**Establishment of an Environmental Control Technology Laboratory
with a Circulating Fluidized-Bed Combustion System**

Quarterly Technical Progress Report

July 1 – September 30, 2004

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ABSTRACT

This report is to present the progress made on the project “Establishment of an Environmental Control Technology Laboratory (ECTL) with a Circulating Fluidized-Bed Combustion (CFBC) System” during the period July 1, 2004 through September 30, 2004. The following tasks have been completed. First, renovation of the new Combustion Laboratory and the construction of the Circulating Fluidized-Bed (CFB) Combustor Building have started. Second, the design of the component parts of the CFBC system have been reviewed and finalized so that the drawings may be released to the manufacturers during the next quarter. Third, the experiments for solid waste (chicken litter) incineration have been conducted using a Thermogravimetric Analyzer (TGA). This is in preparation for testing in the simulated fluidized-bed combustor. The experimental results from this study are presented in this report. Finally, the proposed work for the next quarter has been outlined in this report.

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1. EXECUTIVE SUMMARY

In this quarter (July 1, 2004 through September 30, 2004), progress was made on renovating the new Combustion Laboratory, constructing the Circulating Fluidized-Bed (CFB) Combustor Building, finalizing the component parts drawings of a multi-functional Circulating Fluidized-Bed Combustion (CFBC) Facility, and conducting experiments for pyrolysis and incineration of solid waste (chicken litter). Based on the work conducted during the previous quarter of the project, the following progress have been made. First, the contracts for renovation of the new Combustion Laboratory and the construction of the CFB combustor building have been awarded to the contractors. Second, the design of the component parts of CFBC system have been reviewed, and all drawings are being finalized before being released to the manufacturers in the next quarter. Third, the selected solid waste, chicken litter, has been analyzed for elemental composition, and proximate and absolute analysis characteristics. Fourth, the pyrolysis and incineration of chicken litter have been studied with a Thermogravimetric Analyzer (TGA) before it is burned in a simulated fluidized-bed combustor. Also, the work expected to be completed in the next quarter is briefly introduced, and the reasons for delays incurred in some of the tasks are explained.

2. EXPERIMENTAL

2.1. Renovation of Combustion Laboratory and Construction of CFB Combustor Building

The construction bids for renovation of Combustion Laboratory and the construction of the CFB Combustor Building have been closed. Construction contracts for both tasks have been awarded in this quarter. Renovation of the new Combustion Laboratory and the construction of the CFB Combustor Building were started in September 2004. Construction is expected to be completed in March 2005 according to the schedule.

2.2. Review and Finalization of Drawings of Component Parts for CFBC Facility

The detailed component parts of the CFBC Facility have been designed and drawn individually based on the final concept design of the CFBC Facility and the drawings of

assembly parts. All drawings of component parts have been reviewed. These drawings are being finalized for release of fabrication contracts to the manufacturers in the next quarter. This work is essential and vital to construct the CFBC Facility. A three-dimensional video file for the CFB combustor and the new Combustion Laboratory have been drawn by using AutoCAD to simulate the real effect. This video file is attached with this report.

2.3 Pyrolysis and Incineration Studies of Chicken Waste

2.3.1 Background

Commercial chicken farms generate 12.3 million tons of chicken waste per year in Kentucky alone. Current practices for chicken litter disposal include its use as a fertilizer and in its stockpiling in designated plots of land. Chicken waste is quickly becoming a major concern of the U. S. Environmental Protection Agency (EPA) because of the significant damages it causes to the air and water quality. The methane, ammonia, and other hydrocarbon emissions of chicken waste pollute the air and generate unpleasant odors. When spread on cropland, chicken waste serves as a major contributor of phosphates. Excess phosphates not successfully utilized by the topsoil and/or crops migrate into runoff water and can leach into the water table. Excess phosphates in the water serve as a major energy source for aerobic algal population which significantly increases its reproduction rate. Large populations and sudden population explosions of algae deplete the water of oxygen killing wildlife within the water systems in a process known as eutrophication.

One suggested disposal method for chicken waste is cofiring with coal. Chicken litter is a carbonaceous material high in calcium content that may be suitable for providing activated carbon sites to trap mercury. Before chicken waste can be used as a cofiring agent, the decomposition of chicken waste must be mapped. In recent studies, chicken waste is characterized by proximate, absolute, and elemental analyses and further the decomposition is studied using evolved gas analysis.

2.3.2. Experimental Method

Much like coal, chicken waste is a very heterogeneous material. To successfully characterize chicken litter, a sample preparation method was developed to resemble the preparation of a coal laboratory sample. Approximately 9.5 kg of chicken waste was collected from a local commercial farm. The sample was air dried at approximately 35°C overnight. The

absorbed moisture necessitated removal for the subsequent milling and separation steps to be successfully completed. After air-drying, the sample was milled. The milling process served to homogenize the sample as well as to break apart large aggregates of chicken manure. The milled chicken waste sample was divided in half using a hand riffle. When the entire sample was divided, half was discarded and the remaining half was divided again. The previous riffing steps were repeated until the contents remaining filled a 64 oz bottle. Although the milling and riffing processes decreased the gross heterogeneous nature of the sample, some minor heterogeneity remained with regards to particle size. The sample was then divided into three particle size distributions using sieves of 140 and 325 mesh. Table 1 describes the composition of each sample.

Table 1. Sample Classification

Sample Name	Composition
Mill	no division
A	greater than 140 mesh
B	between 140 and 325 mesh
C	less than 325 mesh

From visual inspection, the largest fraction appeared to be composed of wood chips that comprise the bedding material in the chicken houses. The middle fraction appeared to be composed of fine organic material and feather particles. The smallest fraction appeared to be primarily soil matter that may have been collected with the chicken waste when removing it from the houses.

The collected samples were analyzed to determine the elemental compositions, and test the proximate and absolute analysis characteristics. Thermogravimetric Analyzer (TGA)-Mass Spectrometry (MS), TGA-Fourier Transform Infrared (FTIR), and pyrolysis-Gas Chromatograph (GC)/MS were used to investigate the characteristics of pyrolysis and incineration of chicken waste.

3. RESULTS AND DISCUSSION

3.1 Elemental Compositions of Chicken Waste

Table 2 shows the elemental composition of the chicken waste as determined by ASTM Methods D4326 and D6349. Take note of the increasing Silicon Dioxide (SiO_2), Aluminum Trioxide (Al_2O_3), Ferric Oxide (Fe_2O_3), and Titanium Dioxide (TiO_2) as particle size decreases. The aforementioned trend indicates that soil matter is the primary component of Sample C. An interesting trend in the elemental analysis is observed in the Calcium (Ca) and Sodium (Na) contents. Note that the lowest concentration observed in both cases is for Sample C. This indicates that the primary sources of Ca and Na are from the uptake of mineral matter by the trees i.e. the bedding material and/or the chicken manure. Another interesting trend is observed in the sulfur content. The sulfur content measured as sulfite (SO_3) is greatest in the smaller particle sizes indicating that the sulfur in the chicken waste is in the form of inorganic sulfates.

Table 2. Summary of Elemental Composition

	Weight Percent in Chicken Waste									
Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	TiO_2	SO_3
Mill	9.83	1.36	0.58	3.72	1.26	1.61	3.34	4.23	0.06	1.91
A	7.23	1.02	0.44	4.29	1.21	1.73	3.44	4.54	0.03	1.89
B	11.45	1.82	0.74	4.32	1.88	1.59	3.63	5.71	0.09	2.54
C	31.29	3.64	1.26	3.49	1.99	1.22	3.41	4.75	0.33	2.51

3.2 Proximate and Absolute Analysis of Chicken Waste

Table 3 shows the proximate and absolute analysis characteristics of the chicken waste. The heating value of the chicken waste sample was found to be slightly above 5000 Btu/lb, which is of similar calorific value to lignite coals. Sample A has the highest calorific value because it contains less mineral matter than the other samples; thus, the sieving process is analogous to the washing of coal.

Table 3. Summary of Proximate and Absolute Analysis

Sample	Moisture	Ash	Volatile Matter	wt % C Carbon	wt %N Nitrogen	wt %H Hydrogen	wt %S Sulfur	Btu/lb Heating Value
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Mill	10.59	26.58	54.72	29.09	3.44	5.11	0.80	5166
A	10.43	25.27	54.43	30.66	3.35	5.07	0.76	5299
B	11.43	34.62	49.25	26.13	4.74	4.69	1.28	4281
C	9.44	53.85	34.83	16.75	3.68	3.35	1.24	2915

3.3 Studies of Pyrolysis and Incineration of Chicken Waste

Figure 1 is a TGA overlay showing the four chicken waste samples. The four samples exhibit similar weight loss profiles indicating that the identity of the components within each sample are comparable and are undergoing analogous reactions; however, the differing amounts of each component signifies the amount of these components varies from sample to sample.

Figure 1. TGA Overlay of Four Chicken Waste Samples in Air

From the proximate, absolute, elemental, and thermogravimetric analyses, Sample A was determined to be representative of actual chicken waste excluding mineral matter and Sample C was determined to be primarily comprised of mineral matter. The characterization of the different samples is vital for evolved gas analysis. Understanding the initial sample composition and having the most homogenous sample, allows fewer assumptions to be made in evolved gas analysis.

Sample A and C were studied by multiple evolved gas analysis. Sample A and C represent the extreme compositions of the chicken waste: organic matter and mineral matter. Thermogravimetric Analyzer (TGA)-Mass Spectrometry (MS), TGA-Fourier Transform Infrared (FTIR), and pyrolysis-GC/MS were used to investigate the decomposition of Sample A.

Figure 2 shows the temperature resolved FTIR of Sample A in air. Using the FTIR software, a single wavenumber can be plotted showing an intensity at that discrete wavenumber value as a function of temperature. The FTIR shows that methane (CH_4) and carbon dioxide (CO_2) emissions occur over similar temperature ranges. Ammonia (NH_3) is shown to evolve at three distinct temperature ranges. Each release of ammonia correlates to a unique decomposition mechanism, implying three components of chicken waste decompose to generate ammonia.

Figure 2. FTIR as a Function of Temperature

The TGA-MS data shown in Figure 3 indicates that the initial weight loss is moisture (molecule weight 18) that can be attributed to absorbed water and higher temperature evolutions can be due to water of hydration. The CO_2 (molecule weight 44) data shows good agreement with the TGA-FTIR data in the evolution by two mechanisms. The decrease in O_2 (molecule weight 32) occurring simultaneously with the second CO_2 evolution indicates that char combustion occurs at this temperature.

Figure 3. TGA-MS for Sample A in Air

Figure 4. Summary of Evolved Gases

Figure 4 is a TGA curve divided into four main decomposition processes, with the corresponding evolved gases for each region annotated based on the collective TGA-FTIR and TGA-MS experiments.

Figure 5 shows TGA-FTIR results collected by analogous methods using an inert nitrogen atmosphere. Fewer volatiles are detected for pyrolysis and the successive releases of CO_2 are more separated. Under the assumption that the second CO_2 evolution is indeed char combustion explains the shift of these peak to higher temperatures. Under the depleted oxygen (O_2) conditions of pyrolysis, higher temperatures are required to support combustion.

Figure 6 shows the TGA-MS of Sample C in nitrogen. The CO_2 observed at higher temperatures relates to trends identified by elemental analysis. The release of CO_2 at high temperatures is indicative of the decomposition of carbonate salts into CO_2 and the respective metal oxide.

Figure 5. TGA-FTIR for Sample A in Nitrogen

Figure 6. TG-MS of Sample C in Nitrogen

Figure 7. FTIR for Sample A in Nitrogen

Figure 7 shows that during pyrolysis, some organics are released indicated by the peaks slightly below 3000 cm^{-1} and also those at approximately 1700 cm^{-1} ; however, the complex

FTIR spectra make it difficult to assign specific structures to the evolved gases. GC/MS is a useful technique in simplifying complex decomposition phenomenon. Using a Thermex-GC/MS system, a solid sample can be pyrolyzed in the carrier gas atmosphere. As the sample is decomposed, the evolved gases are trapped in a cryogenic trap cooled to -100°C. At the end of the thermal method, the evolved gases are flashed from the trap and sent to the GC/MS where the compounds can be separated and identified with higher confidence.

Table 4 shows the most abundant compounds determined using the Thermex-GC/MS system to analyze Sample A. The compounds within the table show a wide variety of functionalities such as fatty acids, cholesterol derivatives, amines, and sulfur compounds. To further understand the decomposition mechanism, the chicken waste sample was extracted using methylene chloride. The extracted solution was directly injected into the GC/MS bypassing any possibility for pyrolysis. The compounds eluted in this experiment represent the compounds that potentially serve as the reactants to the evolved gas products. Table 5 shows some compounds identified by the GC/MS experiment.

Table 4. Summary of Compounds from Sample A Identified by Thermex-GC/MS

Carboxylic acids	Heterocyclic	Benzene derivatives	Amines	Phenols
acetic acid	furfural	methylated benzaldehyde	N-butyl tert butylamine	2-methyl phenol
3-methyl butanoic acid	2-furanmethanol	benzene acetic acid	-----	dimethylated phenols
hexanoic acid	indole	dibutyl phthalate	-----	2,4,6 trimethyl phenol
carbamic	-----		-----	2-methoxy-4-vinyl-phenol
Amides	Organic acid	Sulfides	Fatty acids	Steroids
acetamide	phosphonic acid	dimethyl sulfone	propanoic acid ester	cholesterol derivative

Table 5. Summary of Compounds from Sample A-Extract Identified by GC/MS

Hydrocarbons	Phenols	Benzene Derivatives
pentadecane	butylated hydroxy toluene	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester
undecane	-----	dibutyl phthalate
hexadecane	-----	
Fatty Acids	Esters	Steroids
dodecanoic acid	propanoic acid, 2-methyl-, 1-(1,1-dimethylethyl)-2-methyl-1,3-propanediyl ester	cholesterol
tetradecanoic acid	undecanoic acid, methyl ester	á-Sitosterol
hexanoic acid	-----	-----

Figure 8 is a chromatogram overlay for Samples A and C. The GC/MS results verify the TGA-FTIR and TGA-MS data showing that the identities are similar, but the compositions vary.

Table 6 and Figure 9 show GC/MS overlays from data collected using Thermex-GC/MS to analyze the residues from both samples. Figure 9 shows that the residue of Sample C contains significantly less organic material than Sample A does.

Figure 8. Overlay of Sample A and C Extracts

Table 6. Summary of Compounds from Sample A Residue by Identified by Thermex- GC/MS

Heterocyclic	Ester	Amides	Phenols
pyrimidine, 4-methyl-	1,2-Ethanediol, diacetate	acetamide	phenol, 2-methoxy-
furfural	-----	-----	-----
2(5H)-Furanone	-----	-----	-----
2-Furanmethanol	-----	-----	-----
1H-Pyrrole-2-carboxaldehyde	-----	-----	-----
2-Methyliminoperhydro-1,3-oxazine	-----	-----	-----
Aminoalcohols	Hydroxyaldehydes	Thiols	Carboxylic acids
4-amine-1-pentanol	glycidol	methane thiol	acetic acid

Figure 9. Overlay of Sample A and C Residues

The compounds shown Table 6 represent the evolved gases produced by the pyrolysis of the residue. Some of these compounds do exist in the pyrolysis of the original sample; however,

because of the removal of some compounds upon extraction, the mechanism may be altered. Approximately 40% of the identified compounds from the residue contain nitrogen compounds. This suggests that methylene chloride is not an effective solvent at extracting the nitrogen compounds from the chicken waste.

By extracting the chicken waste sample with multiple solvents and analyzing both the extract and the residue simplifies the decompositions and allows one to more accurately map how specific compounds or classes of compounds decompose.

Figure 10. TGA Comparison of High Sulfur Coal, 30/70 Sample A/Coal Blend, and Sample A

Figure 10 is an overlay of some work completed with 30/70 a blend of chicken waste and a high sulfur bituminous coal. Figure 10 shows that the blend is intermediate to the two pure samples. The two lower temperature weight losses occurring below 500°C in the blend occur to

a lesser extent than the pristine chicken waste. It is remarkable to note that the residual weight is a function of the ash content, which increases by only 2% on an absolute basis.

4. CONCLUSIONS

During this quarter, the following tasks have been completed:

- ◆ Construction contracts for the renovation of the new Combustion Laboratory and the construction of the CFB Combustor Building were awarded. Both tasks were initiated in September 2004. According to the construction contract, the two tasks will be completed in March 2005.
- ◆ The drawings of the component parts of the CFBC facility have been reviewed. All these drawings are being finalized in order to permit the award of the manufacturing contract during the next quarter. A 3-dimensional video file for simulating the CFBC System and the new Combustion Laboratory has been generated by using AutoCAD.
- ◆ Since a substantial amount of chicken waste is available in Kentucky, chicken waste was chosen as the solid waste to burn with high sulfur coal in the CFBC System. The elemental composition, proximate and absolute analysis characteristics of chicken waste were determined and analyzed.
- ◆ The pyrolysis and incineration of chicken waste in a blend with high sulfur coal were investigated using TGA. The products from pyrolysis and incineration of chicken waste were determined with GC/MS and FTIR.

5. FUTURE WORK AND UPDATED SCHEDULE

5.1 Future Work

During the next quarter, work efforts will concentrate on the following tasks:

- ✦ Finish finalizing the drawings of all component parts of the CFBC Facility.
- ✦ Bid invitation for manufacturing the parts of the CFBC Facility will be released and bid proposals will be evaluated.
- ✦ Continue to work with architects and their engineers on renovating the new Combustion Laboratory and constructing the CFB Combustor Building.

- ✦ Conduct experiments on the modified laboratory-scale simulated FBC facility.
The following experiments will be carried out on this laboratory-scale simulated FBC facility in the next quarter:
 - ❖ Investigate conditions for co-firing of chicken waste and high sulfur coal.
 - ❖ Monitor pollutant emissions from co-firing of chicken waste and high sulfur coal.
 - ❖ Study pyrolysis of chicken waste.

5.2 Updated Schedule

Based on the current progress made on the project, the updated schedule for Fiscal Year 2005 is shown in Table 7.

Table 7. Updated Schedule for Fiscal Year 2005

Task	Updated Schedule
Close bid invitation and begin evaluation of bid proposals for manufacture of component parts of CFBC Facility	December 20, 2004
Award manufacture contracts of component parts of CFBC Facility	January 15, 2004
Complete renovation of the new Combustion Laboratory and construction of the CFB Combustor Building	March 30, 2005
Complete manufacture of component parts of CFBC Facility	April 20, 2005
Initiate installation the bench-scale 0.6MW _{th} CFBC Facility.	May 1, 2005
Start to do the experiments for fundamental research on the laboratory-scale FBC Facility	December 1, 2004
Complete the experiments for fundamental research on the laboratory-scale FBC Facility	July 30, 2005

ACRONYMS AND ABBREVIATIONS

Al ₂ O ₃	Aluminum Trioxide
Btu	British Thermal Unit
C	Carbon
Ca	Calcium
CaO	Calcium Oxide
CFB	Circulating Fluidized-Bed
CFBC	Circulating Fluidized-Bed Combustion
CH ₄	Methane
CO ₂	Carbon Dioxide
DOE	U.S. Department of Energy
ECTL	Environmental Control Technology Laboratory
EPA	U. S. Environmental Protection Agency
FBC	Fluidized-Bed Combustion
Fe ₂ O ₃	Ferric Oxide
FTIR	Fourier Transform Infrared
GC	Gas Chromatograph
H	Hydrogen
H ₂ O	Water
K ₂ O	Potassium Oxide
lb	pound
MgO	Magnesium Oxide
MS	Mass Spectrometry
N	Nitrogen
Na	Sodium
Na ₂ O	Sodium Oxide
NH ₃	Ammonia
O ₂	Oxygen
P ₂ O ₅	Phosphorus Pentoxide
S	Sulfur
SiO ₂	Silicon Dioxide

SO ₃	Sulfur Trioxide
TGA	Thermogravimetric Analyzer
TiO ₂	Titanium Dioxide
wt	Weight

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