron microscope (CCSEM) analysis of the Illinois 6 and PRB coal samples. During the past month, UCONN continued their analysis of these results and focused on examining the mineral size distributions and compositions for both excluded and included minerals for each coal.

Figure 1 displays the mineral particle size distribution (psd) of the excluded minerals for each coal. For the Illinois and Pittsburgh 8 bituminous coals, more than 80% of the excluded minerals are larger than 22 μm . For the PRB coal, the excluded minerals are

Figure 1. Particle size distribution for excluded minerals.

slightly smaller in size; here, only 63% of the excluded mineral matter is greater than 22 μm . The main component for excluded minerals in Illinois and Pittsburgh #8 coals is pyrrhotite. For the PRB coal, the excluded minerals are mainly kaolinite and quartz.

Figure 2 shows the particle size distribution for the *included* minerals, i.e. those associated with the carbon of the coal. The mode of the PRB coal mineral distribution lies in the 4.6 – 10 μm size range, whereas it is slightly smaller for the Pittsburgh #8 coal (2.2 – 4.6 μm) and larger for the Illinois 6 coal (22-46 μm). This suggests that mineral coalescence may be more limited during combustion of the Illinois coal than during combustion of the other two program coals.

The size of the included minerals is important in the different transformations of the ash formation, but the composition of these ranges is relevant as well. Figures 3 to 8 show the composition of included minerals for the different mineral size groupings extracted from the CCSEM analysis for the three coals. As seen in the figures, for the Illinois and PRB coals, the smallest mineral size ranges (1-2.2 μm and 2.2-4.6 μm) are dominated by quartz. For the Pittsburgh #8 bituminous coal, kaolinite and illite (K-Al-silicates) are the main minerals identified at sizes less than 10 μm . In the 4.6-22 μm size range, the Illinois coal is dominated by pyrrhotite and quartz; pyrrhotite also dominates the two larger particle ranges (22-46 and 46-100 μm). Quartz and kaolinite

are the main components of the included minerals for the PRB coal for minerals larger than 4.6 μm . For the Pittsburgh #8, pyrrhotite and illite are the main components of particles in the range between 10-22 μm ; and only illite is important in the largest minerals.

Figure 2. Particle size distribution for included minerals.

Figure 3. Mineral composition for included minerals in the size range: 1-2.2 μm .

Figure 4. Mineral composition for included minerals in the size range: 2.2-4.6 μm .

Figure 5. Mineral composition for included minerals in the size range: 4.6-10 μm .

Figure 6. Mineral composition for included minerals in the size range: 10-22 μm .

Figure 7. Mineral composition for included minerals in the size range: 22-46 μm .

Figure 8. Mineral composition for included minerals in the size range: 46-100 μm .

During the last month, UCONN conducted initial pressure testing of the low pressure cascade impactor and pre-separator cyclone. The seals at the inlet to the cyclone were found to leak at any elevated pressure, suggesting that it will not be possible to use the cyclone in the HPBO experiments at SRI. Initial tests of the low pressure cascade impactor indicated that it did not leak at pressures to 50 psi. Higher pressure clamps, which should permit operation to at least 10 bar, were ordered and are expected to arrive before early January.

Scanning Electron Microscopy (SEM) analysis was conducted of some of the filter samples provided by SRI to determine whether it would be possible to characterize ash particles in these samples. As expected, the particles are embedded within the fiber mat and cannot be readily characterized in the as-received sample. We will continue our analysis of the corresponding char samples from those experiments during January, and may re-visit the filter samples at a later date if the planned impactor testing does not provide the small particle samples needed to characterize the ash.

In previous reports, UCONN indicated that the CCSEM analysis of the Pittsburgh coal suggested a much higher than expected ash content. UCONN therefore followed standard ASTM D3174-93 method to determine the ash content of the two Pittsburgh coal samples provided by SRI and confirmed a discrepancy between the CCSEM results and the actual coal samples. The Pittsburgh sample sent in September had an ash content of 13.2 weight percent and the samples sent in November, an 11.3 weight percent ash content. UCONN is examining possible reasons for the supriously high ash content reported by CCSEM and expect to analyze a new sample of the Pittsburgh coal (the November sample) in January or February, 2003.

Task 4.0 Deployment in Design Codes

Task 4.1-4.2

No work has been done for this task, as no models have been made available for implementation in Aspen Plus. Work will start when the sub-models become available

Task 4.4

Development work has started to bring sub-models into Fluent.

Task 5.0 Vision 21 Design Analysis

Task 5.2 Conceptual Design of Vision 21 Process

FWC is in the process of evaluating the ASPEN module created by Air Liquide to incorporate PC Coal Lab as part of Task 5.3. The ASPEN module will be evaluated in terms of usefulness and suitability of including the module in the FW Vision 21 Plant ASPEN simulation (Pressurized Pulverized Coal Combustor). In order to directly explore the capabilities of PC Coal Lab and be better equipped to review its implementation in Aspen Plus, FWC has requested a copy of LP Coal Lab from NEA.

Task 5.4 (Component Level Analysis)

No significant work in this area was performed.

Task 6.0 Reporting

Task 6.1 Program/Project Management Plans

Monthly emails are being sent to Kamalendu Das (NETL) as requested to support Fluent Inc. invoices and summarize monthly technical progress.

Task 6.2 Technical Reports

The fourth quarterly report is being prepared.

Task 7.0 Project Management

Monthly emails are being sent to Kamalendu Das (NETL) in support of each monthly invoice from Fluent Inc. As requested these emails breakdown the invoice at the task level and track percent completion of both labor and job completion for the first year of the HPCCK project. Monthly phone conferences are being conducted with full participation from each of the HPCCK team members.

2. Issues and Resolutions

None to report

3. Progress Forecast for the Next Quarter

Task 0 Planning

Task 1 Submodels for Pollutant Formation

Task 1.2 NBFZ Tests

Begin HPBO tests.

Task 1.4 Fuel-N Conversion Development

Continue model development.

Task 2 Submodels for Char Oxidation

Task 2.5 Char Oxidation Mechanism

Complete development of CBK/CFD and complete the work to provide swelling factors.

Task 3 Submodels for Flyash and Fumes

Continue model development.

Task 4 Deployment in Design Codes

Task 4.1 Couple PC Coal Lab and ASPEN Plus

Begin to get feedback from FWC and other members of the HPCCK group on improvements.

Task 4.4 Incorporate submodels in Fluent

Begin to incorporate submodels into Fluent.

Task 5 Vision 21 Process Design Analysis

Begin using PC Coal Lab/AspenPlus software and provide feedback to team members.

Task 6 Reporting

Task 6.1-6.5

Continue reporting as required

4. Personnel and Affiliation, List of Abbreviations

<u>Personnel Name</u>	<u>Affiliation</u>
------------------------------	---------------------------

Al Alhuwalia	FWC
Verna Bungay	Fluent
Soung Cho	FWC
Lewis Collins	Fluent
Don Ekstrom	SRI
Joe Helble	UConn
Bob Hurt	BU
Usman Ghani	AAL
Chris Guenther	Fluent
Ovidiu Marin	AAL
Steve Niksa	NEA
John Rockey	NETL
Bill Rogers	Fluent

<u>Name</u>	<u>Description</u>
--------------------	---------------------------

AAL	American Air Liquide
BU	Brown University
CBK	Carbon Burnout Kinetics Model
CFD	Computational Fluid Dynamics
ECT	Electric Charge Transfer Device
FWC	Foster Wheeler Corporation
HPBO	High Pressure Burnout Testing Mode
HPCCK	High Pressure Coal Combustion Kinetics
NBFZ	Near-Burner Flame Zone Testing Mode
NEA	Niksa Energy Associates
NETL	National Energy Technology Laboratory
PRB	Powder River Basin
SRI	SRI International
SRT-RCFR	Short Residence Time Radiant Coal Flow Reactor
UConn	University of Connecticut

5. Appendix A: Project Milestone Chart (Update 12-26-01)

	Lead	Year 1				Year 2				Year 3			
		Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4
Task 0. Planning	Fluent												
Task 1. Submodels for Pollutant Formation													
1.1 NBZF Test Characterization	SRI												
1.2 NBZF Tests	SRI												
1.3 RCFR Simulations for NBZF Tests	NEA												
1.4 Fuel-N Conversion Development	NEA												
1.5 NOx Production Submodel	NEA												
1.6 Hg Transformations	NEA												
Task 2. Submodels for Char Oxidation													
2.1 HPBO Test Characterization	SRI												
2.2 HPBO Tests	SRI												
2.3 HPBO Char Analyses	BU												
2.4 RCFR Simulations for HPBO Tests	NEA												
2.5 Char Oxidation Mechanism	BU												
2.6 Char Oxidation Submodel	NEA												
Task 3. Submodels for Flyash and Fumes													
3.1 HPBO Tests	UConn												
3.2 NBZF Tests	UConn												
3.3 PPC Ash Mechanism Development	UConn												
3.4 Flyash Formation Submodel	UConn												
Task 4. Deployment in Design Codes													
4.1 Couple PC Coal Lab® and ASPEN Plus	AL												
4.2 Incorporate submodels in ASPEN Plus	AL												
4.3 Couple PC Coal Lab® and FLUENT	Fluent												
4.4 Incorporate submodels in FLUENT	Fluent												
Task 5. Vision 21 Process Design Analysis													
5.1 Advisory Review	FWC												
5.2 Conceptual Design of Vision 21 Process	FWC												
5.3 System-Level Analysis	AL												
5.4 Component-Level Analysis	FWC												
Task 6. Reporting													
6.1 Program/Project Management Plans	Fluent	1	2	1	2	1	2	1	2	1	2	1	1
6.2 Technical Reports	NEA												
6.3 Environmental Reports	SRI	4											4
6.4 Property Reports	Fluent												5
6.5 Exception Reports	Fluent												6
Task 7. Project Management	Fluent												