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Co-firing High Sulfur Coal with Refuse Derived Fuels

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1. Abstract

The objectives for this quarter of study on the co-firing of high sulfur coals with refuse derived fuels were two-fold. First, the effects of different experimental parameters such as temperature, flow rates and reaction times on the formation of chlorinated organic compounds were studied using the tubular furnace as a reactor followed by GC/MS analysis. Secondly, the effect of fuel/air ratio on the flue gas composition and combustion efficiency were studied with the AFBC system.

2. Introduction

The proposed pathway for the formation of chlorinated dioxins from the combustion of chlorine rich fuel mixtures is indicated below.

$$4\,HCl + O_2 \rightarrow 2\,Cl_2 + 2\,H_2O \qquad [1]^{1-4}$$

$$Cl_2 + \text{phenol} \rightarrow \text{chlorinated phenols} \qquad [2]^{4-6}$$

$$\text{Chlorinated phenols} \rightarrow \text{PCDDs} \qquad [3]^{4,7-9}$$

One of the objectives of investigation of combustion with the tubular furnace is to study the conditions under which the chlorinated toxins are formed, or rather the conditions for the progress of the above three steps. Previous studies have identified phenols, as well as many other organic compounds, from the combustion of coal, newspaper, RDF, and cellulose.[10] The conditions for the reaction between phenol and molecular chlorine have been studied. This part of the study is focussed on the experimental proof for the hypothesis postulated above.

The results of studies conducted using the tubular furnace will help us better understand the conditions for the formation of organic compounds in the AFBC system.

The simulation of our AFBC system to model that of the TVA Shawnee Steam Plant is underway. The flue gas composition at the TVA plant is ~15% CO_2, 5% O_2 and less than one percent of CO. The problem of resolving leakage and blockage of the gas sampling system in our AFBC system was the major task for this quarter. The automation of our gas analysis system also was developed.

3. Experimental

3.1. Studies with the Tubular Furnace

The first step was to demonstrate the uncatalyzed Deacon Reaction.[10] Compressed air and 10% HCl in nitrogen are mixed in the ratio of 2:1 in a mixing chamber. The mixture then passes through the furnace tube which is kept at a specified temperature. The evolved gases are then trapped by a phenol - methylene chloride solution in a 25 mL Erlenmeyer flask. The gas flow (60 mL/min of HCl in N_2, 120 mL/min of air) and the temperature are maintained constant for a period of three hours.

The second step is to investigate the chlorination and condensation reactions of phenol. Reaction of vaporized phenol in the presence of 0.5% Cl_2 and 99.5% by nitrogen readily produces chlorinated phenols. Condensation and chlorination reactions of phenol were studied by varying the gas flow (from 45 to 70 mL/min), temperature (400°C to 700°C) and the solvent trap (50 mL of methylene chloride or aqueous sodium bisulfite). Reaction time is a factor to be considered only when the reaction is carried out in liquid phase.

The third step is to study the condensation reactions of chlorophenols. The condensation of chlorinated phenols in air (flow rate 140 mL/min) at 400-700° appears to form chlorinated

dibenzofurans [based on the tentative GC/MS identifications]. The solvent used to trap the evolved vapors was 50 mL of methylene chloride.

3.2. Studies with AFBC Systems

Since the last quarterly report, the improvements in the combustor involve: addition of a high temperature flue gas pump and automatic purge gas for flue gas system. These two modifications were necessary since the combustor room was unsuitable for the permanent location of the GC (see last report[10]), and plugging of the port sampling filter continued to be a problem. Specifically, we have placed a high temperature flue gas pump approximately two feet from the combustor. This addition enables us to enjoy a positive pressure system with our flue gas system and reduces the possibility of vacuum leaks. The system is interfaced with an automatic purge gas system, which periodically (every 6 minutes) stops the vacuum pump and introduces 5 seconds of compressed air back through the sampling tip. The vacuum pump acts as a check valve to prevent the purge gas from going towards the FTIR and GC instruments between sampling cycles, and the introduction of the compressed air is programmed to coincide with the waiting period for the GC and FTIR. Currently, the GC is programmed to sample every 18 minutes, while the FTIR is set for every six minutes.

Prior to each combustion run, the flue gas sampling system is calibrated using three different CO_2 concentrations, two different SO_2 concentrations, and two different CO concentrations. These gases are introduced approximately two and one-half feet from the combustor directly after the high temperature flue gas pump. This location allows the gas to travel over 80 feet in a heated line, which enables the gas to equilibrate with the line, and more accurately represents the heated gas found during combustion. Typically, the calibration procedure involves forcing compressed air through the system for approximately one hour, which enables us to set

the baseline for our FTIR instrument. This is followed with one hour of 10% CO_2 gas, one hour of 15% CO_2 gas, and one hour of 20% CO_2 gas. During each hour the FTIR automatically samples the gas every 7 minutes, which provides us with at least four consistent data points. Paramount to obtaining consistent data with the FTIR is keeping the gas flow uniform. This is important, since increased gas flows result in higher FTIR reading, even at constant gas composition. Usually, the system is calibrated for 80 mL per minute. Flow rates for the GC is not a problem since the data is normalized. Introduction of the SO_2 and CO gases follows the same format as above.

Four combustion runs have been performed during this reporting period, on December 12, January 3, January 25, and February 13. These runs, which averaged approximately eighteen hours in length, have given us additional experience in operating the combustor, as well as providing an opportunity for debugging the system and for training of students. The overall goal of these experiments has been to attain 96% combustion efficiency with a CO_2 concentration of 15% using different fuel/air ratios. Illinois coal sample #95011 (high sulfur/low chlorine) and Kentucky limestone have been used exclusively in all experiments.

4. Results and Discussion

The following tentative compound identifications are based on GC/MS analyses and comparison of the mass spectra obtained with the NIST mass spectrum library. Standard compounds, which can provide positive identification, are on order.

Table 1 illustrates the results from the study of the Deacon reaction. At room temperature no chlorinated phenols can be identified in the trap. At 400°C, 2-chlorophenol and 4-chlorophenol are identified. Additionally 2,4-dichlorophenol and 3-chlorophenol are found both

at 600°C and 800°C. The higher the temperature, the more intense these peaks, indicating that the thermal Deacon reaction (conversion of HCl to molecular chlorine) occurs readily above 400°.

Table 2 illustrates the results from the study of the chlorination and condensation reactions of phenol. At a temperature as low as 250°C phenol starts to react with chlorine to produce 2-chlorophenol and 4-chlorophenol, along with lesser amounts of 2,4-dichlorophenol and 2,4,6-trichlorophenol. At temperatures above 400°C, dibenzofuran is formed. At temperatures above 600°C not only chlorinated phenols and dibenzofuran but also naphthalene and related compounds are detected. More interesting is the identification of dibenzofuran during the reaction of phenol, both in the presence of air and in pure nitrogen above 400°C. This is assumed to be from the condensation of phenol itself. 100 mg of phenol was chlorinated using 0.5 % Cl_2 in nitrogen (flow rate 65 mL/min) at 250°C. The trap used was an aqueous solution of $NaHSO_3$. This was then extracted with five 10 mL aliquots of methylene chloride. Repeated analyses show only a small peak for trichlorophenol. Chlorination of 2,4-dichlorophenol is possible but it appears to be less facile than that of phenol.

Dichlorodibenzofuran is formed from 2-chlorophenol or 4-chlorophenol at 700°C. From 2,4-dichlorophenol, tetrachlorodibenzofuran is produced at 400°C (Table 3). At 700°C not only tetrachlorodibenzofuran but also dichlorodibenzodioxin and trichlorodibenzodioxin and a remarkable amount of 2,4,6-trichlorophenol are identified. The mechanisms for the formation of these compounds remains uncertain.

Figure 1 shows a gradual increase in CO_2 concentration from 4:00 to 14:00 hrs (24 hour clock). During this period a constant coal feed rate was maintained with an accelerated lime feed. This allowed us to raise the bed to an optimum level (31 in) for operation. The short drop

in CO_2 concentration at 14:00 hours was due to excessive bed temperatures (Figure 2), which necessitated shutting off the fuel. The remainder of the experiment proceeded at constant feed rates. The combustion efficiency reaches approximately 94% between 14:00 and 15:30 hours (Figure 3).

5. Further Study

So far the pathways to the formation of PCDDs and PCDFs have been explored experimentally. Further study will emphasize

- investigation of the mechanistic pathway for the formation of PCDDs and PCDFs
- testing the suppression of the Deacon reaction by SO_2.
- confirmation of GC/MS identifications using authentic samples
- development of a GC/MS method in the SIM (selected ion monitoring) mode to detect at higher sensitivity the organic compounds formed during the combustion of blends of PVC and RDF (refuse derived fuel) in the tubular furnace.
- addition of a faster and more powerful computer, since the data acquisition/logging of system parameters is overloading the existing system.
- reproducing combustion parameters which have yielded 15% CO_2 and 95% combustion efficiency, with the lowest possible fuel feed rate.

6. References

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Table 1. Study of The Deacon Reaction

$$4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O$$

Temperature (°C)	Tentative product identifications
Room temperature	None
400	2-chlorophenol and 4-chlorophenol
600	2,4- dichlorophenol, 3-chlorophenol 4-chlorophenol, 2-chlorophenol
800	2,4-dichlorophenol, 3-chlorophenol 4-chlorophenol, 2-chlorophenol

Table 2. Chlorination and Condensation Reactions of Phenol

Run	Temperature (°C)	Time (min)	Tentative product identifications.
1	600	15	Dibenzofurans, no chlorophenols
2	800	15	Dibenzofurans, no chlorophenols
3	600	30	Dibenzofuran, mono, di and trichlorophenols
4	800	30	Dibenzofurans, mono, di and trichlorophenols
5*	700	30	Dibenzofuran, mono, di and tri chlorophenols
6*	250	30	Dibenzofuran, mono, di and trichlorophenols
7*	425	30	Chlorinated phenols and dibenzofuran.

* Trap used for the last three runs was aqueous sodium bisulfite.

Table 3. Study of The Condensation Reactions of Chlorophenols

Sample	Temp (°C)	Tentative product identifications
2,4-dichlorophenol	700	Tetrachlorodibenzodioxin, tetrachlorofuran, dibenzodioxin, 2-chlorophenol, 2,6-dichlorophenol, 2,4,6-trichlorophenol, dichlorobenzene, trichlorobenzene, dichlorodibenzofuran.
2,4-dichlorophenol	400	Tetrachlorodibenzofuran, trichlorodibenzodioxin, dichlorodibenzodioxin.
4-chlorophenol	700	Dichlorodibenzofuran, benzene, chlorobenzene.
2-chlorophenol	700	Dichlorodibenzofuran, phenol.

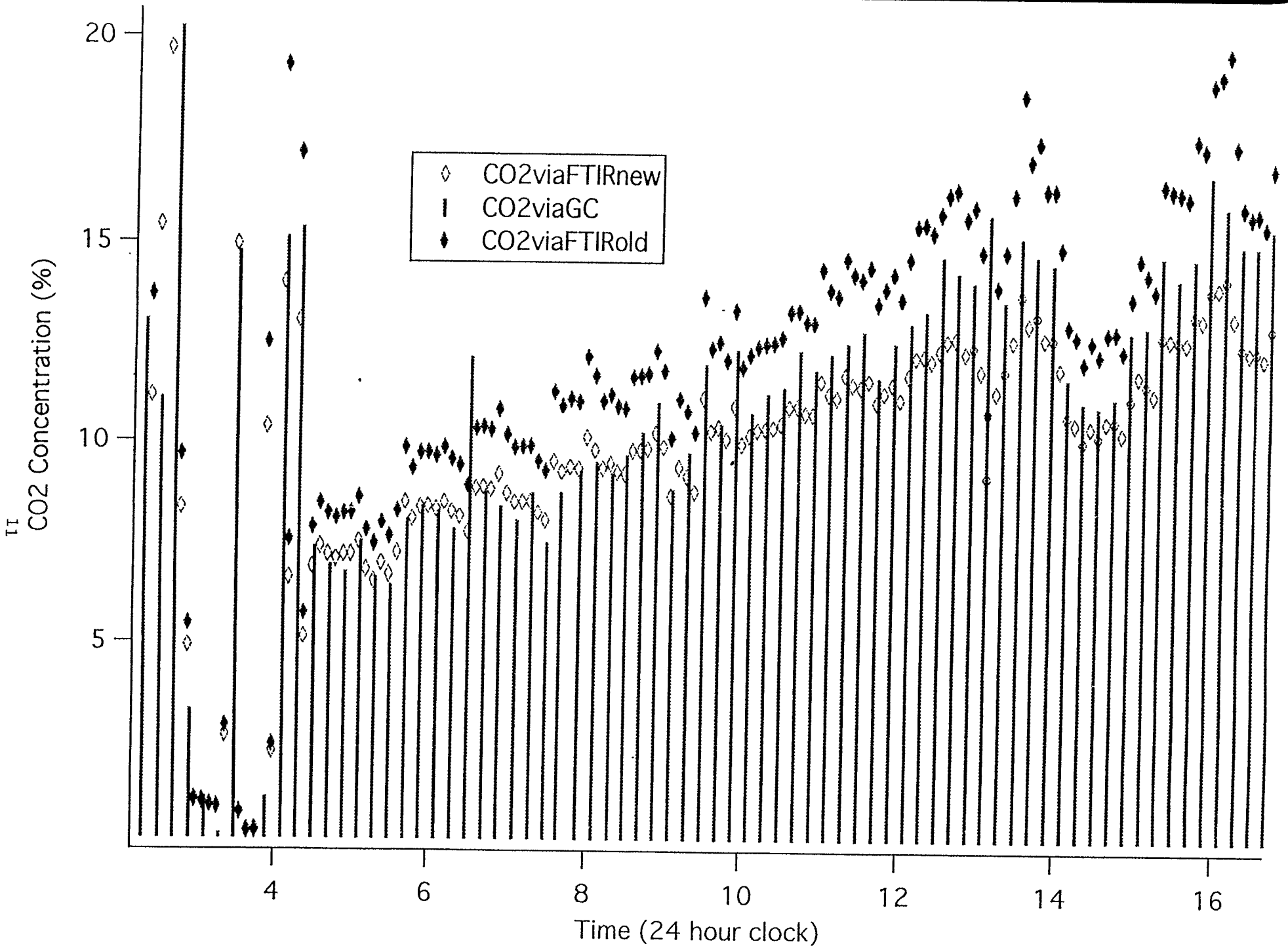

Figure 1. Changes in gas concentrations during the January 26, 1996 combustion run.

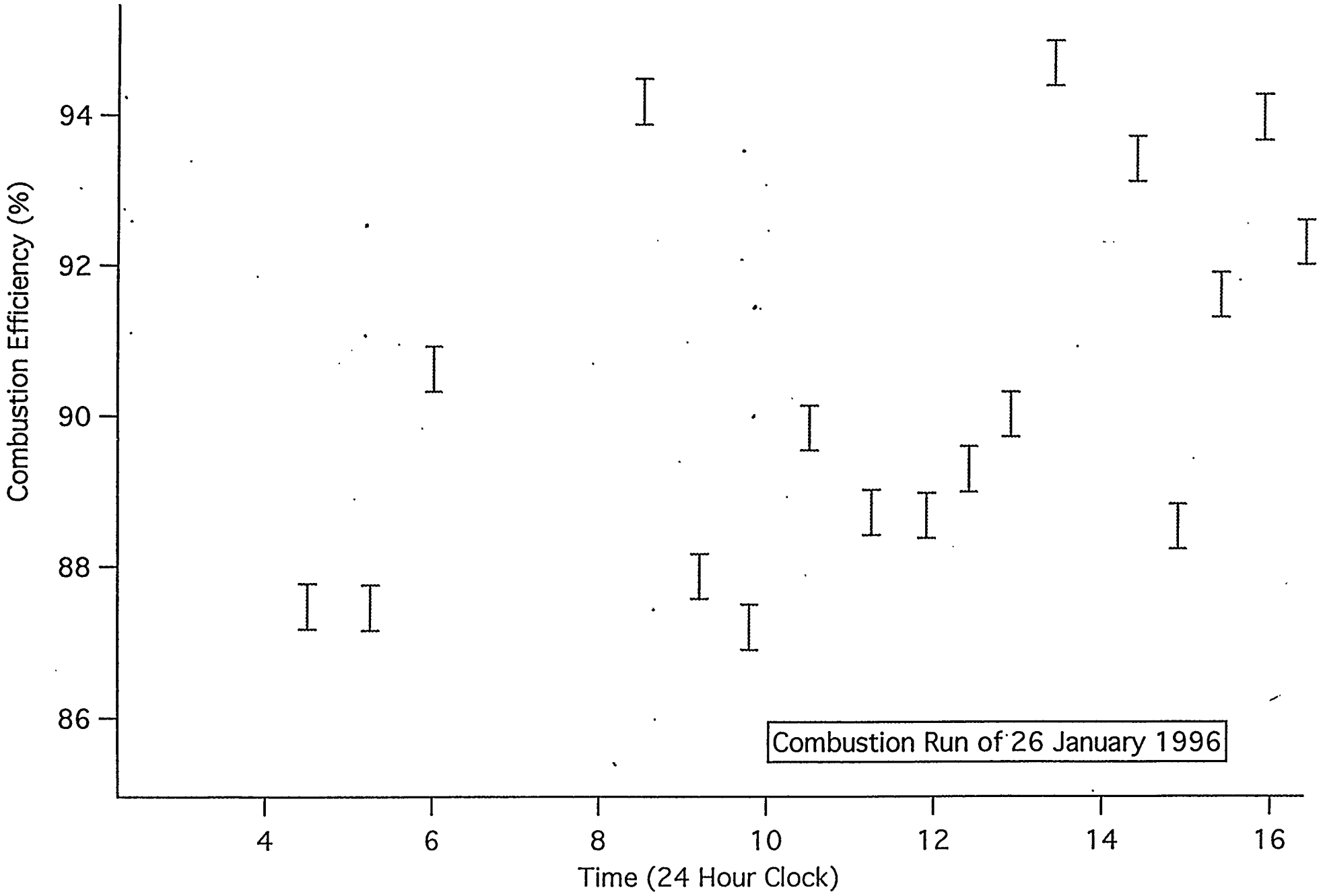

Figure 2. Combustion efficiency vs. time for the January 26, 1996 combustion run.

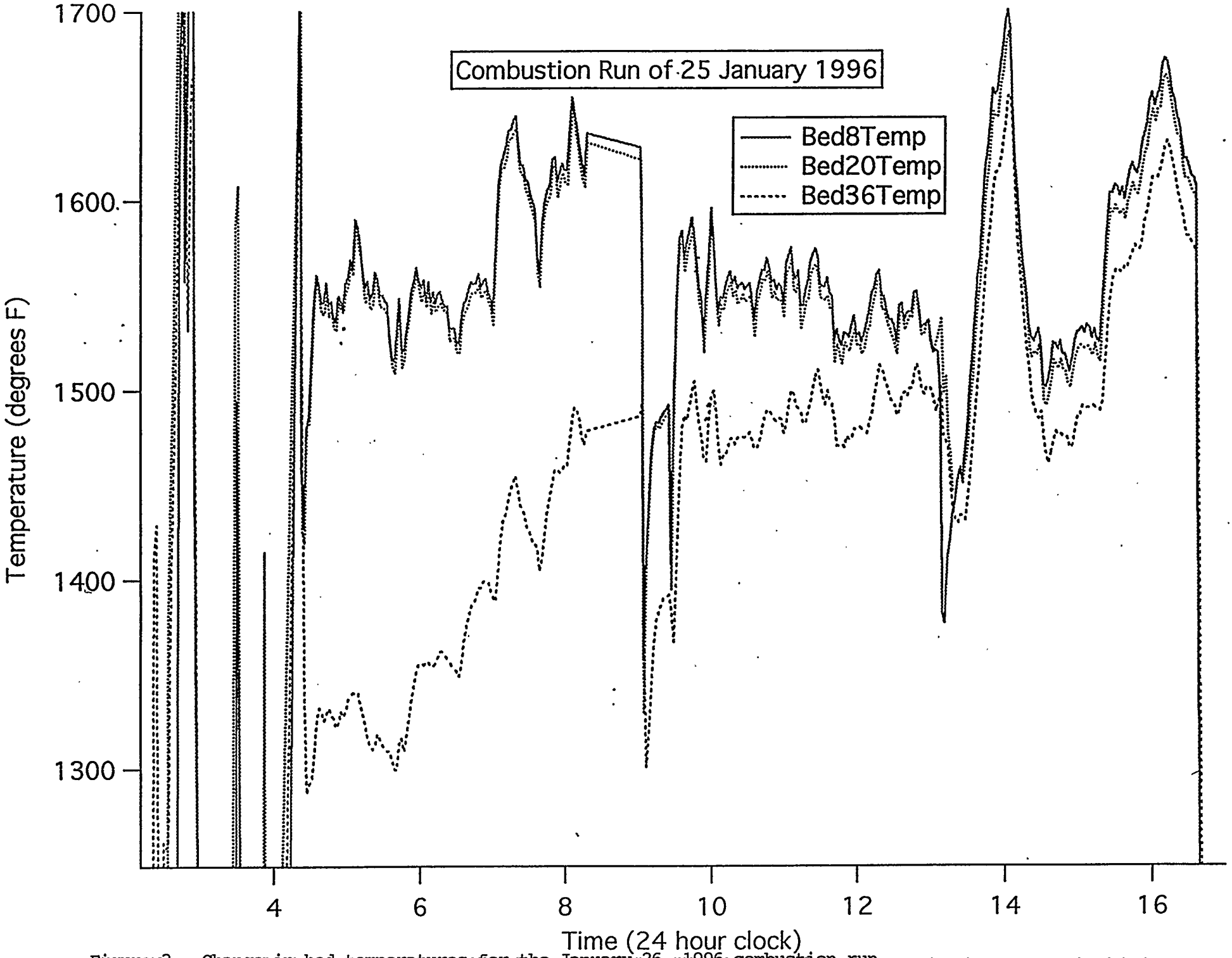

Figure 3. Change in bed temperatures for the January 26, 1996 combustion run.