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Co-firing High Sulfur Coal with Refuse Derived Fuels

Technical Progress Report # 7

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1. Abstract

The objectives for this quarter of study on the co-firing of high sulfur coal with refuse derived fuels project were two-fold. First, the organic compounds tentatively identified as combustion products in the previous report were confirmed by comparing retention times with pure samples. Secondly, a reduced amount of unburned carbon in the fly ash and an oxygen concentration at about 3-6% in the flue gases were achieved by the addition of removable heat exchange tubes in the AFBC system.

2. Tube Furnace Combustion Studies

During this quarter the primary focus of the tube furnace combustion experiments was to confirm the organic compounds identified as combustion products by mass spectrometric library matches and listed in the previous report.[1] The gas chromatographic retention times of the MS-identified compounds were compared to the retention times of pure compounds run under the same conditions. Table 1 gives a comparison of the GC/MS retention times for compounds previously reported. Tables 2 and 3 list the MS-identified compounds from the tube furnace combustion experiments of phenol and 2,4-dichlorophenol, respectively. The other 50 compounds needed to complete the comparison have yet to be purchased and analyzed. It is difficult to obtain good standards for PCDDs and PCDFs.

Incineration of refuse derived fuels may result in the formation of polychlorinated organic compounds such as polychlorodibenzofurans (PCDFs) and polychlorodibenzodioxins (PCDDs). PCDDs/PCDFs have been reported in incinerator emissions and other combustion sources.[2,3] However, the reports given in the literature about the formation of these materials are often contradictory and confusing.[4]

Several mechanisms have been proposed that recognize the existence of molecular chlorine as an important precursor to the formation of chlorinated hydrocarbons during combustion. In our previous work, TG/FTIR/MS studies of the organic compounds evolved during combustion of blends of coal and refuse derived fuels revealed the production of phenols, furans, and various other organic materials during the combustion of paper and other cellulosic materials blended with coals.[5,6] The production of molecular chlorine during the combustion of polyvinyl chloride was also observed. Phenol, furan, and molecular chlorine could provide the important precursors for the formation of PCDDs and PCDFs in combustion processes. TG/FTIR/MS studies done by Lu[5] showed that more hydrocarbons are evolved at a fast heating rate of 100°C/min due to incomplete combustion. These studies indicated there is a greater likelihood for the formation of chlorinated organic compounds at the fast heating rates, due to the concurrent evolution of HCl (which may be converted to molecular chlorine) and hydrocarbons, especially aromatics. Thus, chlorinated organic compounds may be formed at high heating rates, whereas products such as organic acids and alcohols are generally observed at lower heating rates.

These results have prompted us to propose a mechanism for the formation of chlorinated organics and possibly PCDDs and PCDFs during the combustion of refuse derived fuels is which is given in equations 1-3:

$$4HCl + O_2 \leftrightarrow 2H_2O + Cl_2 \quad \text{(Deacon reaction)} \qquad (1)$$

$$C_6H_5OH + Cl_2 \rightarrow \text{chlorophenols} \qquad (2)$$

$$\text{condensation of chlorophenols} \rightarrow \text{PCDDs and PCDFs} \qquad (3)$$

The results of a series of experiments designed to prove, or disprove, this proposed mechanism are given in this report.

2.1 Experimental

Apparatus and Reagents - The TG/FTIR/MS system consisted of a TA Instruments SDT 2960 Simultaneous DTA-TGA system interfaced with a Perkin-Elmer 1650 Fourier Transform Infrared Spectrometer and a Fisons Instruments model VG Thermolab Mass Spectrometer. A Shimadzu QP 5000 system with a NIST/EPA/NIH 62,000 compound database was used for the GC/MS analysis. A twelve-inch Sola Basic Lindberg tube furnace was used for the preheated tube experiments. Reagents used include MC&B reagent grade phenol, EM Scientific HPLC grade dichloromethane, while 2,4-dichlorophenol, 4-chlorophenol, 2-chlorophenol and dibenzofuran were 99+% grade from Aldrich.

To closely simulate conditions in an AFBC combustor, studies were conducted using a preheated quartz tube in the Lindberg tube furnace. The evolved gases were trapped in methylene chloride, concentrated, and analyzed using the GC/MS system. Combustion products of phenol and chlorophenols were also investigated. The detailed experimental conditions are outlined in the following paragraphs.

2.1.1 Production of Molecular Chlorine from HCl and Air

To examine the possibility of producing molecular chlorine via the Deacon reaction, as is illustrated in equation 1, a mixture of air and 10% HCl in N_2 (air:HCl volume ratio of 2:1) was introduced into the quartz tube preheated to different temperatures in the tube furnace. The product gases were trapped in a phenol-methylene chloride solution and the solution analyzed for chlorophenols using the GC/MS system.

2.1.2 Chlorination of Phenol

To examine the gas phase chlorination of phenol, as is illustrated in equation 2, 100 mg portions of phenol were placed in a heated tube and evaporated in the presence of a constant flow 0.5% Cl_2 in N_2. Chlorination took place in the gaseous phase and the products were trapped in an aqueous solution of $NaHSO_3$, extracted by CH_2Cl_2, and analyzed using the GC/MS system.

2.1.3 Combustion of Chlorinated Phenols

The combustion of chlorinated phenols, which may lead to the reaction illustrated in equation 3, was examined by heating 100 mg portions of 2,4-dichlorophenol in the presence of air in the tube furnace. The combustion products were adsorbed by CH_2Cl_2 and identified using the GC/MS system. The reaction was also studied in a series of experiments in which 10 mg portions of 2,4-dichlorophenol were heated in air at a rate of 10°C/min in the TGA and the evolved gases were monitored (on-line) using the FTIR and MS spectrometers.

2.2 Results and Discussion

The production of molecular chlorine by heating HCl in air followed by the chlorination of phenol in solution is an indication that the Deacon reaction (equation 1) takes place in the heated tube. Figure 1 shows the GC/MS results from these experiments conducted at different temperatures. The chromatograms indicate that the higher temperatures favor an increase in the production of chlorophenols. This indicates the Deacon reaction is favored at higher temperatures, which is consistent with thermodynamic calculations that show the Deacon reaction is favored above 590°C.

The gas phase chlorination of phenol (equation 2) experiments produced 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol, as identified by NIST library matches and GC retention times of the pure materials. The chlorination of phenol began at temperatures around 250°C. At higher temperatures, dibenzofuran was produced. At still higher temperatures near 600°C, naphthalene was produced.

To examine the possible condensation of chlorophenols during combustion reactions, as is illustrated by equation 3, the compound 2,4-dichlorophenol was heated in air inside the tube furnace. The combustion products were trapped in methylene chloride, concentrated, and analyzed by GC/MS. Figure 2 shows examples of chromatograms for the combustion products. The products are indicated to be mainly 2,4,6-trichlorophenol, tetrachlorodibenzofuran, and dichlorodibenzodioxin, as identified by NIST library searches. The TG/MS experiments indicated the products of combustion include CO_2 (m/z = 44), H_2O (m/z = 18), HCl (m/z = 36) and trichlorophenol (m/z = 196), as is illustrated by the mass spectra profiles shown in Figure 3. This profile also shows the formation of chlorinated hydrocarbons at relatively low temperatures, which begins around 200°C. The small amount of material used, the slow heating rate, and the 300 amu limitation of the TG/MS system made it impossible to observe any larger chlorinated hydrocarbon product in this particular experiment. FTIR analysis of the evolved gases confirmed the emission of CO_2, CO and H_2O, and HCl, as labeled on the three dimensional plot in Figure 4.

2.3 Conclusions

Based on the information presented in this report summary statements that can be made include:

- The Deacon reaction for the production of molecular chorine is generally favored at temperatures over 600°C.
- The gas phase chlorination of phenol is generally favored at temperatures over 600°C.

- Tetrachlorodibenzofuran, dichlorodibenzodioxin, and other chlorinated organic compounds are formed during the combustion of 2,4-dichlorophenol.
- The proposed three-step mechanism appears to be a possible pathway for the production PCDDs and PCDFs in combustion processes.

3. Fluidized Bed Combustion Studies

Since the last quarterly report, four combustion runs have been performed with the AFBC system. The dates and run times are mentioned in Table 4. The overall goal of these experiments was to attain steady combustion and less than 15% unburned carbon in the fly ash, while maintaining O_2 concentration in the flue gas at about 3-6%. Western Kentucky University coal sample #95011 and Kentucky limestone have been used in all experiments.

According to combustion theory, combustion efficiency (CE) is now defined as follows:[7,8]

$$CE = \frac{[W_c H_0 - H_c(C_t - C_i)W_f - H_{co}N_{co}Q_g]}{(W_c H_0)},$$

where:

W_cH_0 = Total input thermal energy;

$H_c(C_t-C_i)W_f$ = Combustion loss due to unburned carbon in the fly ash;

$H_{co}N_{co}Q_g$ = Combustion loss due to incomplete combustion of CO;

C_t = Total carbon content in the fly ash, weight fraction;

C_i = Inorganic carbon content in the fly ash, weight fraction;

H_0 = Higher heating value of the coal used, kJ/kg;

H_c = Higher heating value of the carbon, 32792.5 kJ/kg;

H_{co} = Higher heating value of the CO, 12633.035 kJ/kg;

N_{co} = Measured CO concentration in the flue gas, %(volume percent, wet basis);

W_c = Coal feed rate, kg/s;

W_f = Fly ash flow rate, kg/s;

Q_g = Flue gas volumetric flow rate on a standard basis, wet, Nm^3/s.

By collecting the fly ash samples, the carbon and ash contents can be determined. The fly ash flow rate can be determined on the basis of bed mass balance, i.e. the ash balance. The flue gas flow rate can be obtained by performing normal combustion calculations. This CE formula has been used to calculate combustion efficiencies in these four tests.

Steadiness of combustion was significantly improved during the combustion run of May 9-11, 1996, due to the addition of new bed heat exchanger. It consists of six individual removable bed cooling tubes. Its surface area for heat transfer is 0-2.4 square feet. The experiment proved that it is an efficient method for the adjustment of bed temperature. Therefore, it is not necessary to change the flow rates of fuel, limestone, and air as frequently to maintain steady bed temperature. Figures 5 and 6 illustrate that operating parameters were almost constant during the combustion run on May 10-11.

The concentrations of CO_2, O_2, SO_2 and CO in the flue gases were measured during each combustion run. Prior to each combustion run, the flue gas sampling system was calibrated using three different CO_2 concentrations, two different SO_2 concentrations and two different CO concentrations. Since the last report, the two modifications (the addition of a high temperature flue gas pump and automatic purge gas for the flue gas system) were proven to be successful. The port sampling filter has never been plugged during the last four combustion runs.

Calculations were also done for predicting CO_2, O_2, SO_2 and H_2O concentrations in the flue gases, and the results were compared with the measured values of CO_2 and O_2. The values obtained were comparable as is illustrated in Figures 7 and 8.

During the May 9-11, 1996 period the combustor performance was steady for a forty-five hour period. This run period was the longest among all the attempts thus far. Major parameters versus time are shown in Figure 9. Wood pellets and coal were used as fuel from 8 am to 8 pm on May 10, and coal was the only fuel used at other times. Two reasonable ranges (A and B) were selected from this combustion run, and individually treated for operating and analysis data. The results are shown in Figures 5-7 and Figure 9. Results of the analysis of the unburned carbon in the fly ash during the range (A), were also obtained as shown in Figure 10.

4. Further Study

The focus of future research work will be:

- to verify the tentative identification of organic compounds by comparing the retention times with pure samples.
- to investigate the effect of the primary air/secondary air ratio on the amount of unburned carbon in the fly ash, so as to reduce this amount. This may be achieved by mounting nozzles to allow tangential flow of secondary air, which will be located at the freeboard section of the combustor.
- to prepare fuel pellets containing PVC, newspaper and plastics.

5. References

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Table 1. Comparison of GC Retention Times for the MS-Identified Compounds with Those for the Pure Compounds.

Compound	Retention Time (min) Experiment	Pure Compound
Furan	-------	less than 4.15^{A}
Toluene	6.08	6.02
Furfuryl alcohol	-------	7.50
Chlorobenzene	7.74	7.68
Cyclohexanone	------	8.61
p-Benzoquinone	8.80	8.71
Styrene	8.79	8.81
Benzaldehyde	-----	10.57
Phenol	10.90	10.77
2-Chlorophenol	11.75	11.75
Benzofuran	12.04	11.96
1,3-dichlorobenzene	12.34	12.43
Benzoic acid	-------	17.44
2,4-Dichlorophenol	17.87	17.68
4-Chlorophenol	18.48	18.44
Naphthalene	18.72	18.71
2,4,5-Trichlorophenol	------	26.10

Table 1. (Continued)

Compound	Retention Time (min) Experiment	Pure Compound
Vanillin	------	26.83
Dibenzofuran	31.92	31.85
Fluorene	34.33	34.40
Anthracene	41.54	42.00
9-Methyl anthracene	------	46.78
Pyrene	51.80	51.69

[A] Since the solvent cut time is about five minutes into the GC program, furan with a retention time of less than five minutes could not be detected as a peak.

Table 2. Compounds Identified by MS Library Matches from Combustion of Phenol at 800°C

Compound	Retention Time (min) Experiment	Retention Time (min) Pure Compound
Benzene(?)[A]	4.66	----
Cyclohexene(?)	4.92	----
Toluene	6.04	6.02
Chlorobenzene (?)	7.64	7.68
Styrene (?)	8.75	8.81
Phenol	10.84	10.77
Benzofuran	11.94	11.96
Indene(?)	13.58	----
Naphthalene	18.72	18.71
Biphenyl (?)	26.75	----
1-Benzosuberone (?)	28.51	----
Acenaphthylene (?)	29.46	----
3-Methyl-4-phenyl-3-buten-2-one(?)	0.52	----
Dibenzofuran	31.81	31.85
Fluorene	34.33	34.40
Phenanthrene(?)	41.54	----
Anthracene	41.89	42.00

[A] (?) Means the SI is less than 80% for tentative identification.

Table 3. Compounds from the Combustion of 2,4-Dichlorophenol That Were Identified by MS Library Searches.

	Retention Time (min)	
Compound	Experiment	Pure Compound
Cyclohexene(?)	4.95	----
2-Chlorophenol (?)	11.75	11.75
1,3-Dichlorobenzene (?)	12.34	12.43
2,4-Dichlorophenol	17.90	17.68
1,3,5-Trichlorobenzene (?)	18.41	----
2,6-Dichlorophenol (?)	19.22	----
2,4,6-Trichlorophenol(?)	25.77	----
5,7-Dichlorobenzofuran (?)	26.33	----
2,7-Dichlorodibenzodioxin (?)	46.48	----
	50.53	----
1,2,4-Trichlorodibenzodioxin (?)	51.51	----
2,3,7,8-Tetrachlorodibenzofuran(?)	56.60	----
3-Butenylbenzene(?)	58.98	----

[A] (?) Means the SI is less than 80% for tentative identification.

Table 4. Summary of Combustion Runs

Number	Date	Run Time (Hours)	Fuel	Oxidant
1	3/20-3/21, 1996	16	coal	air
2	4/4-4/4, 1996	6	coal	air
3	4/25-4/26, 1996	29.5	coal	air
4	5/9-5/11, 1996	45	coal/wood pellets	air

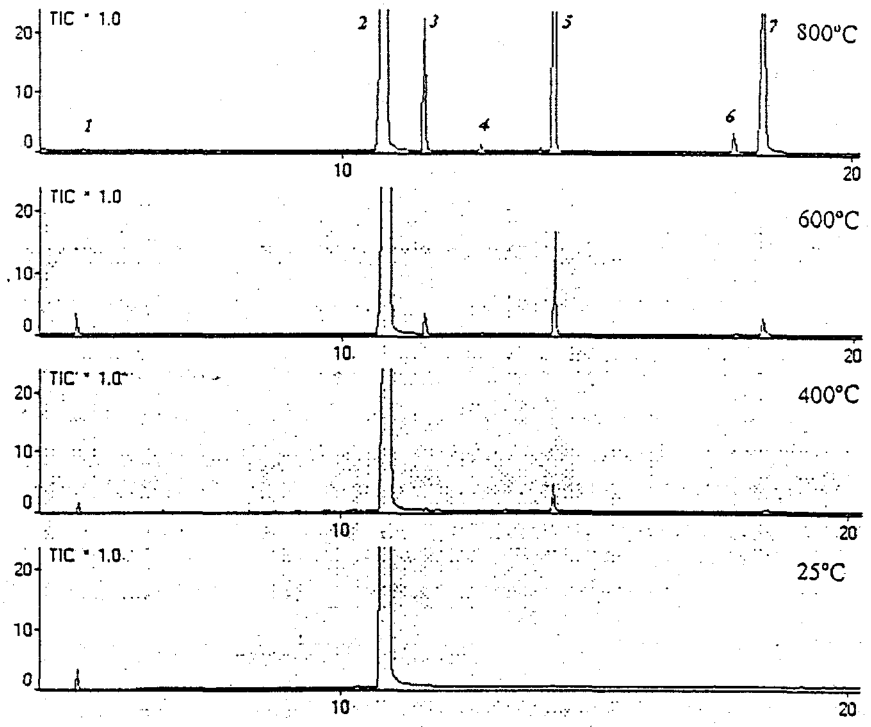

Figure 1. Chromatograms of the products from the reaction of HCl heated in air and trapped in a CH_2Cl_2 solution of phenol, concentrated, and analyzed by GC/MS. The MS assignments (NIST library matches) are as follows: 1 = cyclohexane, 2 = phenol, 3 = 2-chlorophenol, 4 = 2-chloro-cyclochlorocyclohexanol, 5 = *trans*-1,2-dichlorocyclohexene, 6 = 2,4-dichlorophenol, and 7 = 4-chlorophenol.

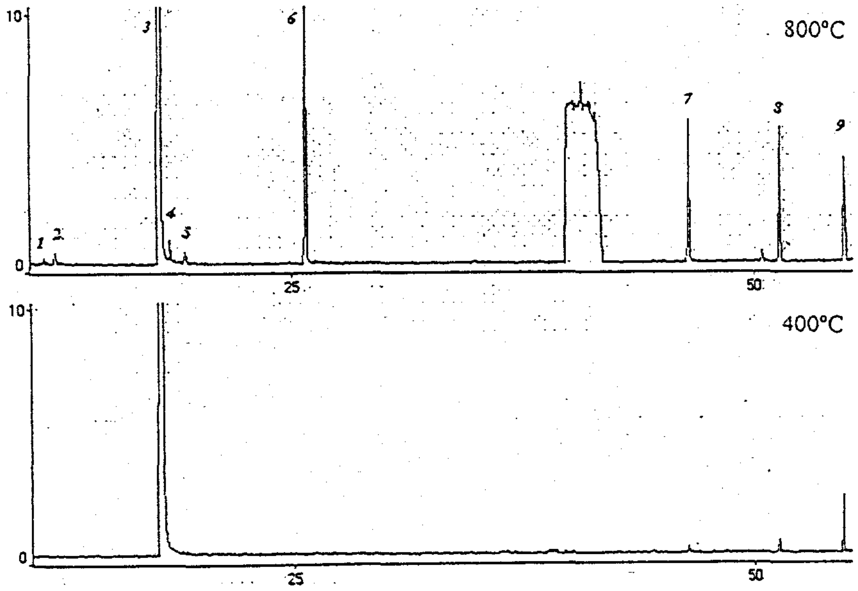

Figure 2. Chromatograms of the reaction products from the combustion of 2,4-dichlorophenol, which were trapped in CH_2Cl_2, concentrated, and analyzed by GC/MS. The MS assignments (NIST library matches) are as follows: 1 = 2-chlorophenol, 2 = dichlorobenzene, 3 = 2,4-dichloro-phenol, 4 = trichlorobenzene, 5 = 2,6-dichlorophenol, 6 = 2,4,6-trichlorophenol, 7 = dichloro-dibenzodioxin, 8 = trichlorodibenzodioxin, 9 = tetrachlorodibenzofuran.

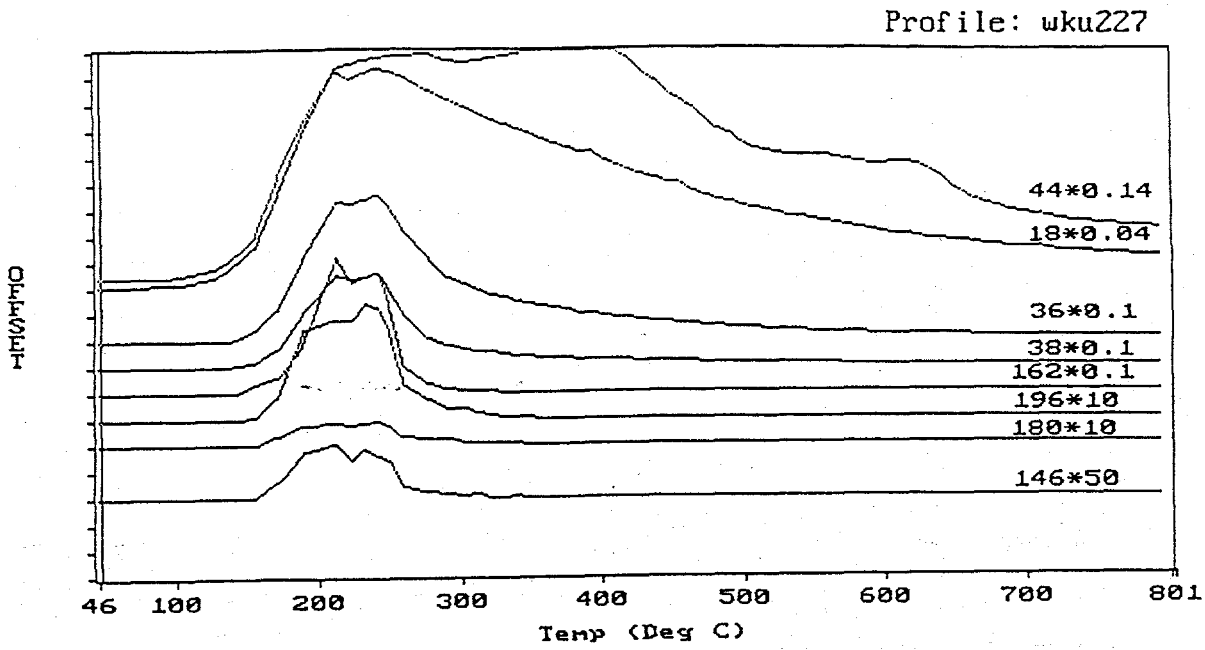

Figure 3. Mass spectra profiles for the combustion products of 2,4-dichlorophenol.

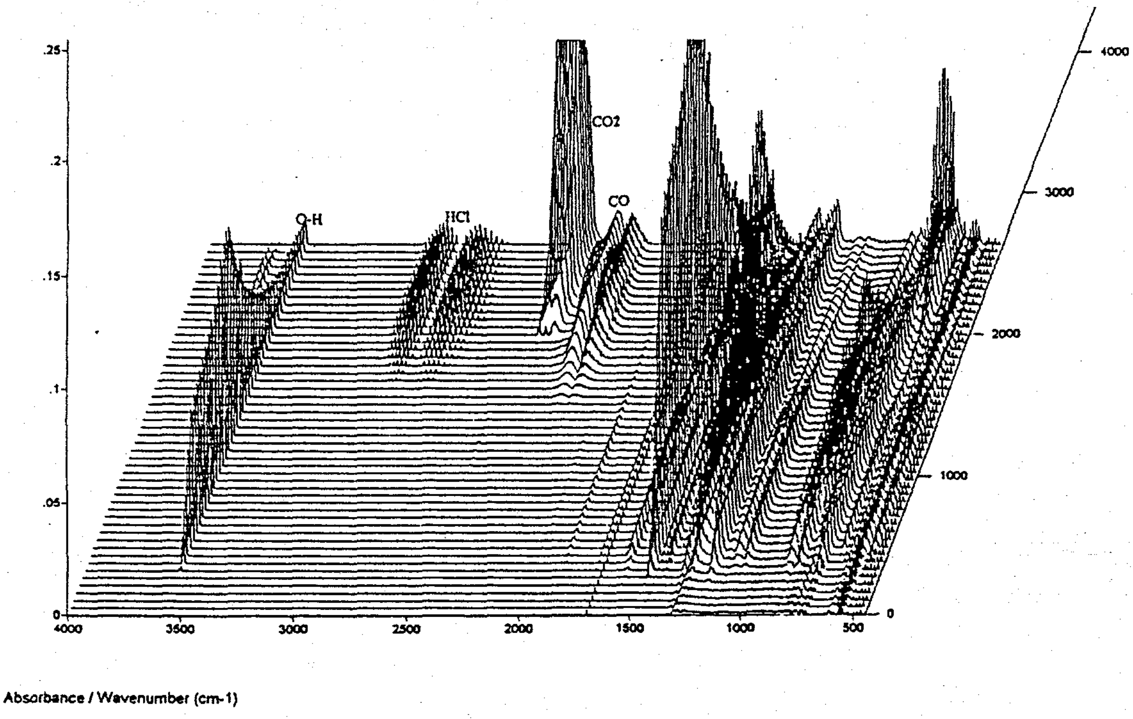

Figure 4. Three-dimensional FTIR spectra of the combustion products of 2,4-dichlorophenol.

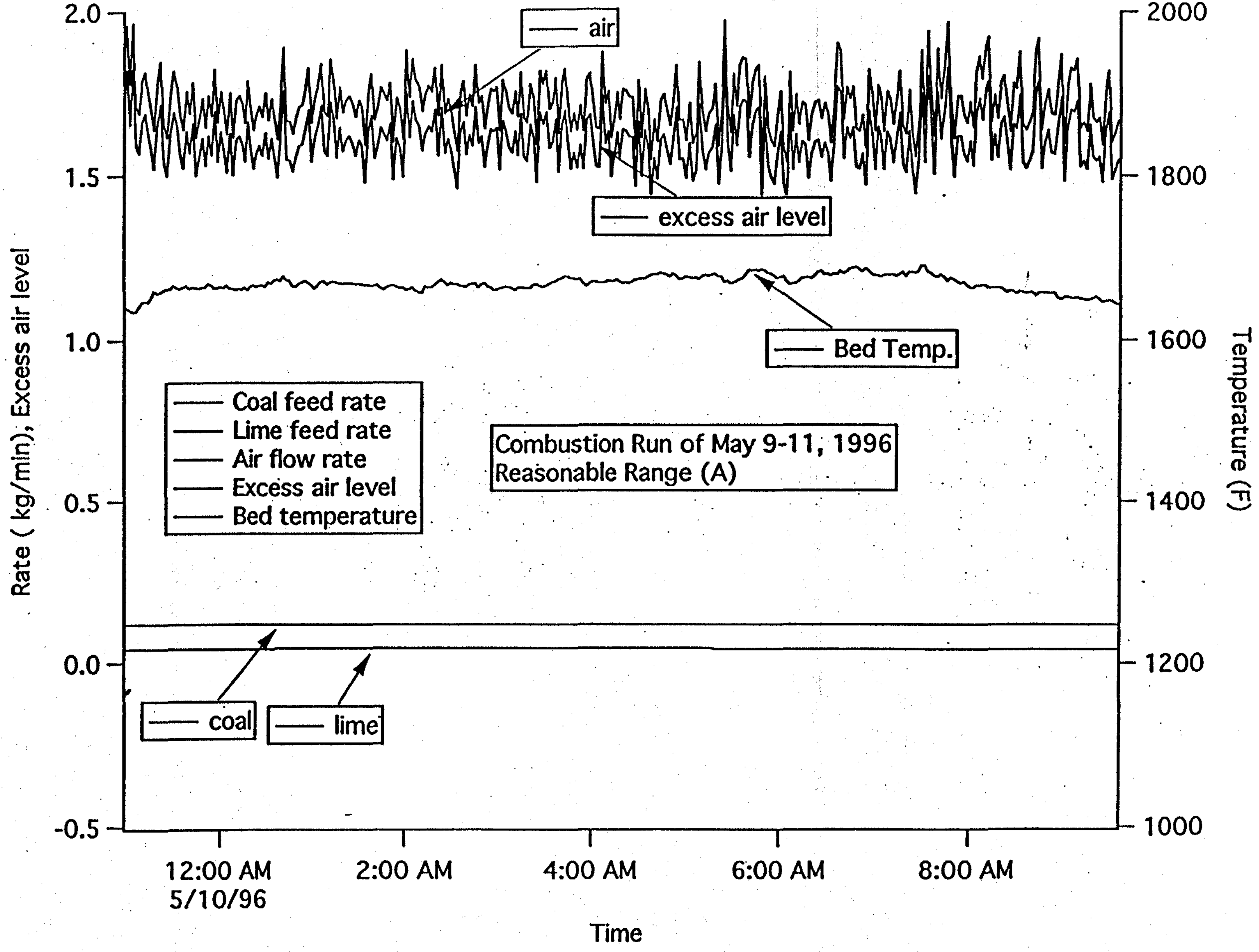

Figure 5. AFBC operating parameters (coal, limestone, air flow rate, bed temperature, and excess air flow rate versus time) illustrating steady combustion in a range (A).

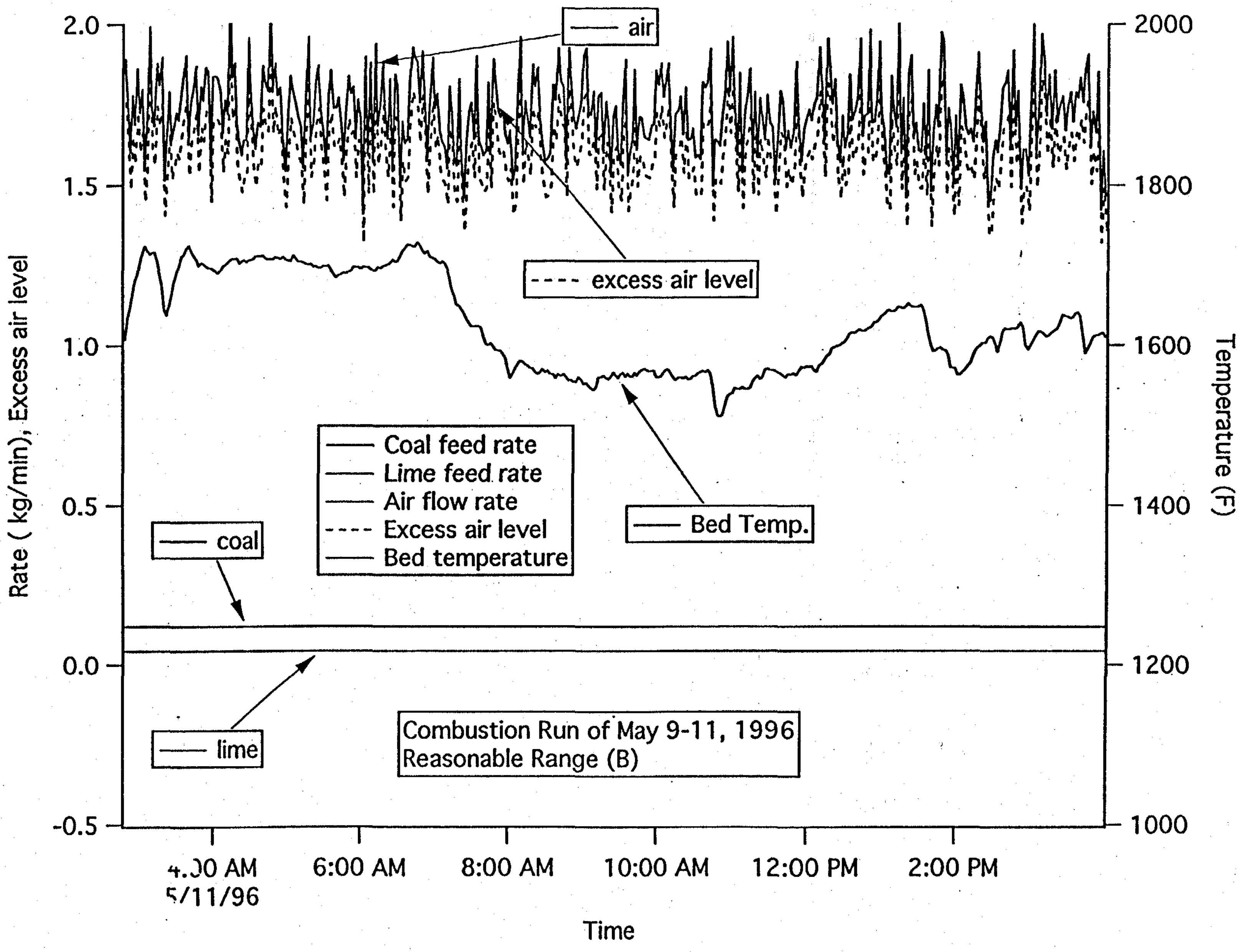

Figure 6. AFBC operating parameters (coal, limestone, air flow rate, bed temperature, and excess air level versus time) illustrating steady combustion in a range (B).

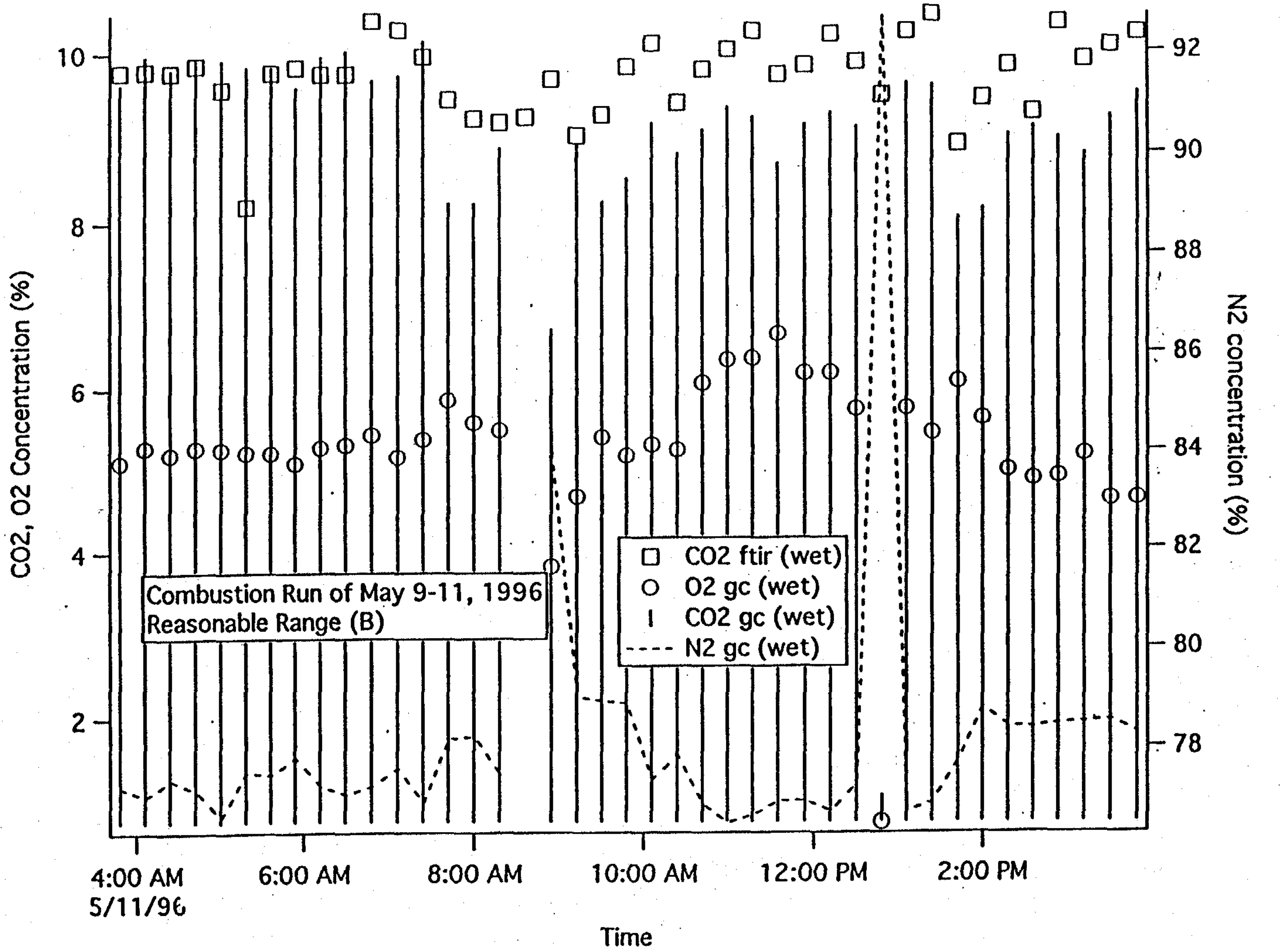

Figure 7. Concentrations of flue gas components CO_2, O_2, and N_2 as measured by FTIR and GC in range (A).

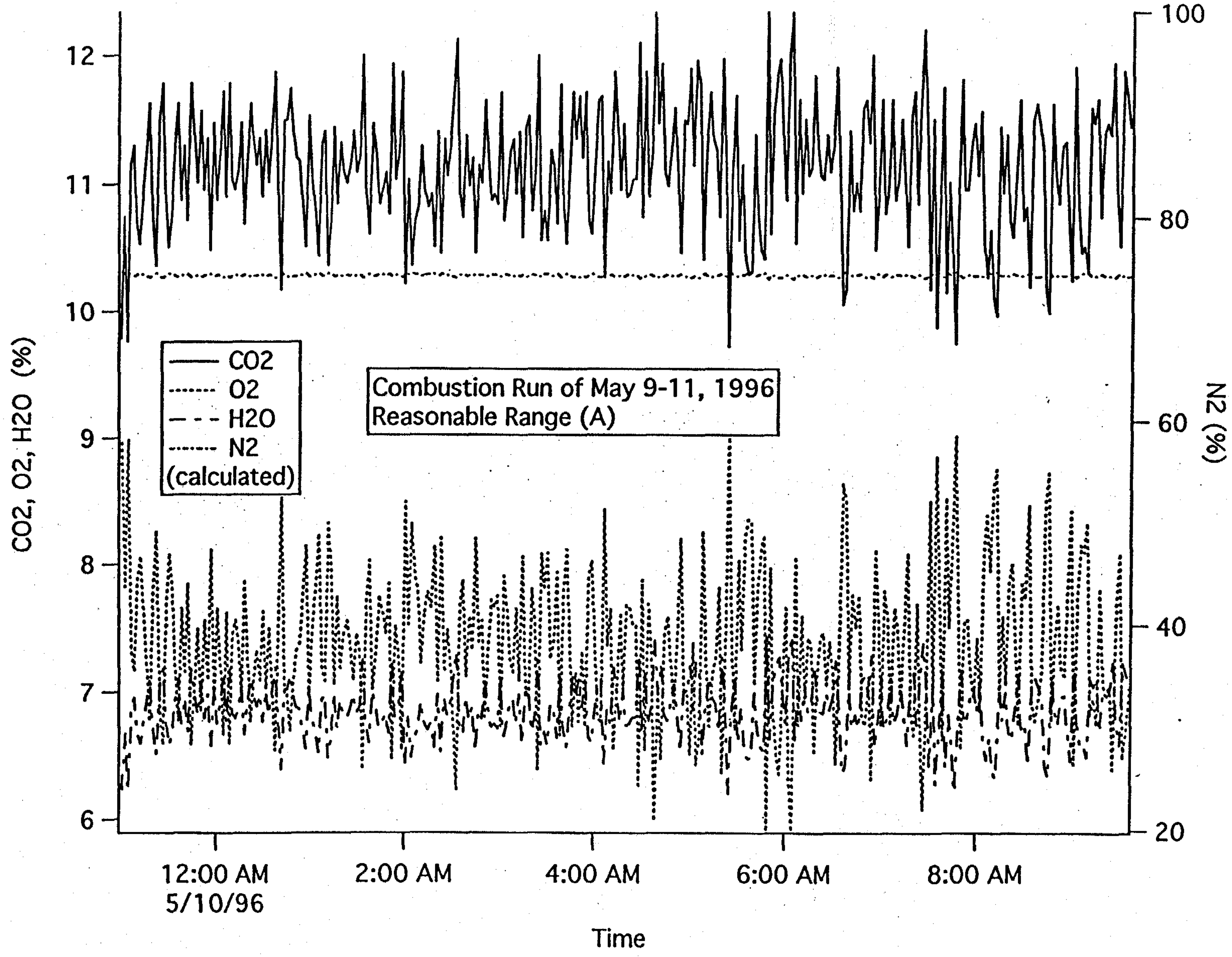

Figure 8. Calculated concentrations of flue gas components CO_2, O_2, N_2, and H_2O in range (A).

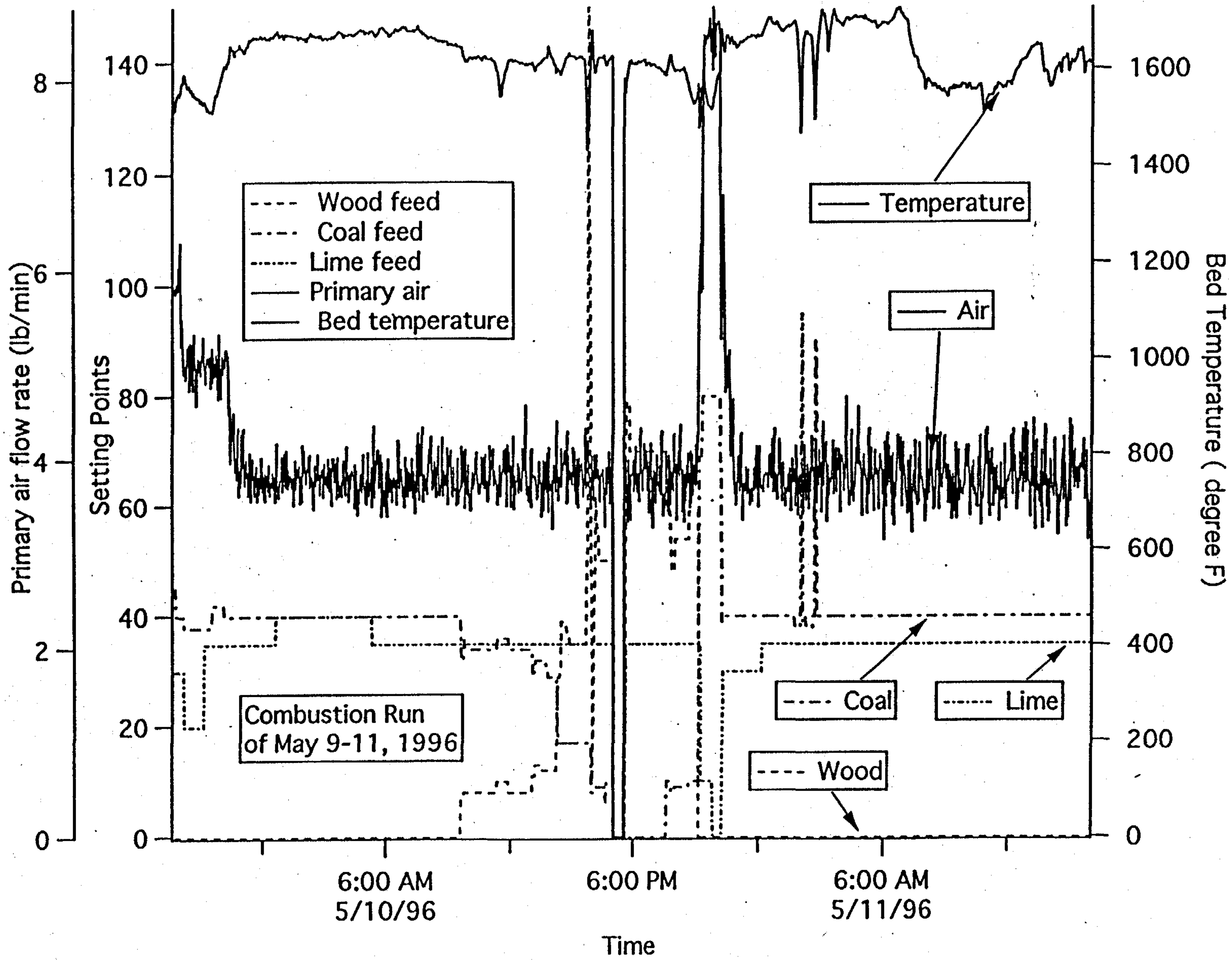

Figure 9. Variation in AFBC operating parameters (coal, limestone, and wood setting points, air flow rate, and bed temperature versus time) for the May 9-11, 1996 combustion run.

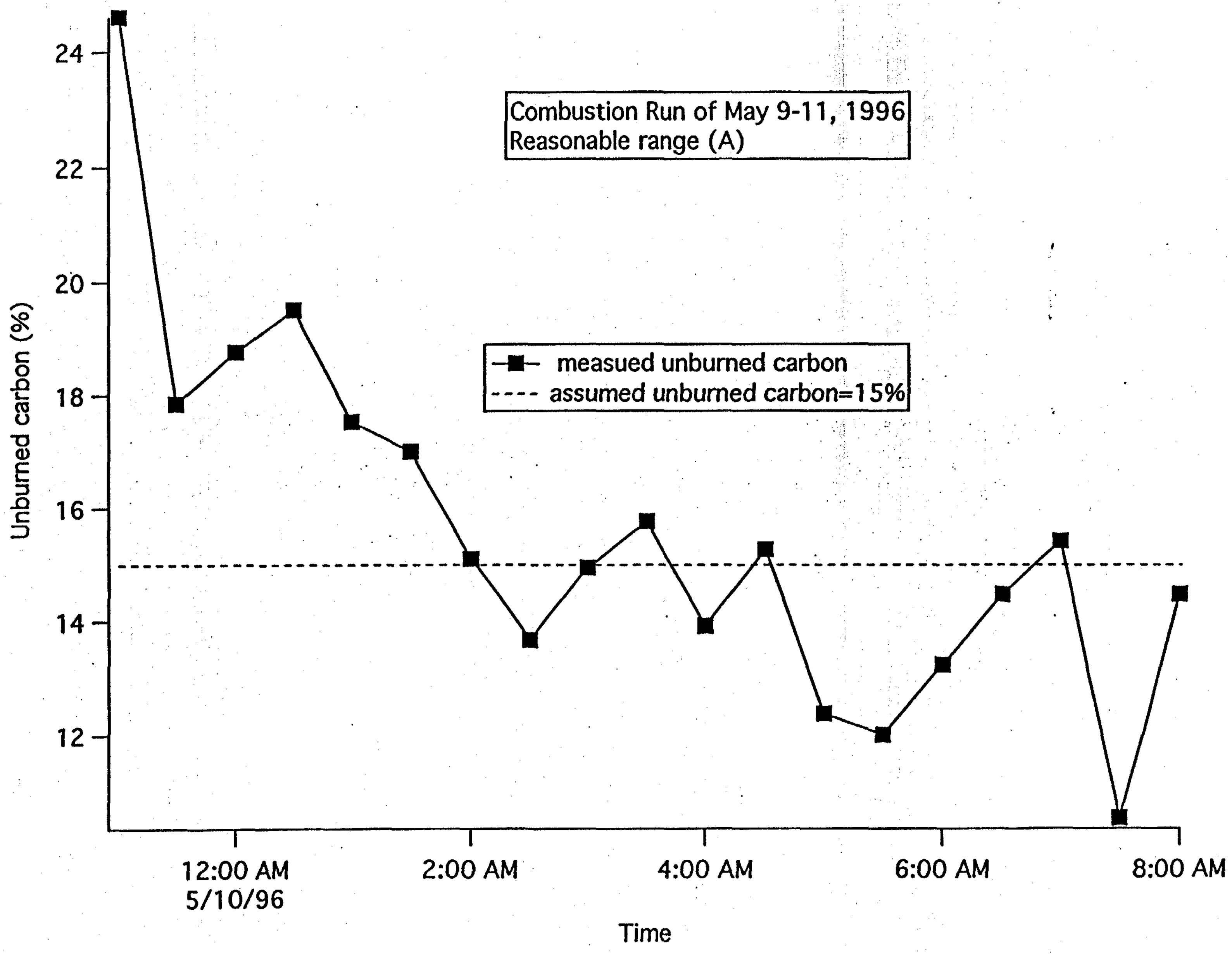

Figure 10. Variation in total carbon for first eight hours of May 10, 1996 combustion run.