Combustion Characterization of Carbonized RDF, Joint Venture Task No. 7

Topical Report

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EXECUTIVE SUMMARY

The overall objective of this research program was to demonstrate EnerTech's and the Energy & Environmental Research Center's (EERC) process of slurry carbonization for producing homogeneous, pumpable fuels from refuse-derived fuel (RDF) with continuous pilot plant facilities, and to characterize flue gas and ash emissions from combustion of the carbonized RDF slurry fuel. Please note that "Wet Thermal Oxidation" is EnerTech's trademark mme for combustion of the carbonized RDF slurry fuel.

Carbonized RDF slurry fuels were produced with the EERC's 7.5-tpd (wet basis) pilot plant facility. A hose diaphragm pump pressurized a 7- 10-wt% feed RDF slurry, with a viscosity of 500 cP, to approximately 2500 psig. The pressurized RDF slurry was heated by indirect heat exchangers to between 5850 -626°F, and its temperature and pressure was maintained in a downflow reactor. The carbonized slurry was flashed, concentrated in a filter press, and ground in an attritor. During operation of the pilot plant, samples of the feed RDF slurry, carbonization gas, condensate, carbonized solids, and filtrate were taken and analyzed.

Pilot-scale slurry carbonization experiments with RDF produced a homogeneous pumpable slurry fuel with a higher heating value (HHV) of 3,000-6,600 Btu/lb (as-received basis), at a viscosity of 500 CP at 100 Hz decreasing, and ambient temperature. Greater-heating-value slurry fuels were produced at higher slurry carbonization temperatures. During slurry carbonization, polyvinyl chloride (PVC) plastics in the feed RDF also decompose to form hydrochloric acid and salts. Pilot-scale slurry carbonization experiments extracted 82-94% of the feed RDF chlorine content as chloride salts. Higher carbonization temperatures and higher alkali additions to the feed slurry produced a higher chlorine extraction.

The carbonized slurry fuel was combusted in a 650,000-Btu/hr atmospheric pulverized-coal boiler simulator. From a storage tank, the carbonized RDF slurry was pumped through the burner gun to the atomizer, where it was mixed with atomizing air. Heated primary air carried the atomized slurry out of the burner gun, while heated secondary air was introduced in an annular section surrounding the burner gun. Heated tertiary air was added through two tangential ports located about 12 inches above the burner gun. The combustion flue gases were analyzed on-line for major pollutants, and extractive samples were taken for analysis of trace pollutants. In addition, samples of the combustion ash were taken and analyzed. The objectives and combustion results are summarized below.

- To determine conditions under which a carbonized RDF slurry will be wet thermally oxidized (combusted).

    - During the combustion test of the carbonized RDF slurry fuel, three combustion temperatures were investigated (1600°F, 1800°F, and 2000°F). Excess air averaged 15%-61 %, depending on the combustion temperature, and was split approximately 11%, 83%, and 6% among primary atomizing air, secondary swirl air, and tertiary overtire air. Percentages of excess air were adjusted manually based upon levels of carbon monoxide in the flue gases. As expected, higher combustion temperatures required less excess air to produce excellent combustion performance. In future combustion tests, excess air initially would be set no higher than 35%.

. To characterize flue gas emissions produced from wet thermal oxidation (combustion) of the carbonized RDF slurry fuel.

- Compared to proposed New Source Performance Standards (NSPS, published September 20, 1994 in the Federal Register), carbon monoxide (CO) emissions were 65%-90% lower at 5-17 ppmv at 7 % O_2 dry, with carbon burnout exceeding 99.9%. Nitrogen oxide (NO_x) emissions also were up to 55% lower than the NSPS at 82 ppmv, without selective **noncatalytic** or catalytic reduction. Since slurry carbonization extracts chlorine from the RDF, hydrochloric acid (HCl) emissions were 17 ppmv, or 32% lower than the NSPS, without any acid gas scrubbing. Mercury emissions also were analyzed at 0.003 mg/dscm, or 96% lower than the NSPS. Cadmium, lead, and **dioxins/furans** emissions were not characterized during these combustion tests. Flue gas emissions from the combustion of the carbonized RDF slurry fuel were well below regulated limits.

- To characterize ash produced from wet thermal oxidation (combustion) of the carbonized RDF slurry fuel.

- Three leaching tests were performed with a representative sample of the combustion ash: U.S. Environmental Protection Agency's Toxicity **charactering** Leaching Procedure (TCLP), Synthetic Groundwater Leaching Procedure (SGLP) for 18 hours, and SGLP for 30 days. Synthetic groundwater was prepared to represent that of Grand Forks, North Dakota, and is unique because of its alkaline pH. For each leaching procedure, no Resource Conservation and Recovery Act (RCRA) Maximum Concentration Limit (MCL) was exceeded, thus this combustion ash would be classified as nonhazardous. All SGLP leaching concentrations were lower than those from the TCLP. In general, the ash exhibited very low leaching characteristics and was 89%-99 % below the RCRA MCL.

COMBUSTION CHARACTERIZATION OF CARBONIZED RDF

1.0 INTRODUCTION

As public concern grows and government regulations become increasingly strict, numerous municipalities and industries face exorbitant costs for solid waste disposal that run head-on into bottom-line profits. Concurrently, markets for lignite coal have been limited primarily because of its high moisture content which results in a low heating value per unit weight and a high transportation cost per unit energy. In addition, most of the North Dakota lignite reserves have sulfur contents that produce emissions that exceed the 1990 Clean Air Act Amendments (CAAA) Phase II emission limits of 1.2 lb SO_2 per MMBtu for power plants.

To address these issues, EnerTech Environmental, Inc., and the Energy & Environmental Research Center (EERC) collaborated to develop a new method of co-utilization of low-rank coals and low-sulfur solid waste materials. The technology, called slurry carbonization, was investigated as a means to efficiently produce homogeneous, high-energy slurry fuels with reduced SO_2 emissions relative to that of the coals, offering a much more environmentally conscious means of utilizing the energy potential of the solid waste.

2.0 BACKGROUND

According to the U .S. Environmental Protection Agency (EPA), the national cost of waste disposal is more than $30 billion a year. Municipal solid waste (MSW) disposal has always been considered an expensive and dirty business. Established landfills are reaching capacity at an alarming rate, and owners are escalating the "tipping fees" they charge to accept MSW. Average fees nearly doubled between 1986 and 1988, from $19.52/ton to $34.69/ton. Later averages are not available, but at this rate of increase, tipping fees would have reached $62/ton in 1990 and exceeded $ 100/ton by 1994. It is critical that out-of-date, expensive waste disposal methods be replaced by more efficient and cost-effective technology. The organizations involved in this project foresee collection trucks delivering waste to a landscaped central site where, after shredding and slurrying, it is processed by compact, enclosed, continuous, and automatically controlled methods of pulping, separating by density, pumping, oxidating, and transferring of heat into energy, harmless vent gas, and ash slurry.

Such a technology has already been developed at the EERC for the preparation of liquid fuels from low-rank coals. In 1991, a project between EnerTech Environmental, Inc., and the EERC applied the technology to a raw RDF. The process, more commonly referred to as hydrothermal treatment and more recently referred to as wet carbonization, expose-s the high-moisture material to high temperature and pressure to essentially squeeze trapped bulk water from within the structure of the material. Hydrothermal treatment is a relatively simple process in which a pressurized, diluted slurry is heated to temperatures above 200°C for up to 10 minutes. When heated under pressure to a final temperature, structural groups attached to the chemical structure decompose to form carbon dioxide, which helps to force liquid water out of the pores and into the carrier medium. Exposure to these or higher temperature conditions also causes both chemical and physical changes that may significantly reduce the propensity for the substance to reabsorb the removed moisture.

Results from EERC studies indicated that an enhanced slurry fuel could be produced with an energy density increase of over 400%, a chloride concentration reduction of 80%, and a sulfur reduction of 50%. Based on these results, the EERC and EnerTech are working to develop a new method of utilization that will reduce lignite moisture and SO_2 emissions and also address one of the greatest environmental challenges facing society—disposal of MSW. In 1993, EERC and EnerTech developed a RDF-lignite slurry fuels program to address these concerns.

The EnerTech-EERC three-step process, illustrated in Figure 1, processes the MSW and/or coal entirely as a fluid through compact, enclosed equipment under automatic control. The wet slurry is moved through EnerTech's boilers, which oxidize the mixture under pressure. The conditions are highly destructive to gaseous pollutants, allowing the MSW slurry to be directly converted to energy without pollution concerns. The process will allow MSW to be processed continuously while recyclables are recovered, and energy is produced, with much less capital investment and no harm to the environment. At the conditions contemplated, even high-sulfur lignites can be converted more efficiently to energy with negligible pollution.

3.0 OBJECTIVES

The objective of testing was to establish the effectiveness of the EnerTech process on the production of a fuel that has desirable combustion properties, including low slagging and fouling tendencies. stable flame characteristics under a variety of load conditions, high carbon burnout, and low emissions. Specific objectives included the following:
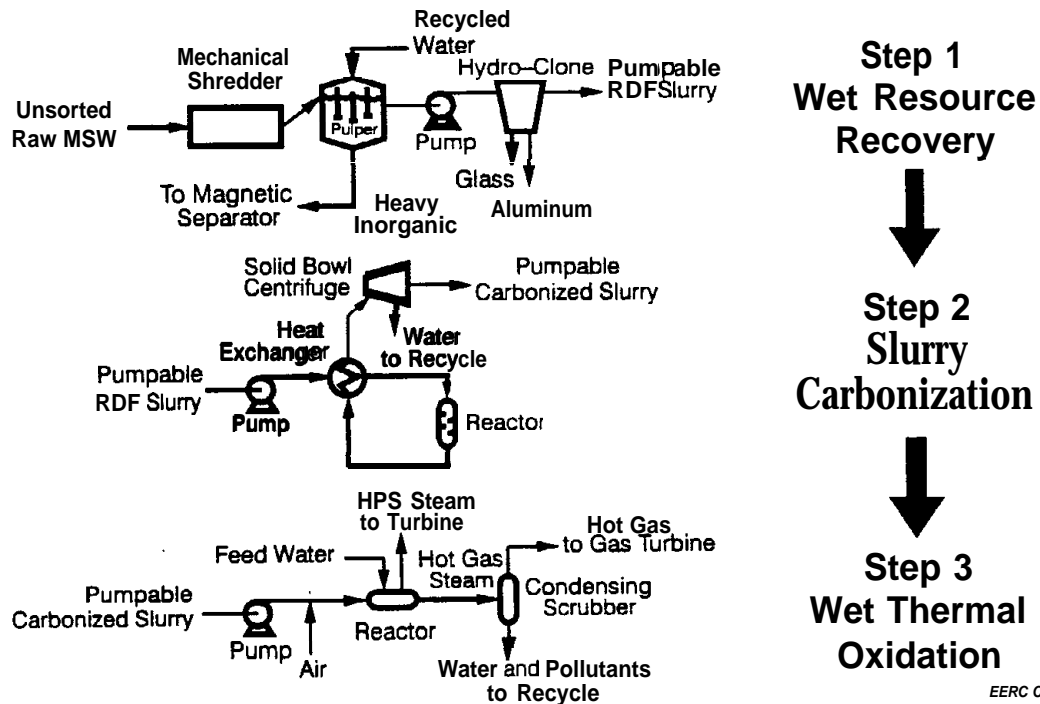
Figure 1. EnerTech-EERC three-step MSW process.

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- Combustion testing to quantify flue gas concentrations of SO_2, NO_x, and hazardous air pollutants (HAPs)

- Evaluation of the fuel's fouling and slagging characteristics

- Evaluation of electrostatic precipitation (ESP) performance

- Flame stability testing to determine the range of swirl required to maintain stable combustion

- Characterization of the leaching potential of the fly ash.

4.0 WORK DESCRIPTION

Research performed under this project, and a separately funded project, was divided into three general tasks. In the first task (funded under a separate program), a commercial source of RDF, produced from a wet-resource-recovery (wet-RR) process, was not available for this research program. Therefore, EnerTech simulated a typical wet-RR RDF slurry from dry RDF pellets. Two samples of dry RDF pellets were procured from local resource recovery operations. Samples were analyzed at the EERC, and compared to a typical wet processed RDF. Based upon this characterization, a sample of RDF pellets from Thief River Falls, Minnesota, was slurry carbonized in EERC's 2-gallon autoclave system (please see Figure 2). Approximately 9 pounds of a 14-wt% RDF slurry were charged to the autoclave after which the autoclave was sealed and evacuated of residual air. External heaters were activated and the temperature controller programmed to 5720 F.
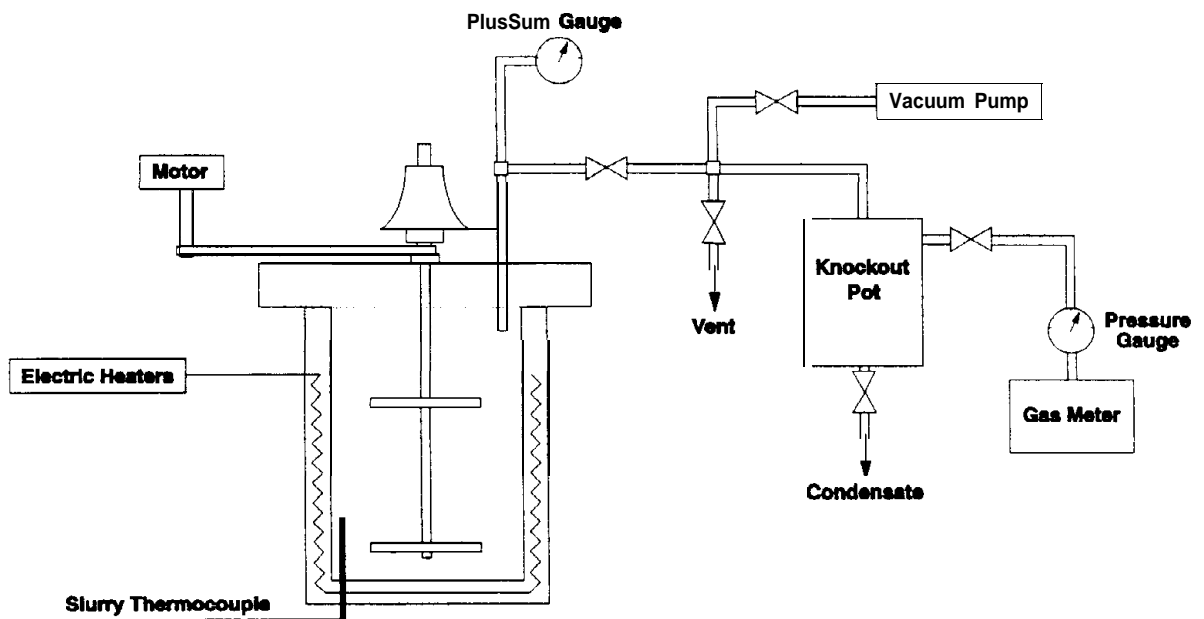
Figure 2. Simplified schematic of EERC's 2-gallon batch autoclave system obtained for EnerTech.

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Heating up to the desired slurry carbonization temperature took approximately 2.5 hours. Slurry temperature and pressure were maintained for a nominal period of 15 minutes, after which the heaters were shut off. Reactor and contents were allowed to cool down overnight prior to product collection. Slurry was continually stirred throughout the heatup, temperature stabilization, and cooldown. After cooldown, carbonization gas was vented via a diaphragm meter to quantify production of noncondensable products. The carbonized RDF slurry was separated into a damp carbonized cake and a water stream via Büchner filtration, and samples were taken and characterized. Based on this data, Thief River Falls' RDF was considered an acceptable source material and approximately 2000 lb were procured.

A second batch characterization experiment was performed with EERC'S autoclave at 617 "F to determine the effects of adding sodium hydroxide (NaOH) on the extraction of chlorine from RDF. During slurry carbonization, polyvinyl chlorine (PVC) plastic in the feed RDF decomposes and forms aqueous HCl in the carbonized slurry. NaOH was added to the feed RDF slurry to neutralize the hydrochloric acid as it forms and enhance the chlorine extraction. Results from this second characterization experiment were used to determine the weight percentage of NaOH to be added to the RDF during pilot plant production of carbonized RDF.

In the second task (also funded under a separate project), the large required volume of carbonized RDF for the combustion experiment was produced with EERC'S continuous 7.5-tpd (wet basis) hot-water-drying pilot plant (please see Figure 3). A hose diaphragm pump capable of pumping slurries of viscosity to 2500 CP at 60 Hz was used to pump the dilute RDF slurry from 35 psig to approximately 2500 psig. From the pump, the pressurized RDF slurry flowed through a series of four heat exchangers. A double-pipe, steam heat exchanger first heated the slurry to approximately 1400 F. Three condensing Dowtherm vapor heat exchangers, connected in series, heated the slurry to its final temperature. Slurry temperature and pressure were maintained for specified residence times in a downflow reactor. From the reactor, the carbonization gas was separated from the carbonized slurry by feeding the hot slurry tangentially into a cyclone-shaped vessel and flashing to atmospheric pressure. The carbonization gas was conducted from the top of
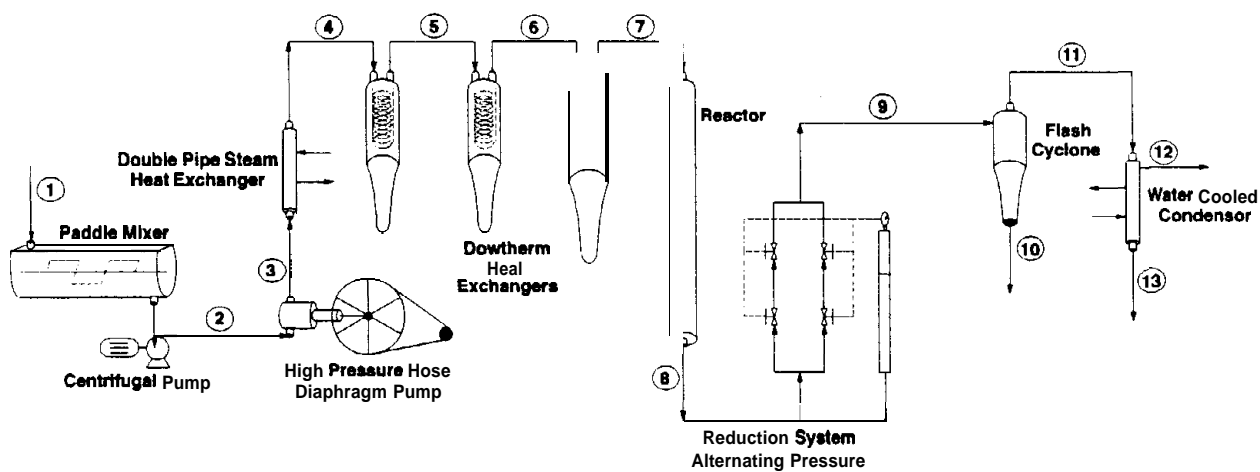
Figure 3.   Simplified schematic of EERC's continuous 7.5-tpd (wet basis) slurry carbonization unit (obtained from EnerTech).

the cyclone to a multipass water-cooled condenser. Noncondensable gas was sampled and sent to a natural gas-fired incinerator where it was flared at 1500°F. The liquid condensate was sampled and pumped to a storage tank for proper disposal. From the bottom of the cyclone, the carbonized slurry was sampled and pumped to a storage tank for dewatering by a filter press at the end of the pilot plant run. All carbonized product was saved and blended for the continuous combustion experiments.

During the carbonized RDF slurry production, a total of five different process conditions were investigated and sampled for analysis. Table 1 summarizes the critical variables and set points for each test condition.

In the third task funded under this project, the carbonized RDF slurry prepared from above was combusted in EERC'S 650,000-Btu/hr atmospheric combustion test facility (CTF). The CTF (please see Figure 4) is a pulverized-coal/oil combustion simulator, which represents the majority of commercial combustion facilities that could utilize EnerTech-EERC's carbonized RDF slurry fuel. The combustion chamber is 30 inches in diameter, 8.2 feet high, and refractory lined. From a continuously stirred storage tank, the carbonized RDF slurry was pumped through the burner gun to the atomizer, where it was mixed with atomizing air prior to entering the burner throat. Heated primary air carried the atomized slurry out of the burner gun, while heated secondary air was introduced in an annular section surrounding the burner gun. Heated tertiary air was added through two tangential ports located in the furnace wall about 12 inches above the burner cone. A simulated waterwall probe and a horizontal probe were positioned just above the flame to evaluate the slag potential of the slurry fuel.

Flue gases passed out of the furnace into a lo-inch-square duct that is also refractory lined. Located in the duct was a vertical, ash fouling test probe bank designed to simulate superheater surfaces in the convective pass of a boiler. After leaving the ash fouling test probe bank, flue gases passed through a series of water-cooled heat exchangers, and then to a five-stage cyclone system before being discharged through an ESP. The five-stage cyclone system was used to determine the size distribution of particulates entering the ESP. The system consists of five cyclones and a backup filter connected in series to provide five, equally spaced particle-size cuts on a logarithmic scale from 0.004 to 0.40 inches.

TABLE 1

Summary of Slurry Carbonization Test Conditions, Continuous Experiment.

	Test #1	Teat #2	Test #3	Test #4	Test #5
Average Maximum Temperature, "F	600.4	621.9	626.4	585.0	615.9
Reactor Residence, min	7.3	8.7	8.3	7.3	8.6
lb NaOH/dry lb RDF	0.090	0.090	0.045	0.090	0.090
Feed Particle Size, in.	1/16	1/16	1/16	1/8	1/8
Feed Solids, wt%	7.0	10.0	7.7	7.0	7.3
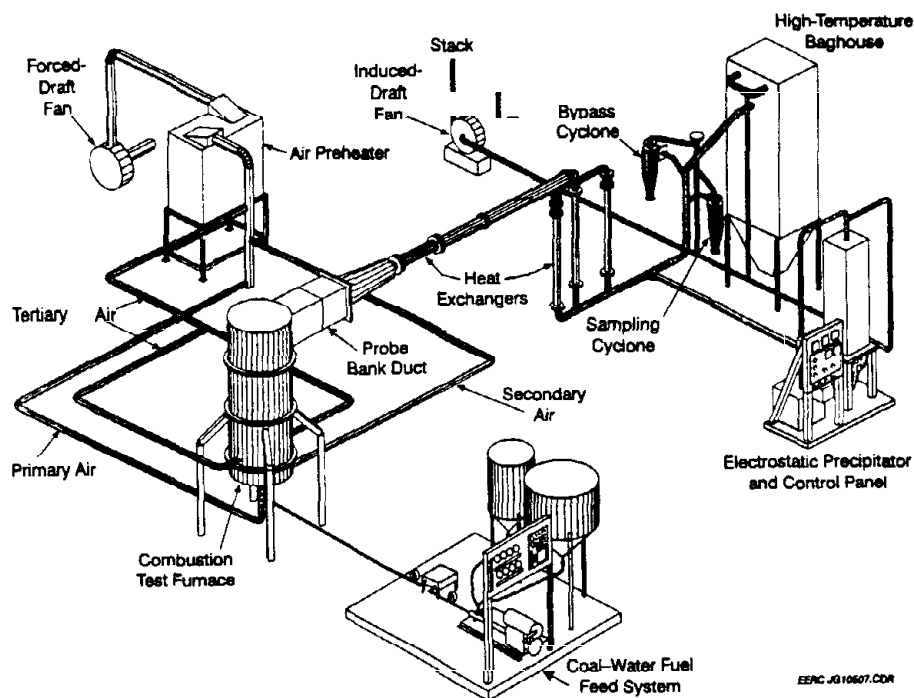
Figure 4. Simplified schematic of EERC'S continuous 650,000-Btu/hr atmospheric CTF.

During the combustion experiment, three different combustion temperatures (1600°F, 1800°F, and 2000°F) were investigated. Samples of the carbonized RDF slurry, fly ash before and after the ESP, and collected fly ash were saved for analysis. Also, combustion ftue gases were continuously monitored for O_2, N_2, CO_2, CO, NO_x, SO_2, and hydrocarbons, and sampled, according to EPA methods, to determine volatilized heavy metals and chlorine.

5.0 RESULTS AND DISCUSSION

5.1 Refuse-Derived Fuel (RDF) Characterization and Selection

Since a commercial source of wet-RR processed RDF was not available for this research program, a RDF slurry was simulated from dry RDF pellets. A sample of RDF pellets from Thief River Falls, Minnesota, was characterized and compared to a wet-RR RDF material that EnerTech has previously slurry carbonized. As can be seen from Table 2, small differences exist in ash, carbon, and nitrogen contents of the carbonized products (please note that oxygen contents were calculated by difference). However, considering the heterogeneous character of RDF and the difficulty in obtaining a representative sample, Thief River Falls and wet-RR RDFs are very similar. Based on this data, the Thief River Falls RDF was considered an acceptable source material and approximately 2000 lb were procured.

TABLE 2

Comparison of Fuel Properties of Raw and Carbonized RDF, Batch Experiment

	Thief River Falls RDF	slurry Carbonized @ 572°F	Wet-Resource-Recovery RDF	Slurry carbonized @ 572°F
Proximate, wt%, dry:				
Volatile Matter	81.8	56.1	82.0	61.3
Freed Carbon	11.6	32.8	11.4	30.0
Ash	6.7	11.1	6.6	8.7
Ultimate, wt%, dry:				
Carbon	47.6	68.0	52.3	72.0
Hydrogen	6.6	7.2	7.9	7.6
Nitrogen	0.2	0.5	0.9	1.6
Sulfur	0.2	0.1	0.3	0.1
Oxygen	38.7	13.1	32.0	10.0
HHV', Btu/lb, dry:	8,650	14,200	9,560	14,060
Ash XRFA[2], wt%				
Silicon	37.8	41.8	45.0	44.0
Aluminum	24.7	36.0	19.7	31.8
Iron	1.0	2.6	6.3	3.4
Titanium	5.1	10.1	4.0	7.7
Phosphorus	1.1	1.6	2.6	2.3
Calcium	15.2	1.9	10.4	4.8
Magnesium	2.6	2.3	2.1	2.2
Sodium	4.2	0.4	2.1	1.0
Potassium	1.6	0.3	1.2	0.7
Sulfur	6.6	3.0	6.7	2.1

' Higher heating value.
[2]X-ray fluorescence analysis.

Figure 5 summarizes the mass balance from the second batch characterization experiment with Thief River Falls RDF. Weight of the filtrate, filter cake, and condensate was determined analytically, while weight of the carbonization gas was determined by difference. This results in a small inaccuracy in the measured and calculated weight of the filter cake and carbonization gas, since a small amount of carbonized RDF remained bonded to the internal components of the autoclave and could not be removed. Carbonized cake contained 33% of the total feed solids (dry basis), while the filtrate contained approximately 31%. Condensate contained less than 1 % of the total feed solids and carbonization gas approximately 35% by difference.

For the mass balance in Figure 5, approximately 0.09 lb of NaOH was added per dry lb of RDF to neutralize aqueous hydrochloric acid formed from the decomposition of PVC. Feed RDF had a total chlorine content of approximately 3.697×10^{3} lb (or 2.71 lb Cl/1000 dry lb RDF) that was reduced to a total chlorine content of approximately 0.064×10^{3} lb in the carbonized cake (or 0.14 lb Cl/1000 dry lb carbonized product), or over 98 %, a substantial removal. Table 3 summarizes chlorine contents and pH of the feed and carbonized RDF.
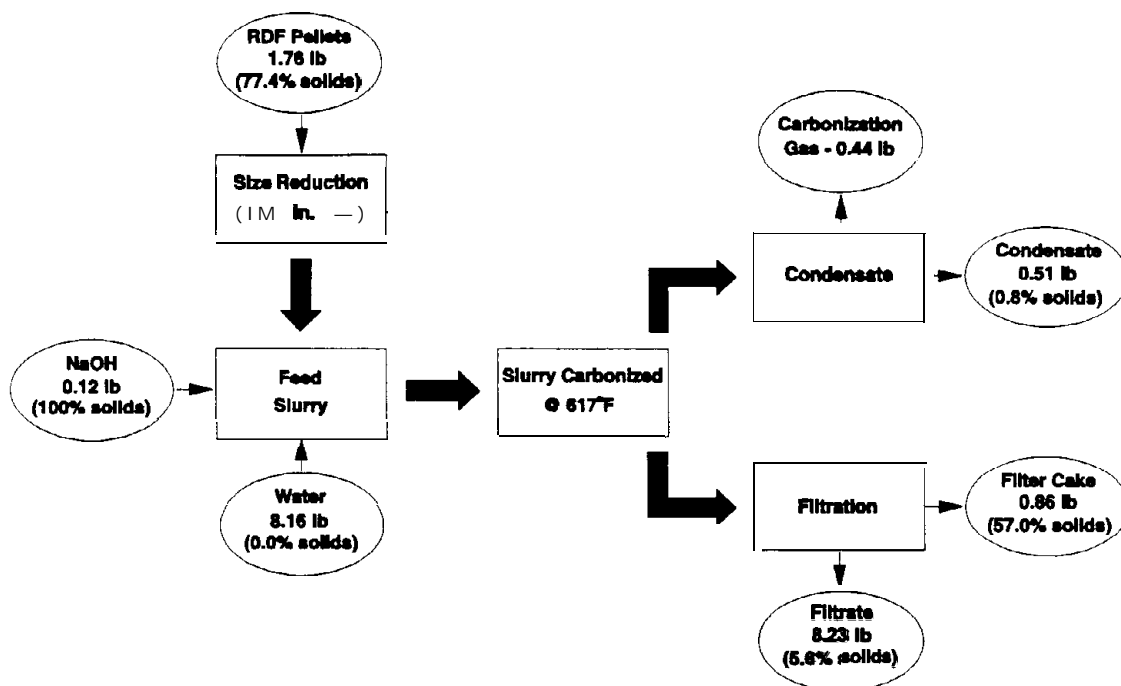
Figure 5. Mass balance of slurry carbonization, batch experiment.

TABLE 3

Chlorine Concentrations of Raw and Carbonized RDF, Batch Experiment

	Feed RDF	Slurry Carbonized RDF @ 617°F
Chloride Concentration (lb/1000 dry lb)	2.71	0.14
Slurry pH	12.84	6.35

Removal of chlorine, through slurry carbonization prior to combustion, provides several important advantages over mass bum and other RDF combustion technologies. Briefly, the advantages include the 1) elimination of acid gas scrubbers for combustion flue gases to remove HCl; 2) reduction in chlorine-resistant construction materials in the boilers and downstream particulate collection systems; 3) potential reduction in formation of organic and chlorinated organic by-products, such as dioxins and furans in combustion flue gases; 4) reduction of combustion inhibition from radical scavenging of chlorine atoms; and 5) emission reduction of many nonvolatile and semi-volatile metals because of metal chloride formation.

For the second batch characterization experiment, the ash fusion temperature of the carbonized product was analyzed to determined the effect of NaOH addition on the fusion temperature of the ash. As can be seen from Table 4, fusion temperature of the ash from carbonized RDF with NaOH was lower than that of the ash from carbonized RDF without the addition of NaOH. However, these temperature are well below typical operating temperatures of pulverized-coal combustors and should not pose a slag problem in boilers.

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TABLE 4

Ash Fusion Temperatures (Reducing Atmosphere) of Raw and Carbonized RDF, Batch Experiment.

	Raw RDF w/ no NaOH	Raw RDF w/ NaOH	Carbonized w/ no NaOH	Carbonized w/ NaOH
Temperatures, "F:				
Initial	2196	2188	2491	2219
Softening	2214	2250	>2800	2388
Hemispherical	2356	2473	>2800	2421
Fluid	2397	2691	>2800	2534

5.2 Pilot-Scale Slurry Carbonization of RDF

The large quantity of carbonized RDF required for combustion experiments was prepared using EERC'S continuous 7.5-tpd (wet basis) hot-water-drying pilot plant (please see Figure 3). A total of five different process conditions were investigated with this pilot plant (please see Table 1), and samples were collected for analysis. The average reactor residence time was calculated based upon feed rate of the high-pressure pump, reactor volume, and estimated density of the feed slurry. In order to eliminate duplicate analysis, the feed solids for Test #2, #3, and #5 were determined from samples taken during the pilot plant run, while the feed solids for Test #1 and #3 were estimated from the weight of water added to the dry, shredded RDF pellets during preparation of the feed slurry.

In conjunction with the simplified schematic of the slurry carbonization pilot plant in Figure 3, Table 5 summarizes average mass flow rates during the slurry carbonization pilot plant run. Flow rates are based upon total pounds of prepared RDF slurry and total pounds of dilute carbonized slurry and condensate collected through the entire pilot plant run. Mass flow rates of the carbonized cake and filtrate are based upon the filter press run performed at the end of the pilot plant run. Carbonization gas mass flow rate was calculated by difference.

Based on Table 5, 34 wt% of the feed solids (dry basis) were recovered in the carbonized cake (dry basis) for a calculated energy yield of approximately 57%. Also, 31 wt% of the feed solids were converted to soluble liquids in the filtrate and 35 wt% to carbonization gas. Less than 1 wt% of the feed solids appeared in the condensate. This mass balance was extremely similar to the mass balance of the batch slurry carbonization experiment shown in Figure 5, and indicates results from EERC'S autoclave are similar to the continuous pilot plant.

Table 6 characterizes the filtrate and condensate from each slurry carbonization pilot plant test in typical industrial wastewater treatment terms. In addition, a sample of the filtrate and condensate from Test #2 was analyzed by gas chromatography-mass spectrometry (GC-MS). Because of the high polarity of many of the soluble organics in the filtrate and condensate, it was necessary to optimize chromatographic conditions, and ultimately, a thick-film capillary column was used (5-pm film x 30-m long DB-1 GC column), rather than a more conventional column. Injections were performed either split or splitless at 100"F (hold 3 minutes) followed by a temperature ramp at 20 °F/minute to 580°F.

TABLE 5

Average Mass Flow Rates of Continuous Slurry Carbonization Pilot Plant Run

No.	Stream Name	Average Mass Flow Rate, lb/hr	Average wt% Total Solids	Average Solids Flow Rate, lb/hr	% of Input Solids
1	Feed RDF Slurry	548	7.2	39.2	100
10	Carbonized Slurry	290	8.8	25.6	65.3
	Carbonized Cake	24	54.8	13.4	34
	Filtrate	265	4.6	12.2	31
11	Carbonization Gas	35	---	---	---
12	Condensate	224	0.06	0.13	0.003

TABLE 6

Filtrate and Condensate Analysis, Continuous Experiment

	Test No. 1		Test No. 2		Test No. 3		Test No. 4		Test No. 5	
	Filtrate	Cond.	Filtrate	Cond.	Filtrate	Cond.	Filtrate	cold.	Filtrate	cold.
pH	4.61	3.92	4.85	2.86	4.40	3.43	4.81	3.87	5.31	—
COD, lb/gal	110.9	44.3	108.6	58.3	106.0	57.9	111.3	56.0	109.8	—
BOD_5, lb/gal	26.5	9.6	32.6	11.0	29.1	11.2	31.8	10.9	32.2	—
TOC, lb/gal	42.8	11.0	50.3	13.4	42.8	12.9	46.9	12.1	46.6	—
TIC, lb/gal	2.3	11.0	<0.4	<0.4	0.4	<0.4	0.8	<0.4	3.4	—
TDS, lb/gal	105.2	0.8	134.4	3.0	110.5	2.1	135.5	0.8	152.2	—
TSS, lb/gal	0.3	0.5	716	<0.1	2.5	<0.1	4.2	1.6	4.2	—

The filtrate and condensate had relatively similar dissolved organic compositions. From the acid fraction extraction, several of the most concentrated organics are guaiacol (methoxyphenol), syringol (dimethoxyphenol) and their derivatives. The identifications of these species are quite certain because of their unique mass spectra. Several neutral organics were found in the acid fraction at high concentrations, and their mass spectra indicate that they are primarily volatile ketones (especially cyclic ketones) and related compounds. Carboxylic acids (particularly acetic acid) were also present in the acid fraction.

The base fraction from both samples contained much lower concentrations of organics, and most of the species detected in the base fraction were also detected in the acid fraction (indicating carryover during the methylene chloride extraction). However, traces of components, such as of pyridine, were found in the base fraction. Please note that organics not present in either fraction for

the filtrate and condensate (at least not at detectable levels) include typical fuel hydrocarbons (benzene, alkylbenzenes, alkanes, etc.), polycyclic aromatic hydrocarbons (PAHs), and chlorinated organics.

Addition of NaOH to the feed RDF slurry had a significant impact upon the solid yield in the carbonized cake. Based upon previous research by EERC and EnerTech, autoclave experiments without any alkali addition resulted in a solid recovery in the carbonized cake averaging 52% with an energy yield above 80%. EnerTech also has performed autoclave experiments with the addition of CaO to the feed RDF slurry and produced a recovery of solids of approximately 48 % and an energy yield of 72 %. EERC and EnerTech theorizes that NaOH is hydrolyzing components in the feed RDF slurry and increasing the soluble hydrocarbon compounds in the carbonized slurry. A hydrolysis effect of NaOH can be viewed as a potential positive or negative. On the negative side, a significant proportion of the feed RDF, mass and energy, has been solubilized which must then be recovered prior to reuse or disposal of the filtrate water.

On the positive side, a carbonized slurry made up of these solubilized hydrocarbons and solid carbonized RDF particles potentially would have a significantly better rheology (i.e., a higher total wt% solids at a comparable viscosity), and hence heating value, than the rheology of a carbonized slurry of pure water and solid carbonized RDF alone. EnerTech must perform more autoclave experiments to either maximize chlorine extraction and minimize conversion of the feed RDF to soluble products or research means of removing the solubilized hydrocarbons from the filtrate and blending them with the solid carbonized RDF particles.

Table 7 summarizes measured process temperatures and pressures during Test #2 for the lines enumerated in Figure 3, as a representative sample of conditions utilized during the slurry carbonization pilot plant run. Please note temperatures of streams #1-#3 (feed RDF slurry) and stream #11 (carbonization gas) are estimated. Temperature and pressure profiles for the remaining four test conditions were similar.

Table 8 summarizes fuel properties of raw and carbonized RDF from the five test conditions of the slurry carbonization pilot plant run. On a dry basis, the feed RDF had a high oxygen content (above 35 wt%) and a low heating value. In general, oxygen is contained in carboxyl acid groups and represents a significant weight percentage but only a minimal energy contribution. High-quality solid fuels, like bituminous coal, have a lower wt% oxygen and a higher heating value, because of the predominance of carbon-carbon and carbon-hydrogen bonds. With EnerTech's slurry carbonization process, an objective is to remove these oxygen functional groups from solid RDF particles, so that the heating value of remaining carbonized particles (now mostly carbon-carbon and carbon-hydrogen bonds) will be higher. As can be seen in Table 7, wt% of oxygen was reduced approximately 43%-76 % (dry basis), while the heating value of the carbonized RDF was improved 51 %-82% (dry basis). Concurrently, slurry carbonization destroys the fibrous structure of RDF. Figurea 6-9 depict, by scanning electron microscopy (SEM), the change in particle shapes and structures from the feed RDF to the carbonized product.

As can be seen in Table 9, the majority of oxygen functional groups were removed from the RDF particles as carbon dioxide gas. The carbonization gas also contains trace amounts of hydrogen, carbon monoxide, and other hydrocarbons. In a commercial facility, this carbonization gas would be conducted to a boiler to oxidize the trace organics and reclaim their heating value.

TABLE 7

Process Temperatures and Pressures of Slurry Carbonization
Pilot Plant Test #2

Line No.	Stream Name	Test #2, °F	Test #2, psig
1	Feed RDF Slurry	60.0	-----
2	RDF Slurry	65.0	23
3	RDF Slurry	70.0	2310
4	RDF Slurry	157.6	-----
	#1 Dowtherm Liquid	483.3	——
	#1 Dowtherm Vapor	468.5	-----
5	RDF Slurry	338.5	2103
	#2 Dowtherm Liquid	567.7	-----
	#2 Dowtherm Vapor	554.9	-----
6	RDF Slurry	483.4	-----
	#3 Dowtherm Liquid	642.9	-----
	#3 Dowtherm Vapor	-----	——
7	RDF Slurry	608.4	2059
8	Carbonized Slurry	625.3	-----
9	Carbonization Gas	541.6	-----
10	Carbonized Slurry	295.9	-----
11	Carbonization Gas	227.3	---
12	Condensate	227.3	---

Based upon these tests, the HHV of the carbonized RDF appears to be a function of maximum carbonization temperature. As can be seen from Figure 10, a higher maximum carbonization temperature produced a carbonized product with a lower oxygen content and higher HHV (dry, ash-free basis).

The feed particle size, feed RDF w%, or grams NaOH per gram feed RDF did not produce a noticeable effect on heating value. Also, average reactor residence time did not produce a noticeable effect on heating value, although the measurement of this variable was approximate and did not vary significantly. More teats are required to refine this relationship and account for differences in the measured heating values of the carbonized RDF at similar maximum slurry carbonization temperatures.

Slurry carbonization of RDF not only improves the heating value of the solid product, but also greatly improves rheology of the carbonized RDF slurry through the removal of oxygen functional groups and reduction in the particle size of the RDF. It is suspected that water bonds with the oxygen functional groups in the large RDF particles through Van der Waals forces, resulting in a high viscosity for the feed RDF slurry. Since slurry carbonization reduces oxygen content and particle size of RDF, viscosity of a carbonized RDF slurry is also dramatically reduced (or the

TABLE 8

Fuel Properties of Raw and Slurry Carbonized RDF, Continuous Experiment

	Test No. 1		Test No. 2		Test No. 3		Test No. 4		Test No. 5	
	Feed	Product	Feed	Product	Feed	Product	Feed	Product	Feed	Product
Proximate, wt%, dry										
Volatile Matter	75.42	69.74	75.42	71.27	82.41	65.40	77.21	70.57	77.21	60.91
Fixed Carbon	9.31	14.67	9.31	12.63	7.90	16.85	7.68	12.86	7.68	9.67
Ash	15.28	15.59	15.28	16.09	9.69	17.75	15.11	16.56	15.11	29.41
Ultimate, wt%, dry										
Carbon	43.32	60.13	43.32	63.16	48.03	63.19	43.03	55.79	43.03	54.91
Hydrogen	5.45	7.63	5.45	7,63	5.89	7.57	4.86	6.42	4.86	6.67
Nitrogen	0.23	0.18	0.23	0.28	0.41	0.34	0.16	0.27	0.16	0.25
Sulfur	0.08	0.11	0.08	0.12	0.16	0.12	0.08	0.12	0.08	0.09
Oxygen	35.63	16.35	35.63	12.72	35.81	11.03	36.76	20.84	36.76	8.66
HHV, Btu/lb, dry	7,395	11,680	7,395	13,450	8,390	12,734	7,418	11,213	7,418	12,017
Ash XRFA, wt%										
Silicon	20.91	45.60	20.91	41.96	30.97	44.87	20.53	39.62	20.53	38.69
Aluminum	27.98	36.89	27.98	34.75	21.28	36.55	28.12	32.11	28.12	34.92
Iron	0.52	2.06	0.52	1.97	0.87	1.94	0.60	2.95	0.60	10.17
Titanium	2.50	1.44	2.50	1.28	3.01	1.42	2.54	2.23	2.54	2.85
Phosphorus	0.16	0.90	0.16	0.83	0.56	0.84	0.16	0.65	0.16	0.55
Calcium	8.01	3.54	8.01	4.65	10.93	3.68	7.80	4.58	7.80	3.43
Magnesium	0.86	2.60	0.86	2.55	1.48	2.58	0.84	2.04	0.84	2.50
Sodium	36.39	5.59	36.39	9.75	26.77	6.62	37.33	13.58	37.33	5.35
Potassium	0.55	0.67	0.55	0.75	0.59	0.68	0.54	0.75	0.54	0.59
Sulfur	2.12	0.71	2.12	1.51	3.55	0.81	1.52	1.49	1.52	0.95
Ash Fusion, °F										
Initial	2556	2271	2556	2115	2125	2268	2557	2188	2557	2201
Softening	2673	2419	2673	2232	2212	2388	2719	2215	2719	2316
Hemispherical	2687	2712	2687	2278	2239	2746	2727	2259	2727	2453
Fluid	2716	2786	2716	2568	2251	2775	2745	2372	2745	2586
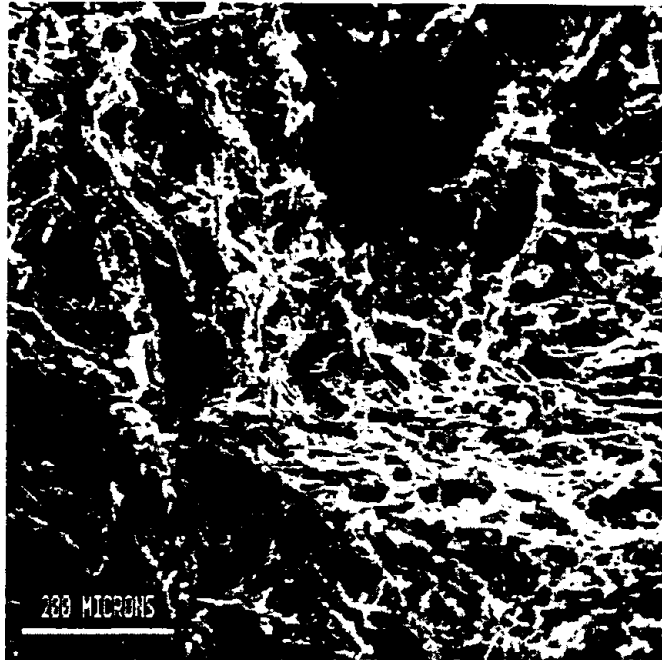
Figure 6. SEM photomicrograph (200 microns) of feed RDF particles.
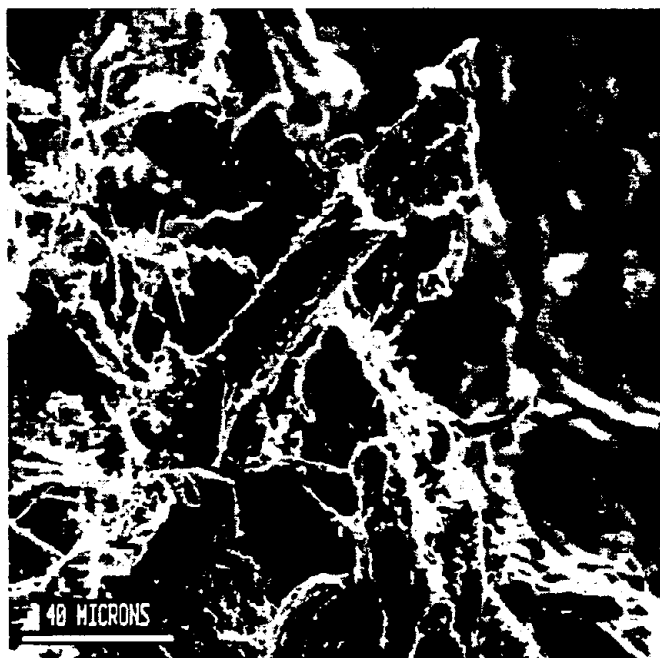
Figure 7. SEM photomicrograph (40 microns) of fed RDF particles.

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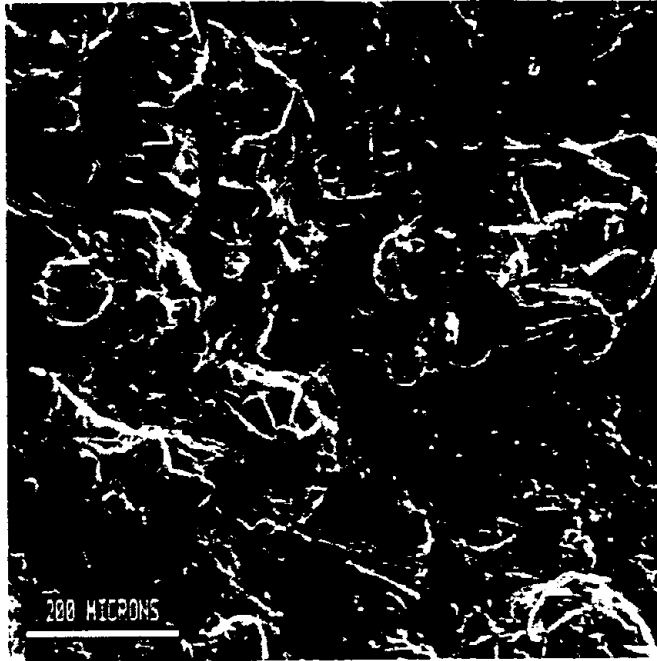
Figure 8. SEM photomicrograph (200 microns) of carbonized RDF particles.
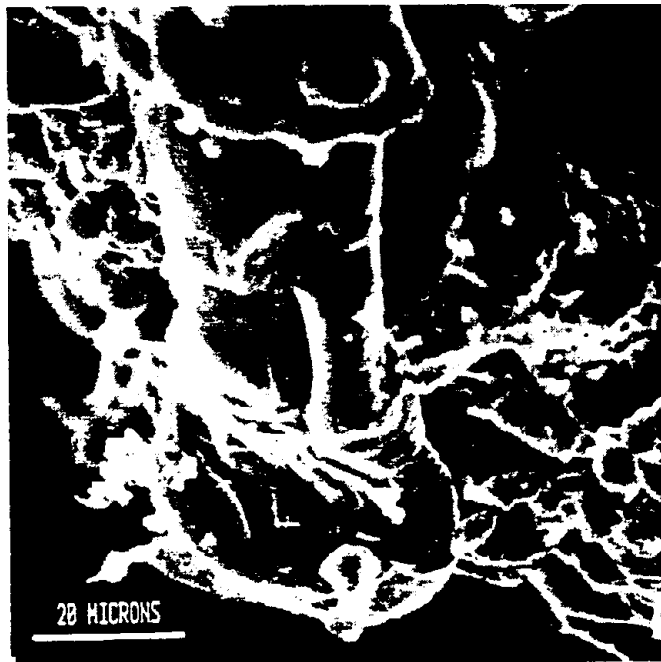
Figure 9. SEM photomicrograph (20 microns) of carbonized RDF particles.

TABLE 9

Composition of Carbonization Gas, Continuous Experiment

	Teat No. 1	Test No. 2
Gas Component, mol %, dry		
Carbon Dioxide	89.22	87.46
Hydrogen	6.64	4.94
Carbon Monoxide	2.73	6.80
Propylene	0.72	0.36
Isobutylene	0.33	0.19
1-Butene	0.15	0.07
trans-2-Butene	0.07	0.04
cis-2-Butene	0.05	0.04
Helium	0.05	0.09
Ethylene	0.04	> 0.00
Methane	> 0.00	> 0.00
Calculated Btu/scf, dry		
Saturated	41.3	43.2
Dry	42.1	44.0
Calculated Specific Gravity	1.305	1.349
Calculated Avg. Molecular Wt.	37.73	38.97
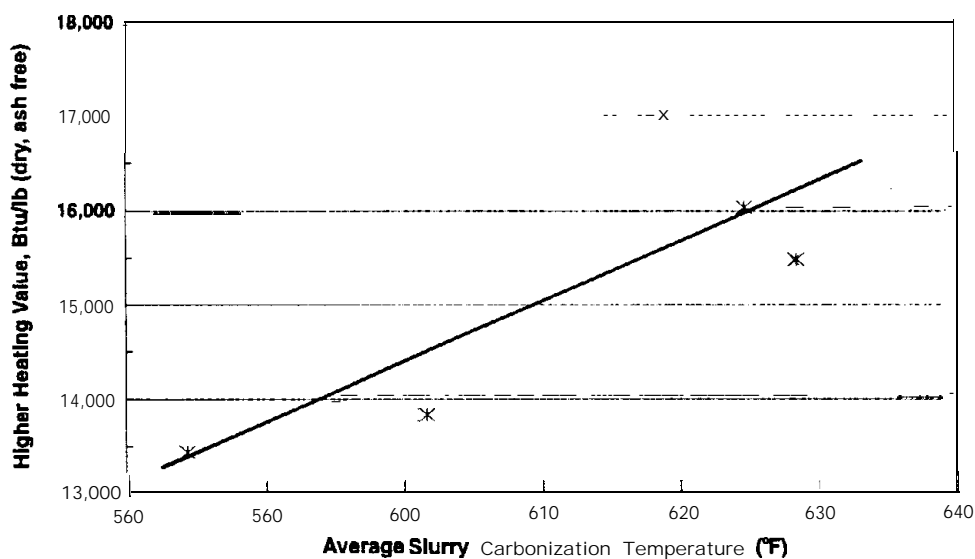
Figure 10. HHV versus average slurry carbonization temperature, continuous experiment.

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weight percentage of **carbonized** RDF can be increased dramatically in a carbonized RDF and water mixture). As can be seen in Figure 11, viscosity of the feed RDF slurry was approximately 500 **cP** (at 100 Hz decreasing) with a 9.1 **wt%** total solids. However, **viscosity** of carbonized RDF slurry for Test #3 at a comparable viscosity was 49.2 wt% total solids, a 440% improvement. A viscosity of 500 **cP** was considered **pumpable** for EERC's pilot plant combustion facility, but the required viscosity will vary according to the combustion facility.

Rheology of the carbonized RDF slurry varied with each test condition. Test #4 yielded the lowest and Test #3 the highest wt% total solids of the five experimental tests. As with the heating value of carbonized product, a higher maximum carbonization temperature produced a carbonized RDF slurry with a higher wt% total solids. Feed particle size, feed RDF wt%, or grams NaOH per gram feed RDF did not produce a measurable effect on the **rheology** of the carbonized RDF. Also, average reactor **residence** time did not appear to produce a measurable effect on the rheology.

Additional variation in rheology at similar maximum slurry carbonization temperatures can be partially accounted for by differences in the particle-size distribution and average particle size of carbonized RDF. Rheology of the carbonized RDF slurry can be improved by reducing particle size of carbonized product. Samples of carbonized RDF slurry were sheared in a laboratory blender and their rheology reanalyzed. As can be seen in Figure 12, the **wt%** total solids for Test #3 were increased from 49.2 % to approximately 51.8%, a 5% improvement at a viscosity of 500 cP. For Test #2, shearing produced a 3% improvement in the wt% total solids loading of the carbonized RDF slurry. Figure 13 summarizes the particle-size distribution of **unsheared** and sheared carbonized RDF slurry for Test #2.
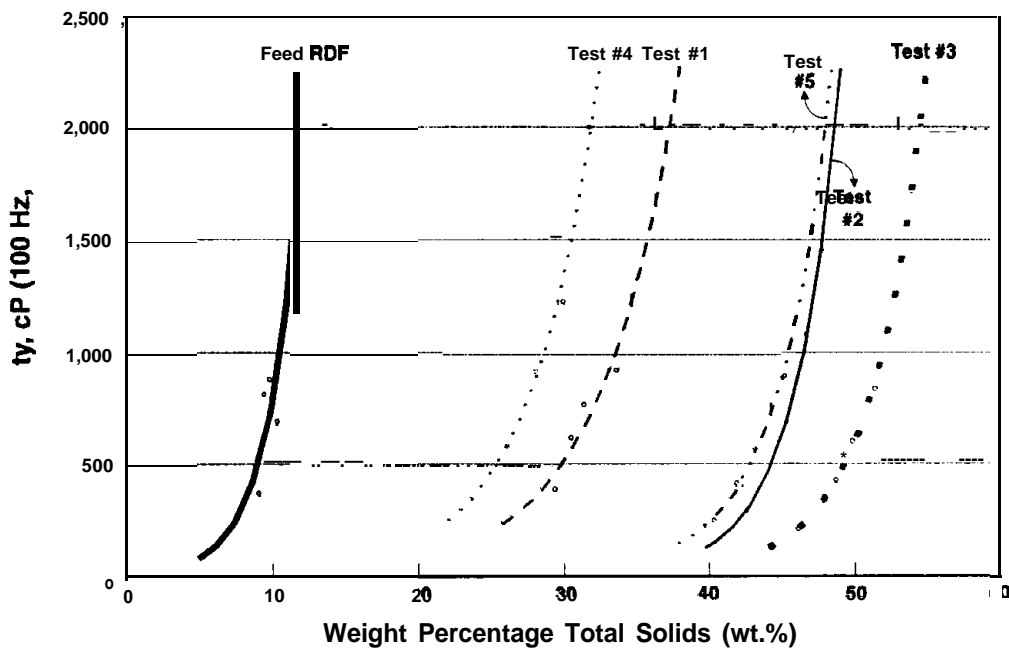

Figure 11. Rheology comparison of feed and carbonized RDF slurry, continuous experiment.
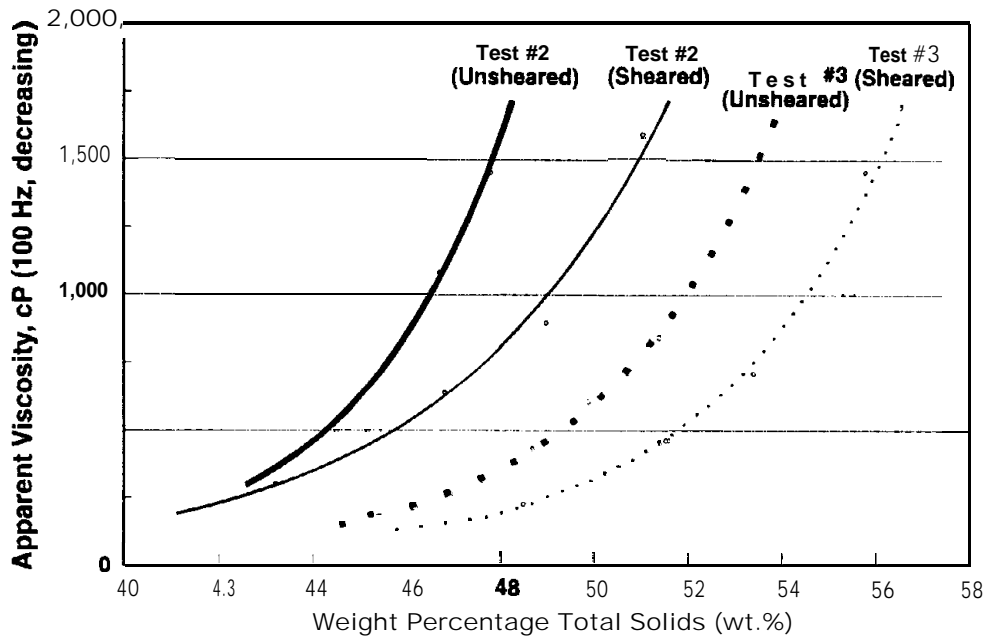
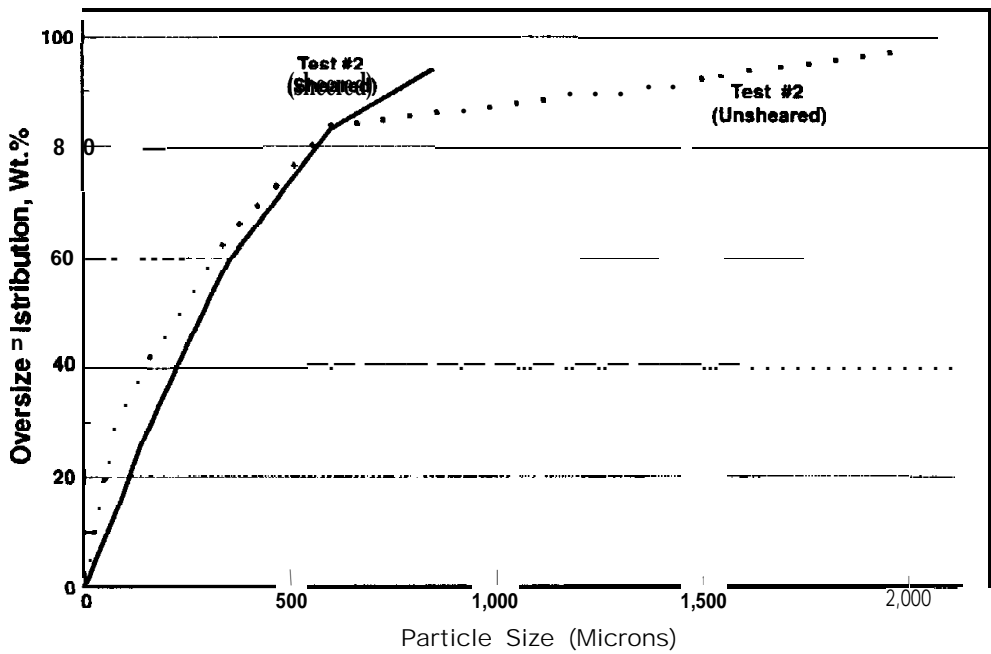Figure 12. Rheology comparison of unsheared and sheared carbonized RDF slurry, continuous experiment.

Figure 13. Particle-size comparison of unsheared and sheared carbonized RDF, continuous experiment.

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Based upon Table 6 and Figure 14, the EnerTech-EERC's slurry carbonization process is capable of producing a slurry fuel with a heating value up to approximately 6,600 Btu/lb (as-received basis) at 500 cP. Figure 14 summarizes HHV of the sheared, carbonized slurry fuel for each test condition and compares it to feed RDF slurry. As can be seen in Figure 14, slurry carbonization improves heating value of feed RDF slurry over 850%.

As discussed earlier, PVC plastic decomposes during slurry carbonization to form hydrochloric acid in the carbonized RDF slurry. NaOH was added to the feed RDF slurry to neutralize extracted hydrochloric acid and potentially enhance decomposition of the PVC. Table 10 summarizes chlorine concentrations of the feed and carbonized RDF, tiltrate, and condensate for each test condition (please note that a condensate sample was not available for analysis from Test #5). Based upon mass balance flow rates in Table 5, feed RDF chlorine concentration was reduced from approximately 0.118 lb/hr (3.00 lb/1000 dry lb) to as low as 0.007 mg/hr (0.50 lb/1000 dry lb) in the carbonized RDF of Test #5, or over 94 %. Please note mass balance closure for chlorine was approximately 126%-191 % because of measurement variation, and any conclusions should be interpreted cautiously. Mass balance closure was calculated by (Cl filtrate + Cl condensate + Cl carbonized Solids) *100/Cl feed RDF.

Chlorine extraction appears to be dependent on the maximum carbonization temperature. As can be seen from Table 10, higher carbonization temperatures produced a higher percentage extraction of chlorine at similar percentage alkali added to the feed RDF slurry. In addition, chlorine extraction appears to be dependent on the percentage addition of NaOH to the feed RDF slurry. Addition of a higher percentage of NaOH produced a higher extraction of chlorine at similar carbonization temperatures. The acidic pH of the filtrate indicates that PVC decomposition equilibrium may be shifted to higher extraction of chlorine utilizing an alkaline pH.
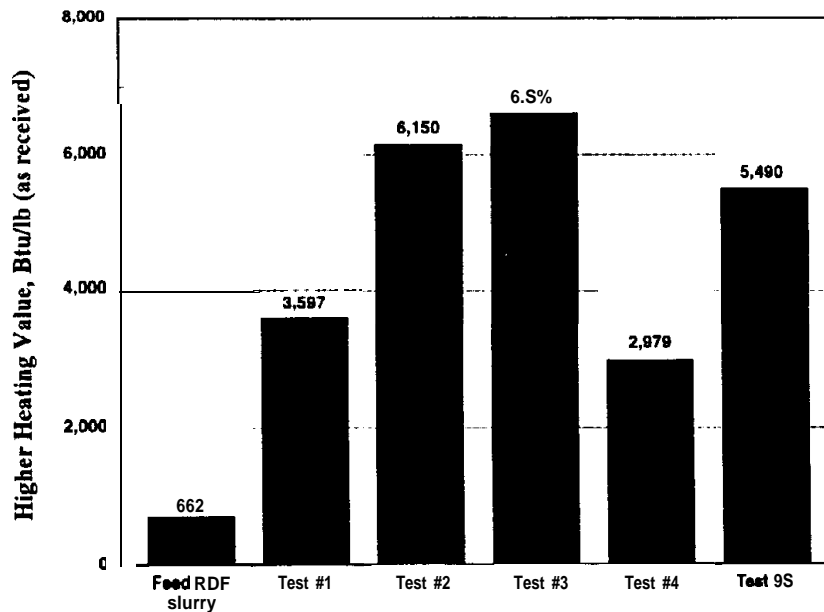

Figure 14. HHV of the feed and sheared carbonized RDF slurry fuels, continuous experiment.

TABLE 10

pH and Chlorine Concentrations of Filtrate, Condensate, and Carbonized RDF,
Continuous Experiment

	Feed RDF	Test No. 1	Test No. 2	Test No. 3	Test No. 4	Test No. 5
Process Temperature, "F	—	600	622	626	585	616
Cl Solids (lb/1000 dry lb)	3.00	0.68	0.75	1.40	1.52	0.50
Cl Filtrate (lb/1000 gal)	—	4.59	6.59	6.76	5.76	5.93
Filtrate pH	11.98	4.61	4.85	4.40	4.81	5.31
Cl Condensate (lb/1000 gal)	—	<0.008	<0.008	0.021	<0.008	—
Condensate pH	—	3.92	2.86	3.43	3.87	—
Calc. Cl Extraction	—	92.3%	91.5%	84.1%	82.7%	94.3%
Mass Balance Closure	—	126%	179%	191 %	166%	159%

As previously discussed, batch autoclave experiments indicated a higher extraction of chlorine, approximately 98% under similar conditions. The autoclave experiments were performed with an average residence time of approximately 15 minutes verses the average reactor residence time of 7-9 minutes in the pilot plant run. The average reactor residence time may be a critical variable in the decomposition of PVC during slurry carbonization, assuming analytical accuracy and precision does not account for differences in measured chlorine extraction, but more research is required to confirm this.

Table 11 summarizes trace metal balances for Test #2 based upon the mass flow rates of Table 2. Because of the heterogeneous character of feed RDF, mass balance closure was low, even for duplicate samples. In addition, actual mass flow rates varied with each test condition,

TABLE 11

Trace Metal Balance for Slurry Carbonization Pilot Plant Test #2

	Feed RDF	Test #2			
	Solids, mg/hr	Cake, mg/hr	Filtrate, mg/hr	Condensate, mg/hr	Difference or Gas, mg/hr
Hg	5.34	1.40	0.23	0.03	3.68
Sb	40.04	33.32	<60.00	<60.03	(113.28)
As	15.84	6.02	0.66	1.93	7.23
Cd	22.78	28.28	<0.60	2.09	(8.19)
Pb	529.48	643.25	1.44	12.06	(127.27)
Ni	59.80	133.50	<6.00	5.17	(84.87)
co	29.37	31.80	<0.60	2.62	(5.65)
Cr	245.61	382.31	<6.00	<5.00	(147.70)
Cu	1509.23	486.69	<6.00	<5.00	1011.54
Mn	1117.69	685.73	<6.00	152.04	273.92
Zn	2909.90	2609.41	44.35	211.84	44.30
Se	10.14	20.63	0.48	1.42	(12.39)
Be	<0.20	1.34	<0.20	0.20	(1.54)

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contributing to poor mass balance closure. However, as art initial analysis, data in Table 11 suggests carbonization gas may contain mercury (Hg) and arsenic (As), and should be further characterized in future research. Table 11 also indicates that the majority of cadmium (Cd), lead (Pb), and cobalt (Co) remained with the carbonized cake, while a notable proportion of feed manganese (Mn) and zinc (Zn) were solubilized in the tiltrate and condensate. Further analysis and more sophisticated sampling and instrumentation are required before any initial conclusions cart be drawn for antimony (Sb), nickel (Ni), chromium (Cr), copper (Cu), selenium (Se), or beryllium (Be). Note that the feed RDF for these experiments was not prepared by wet RR which is expected to remove a higher percentage of the heavy metals than a typical dry RR.

5.3 **Pilot-Scale Combustion of the Carbonized RDF Slurry Fuel**

As discussed, the dilute carbonized RDF slurry produced from pilot-scale carbonization experiments was blended and dewatered in a single filter-press run. Since a reduction in particle size had previously been shown to improve rheology, the filter-press cake was ground in a pilot-scale attritor and its rheology determined. As can be seen in Figure 15, solids loading of this attrited fuel was lower than samples from the filter-press cake. Differences in rheology before and after attriting are not well understood. The attritor is suspected to have produced a small amount of very tine particles that formed a gelatinous structure and adversely affected the viscosity of the slurry. In addition, the attritor did not effectively reduce the size of larger particles, producing a carbonized RDF slurry fuel with an average particle size of 356 microns, approximately 60% larger than the average particle size of the sheared filter cake sample. Because of the size of the filter-press cake, it could not have been cost effectively sheared in the laboratory blender. If additional research funds are awarded, a pilot-scale shear unit will be rented. Also, please note that the rheology of samples from the filter-press cake was lower than that from Test #3, since the filter cake was a blend of all five carbonization tests (including Test #4 which had the worst rheology).
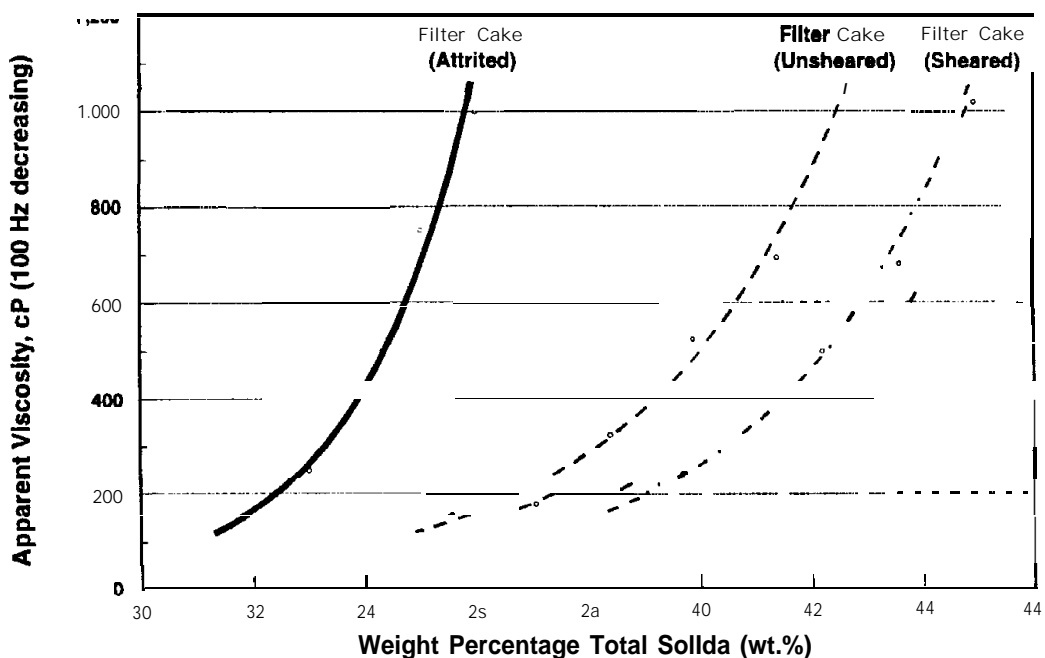

Figure 15. Rheology of the blended carbonized RDF slurry fuel.

Since viscosity was higher and, hence, heating value lower, the carbonized RDF slurry fuel was divided into three samples for the combustion test. First used was the attrited slurry fuel without any additives. During the combustion test with this first fuel, the slurry fuel pump was at its maximum output, and the heat input to the combustor was limited. This resulted in a final steady-state combustion temperature of approximately 1600°F. In order to increase heat input to the combustor, a second sample of the attrited slurry fuel was mixed with 1.5 wt% ammonium lignosulfonate (ALS) viscosity reducing agent, so that the rate of charging the carbonized slurry fuel could be increased. This resulted in a steady-state combustion temperature of approximately 1800°F. The third sample of the attrited fuel was mixed with 1.5 wt% ALS and 7.5 wt% No. 6 diesel fuel to further increase heat input to the combustor. This resulted in a steady-state combustion temperature of approximately 2000°F. Table 12 summarizes fuel properties of the three slurry fuel samples. Please note that chlorine content of the slurry fuels were lower that the samples analyzed during pilot plant production of the carbonized product, possibly since the carbonized cake was washed during the filter-press run.

Table 13 summarizes average operating conditions of each combustion test. These conditions represent the averages over the entire test period, not just the steady-state conditions. The averages were used since samples were collected over the entire routine, and not just from steady-state operation. As can be seen in Table 13, combustion air was split approximately 11%, 83%, and 6% among primary atomizing air, secondary swirl air, and tertiary overfire air, respectively, for each combustion test. Air splits were adjusted manually and were based upon experience with combustion of slurry fuels. Secondary and tertiary air streams were preheated in an electric preheater. Excess air averaged between 15% and 60% and was manually adjusted based upon carbon monoxide content in the flue gas. For the slurry fuel without additives, excess air initially was set high, as a conservative start, and was adjusted to approximately 35% (resulting in an average of 61 % excess).

TABLE 12

Fuel Properties of the Three Combustion Slurry Fuels

	Slurry Fuel WI no additives	Slurry Fuel WI 1.5% ALS	Slurry Fuel w/ 1.5% ALS and 7.5% Diesel
Ultimate, wt%, dry			
Carbon	62.01	62.53	68.25
Hydrogen	6.54	7.17	8.09
Nitrogen	0.56	0.32	0.28
Sulfur	0.24	0.29	0.34
Oxygen	14.99	14.70	9.18
Ash	15.66	14.98	13.85
Chlorine, mg/g	0.46	0.46	0.36
Rheology			
Viscosity	750	ND'	ND
Wt % Solids	34.6	35.3	35.3
Higher Heating Value, Btu/lb	12,271	12,876	15,216
Dry Slurry	4,240	4,545	5,371

[1] Not determined.

TABLE 13

Average Operating Conditions of EERC's 650,000-Btu/hr Combustion Test Facility

	Slurry Fuel no additives	Slurry Fuel 1.5% ALS	Slurry Fuel 1.5% ALS and 7.5% Diesel
Slurry Feed Rate, lb/hr	127.4	127.4	127.4
Combustion Air			
Primary, scfm	13.2	9.3	14.1
Secondary, scfm	89.6	86.8	96.5
Tertiary, scfm	6.8	7.2	5.3
Total Excess, %	60.6	40.3	15.0
Combustion Temp; "F			
Primary Air	113.7	109.9	120.5
Secondary Air	609.9	640.2	693.7
Combustor	1719.3	1716.3	1970.2
Flue Gas Exit	270.7	298.5	302.4
Length of Test, hr	1.23	1.43	1.87

If additional research funds are awarded, excess air initially would be set no higher than 35%. Since higher combustion temperatures were achieved with the slurry fuels with ALS and the ALS-diesel mix, carbon monoxide emissions were lower, and excess air requirements were adjusted to 15%, which are more typical.

Prior to the test, the combustor was heated by tiring natural gas and then switching to the slurry fuel. As previously discussed, the combustion temperature of the carbonized slurry fuel with no additives dropped from a preheated temperature of approximately 2000°F to slightly above 1600°F because of pumping limitations of the low solids loading fuel. If the expected solids loading had been achieved, as previously discussed, the pump would have been more than adequate. This first combustion test resulted in a skewed average combustion temperature of 1719°F, but the temperature actually stabilized at approximately 161O°F. Upon switching to the slurry fuel with 1.5 % ALS, the combustion temperature rose and stabilized at approximately 1780°F, resulting in an average combustion temperature of 1716°F. With all three slurry fuels, the feed pump was at its maximum output.

As can be seen in Table 14, emissions from combustion of all three slurry fuels were exceptionally low, even when compared to the proposed New Source Performance Standards (NSPS, published September 20, 1994, in the Federal Register). Carbon monoxide (CO) emissions were 90%-65 % lower than the lowest NSPS regulation limit, but only 15%-60% excess air was utilized. Carbon burnout also was excellent at 99.9%. Carbon burnout was averaged across all three combustion tests and was based upon the carbon content of the ESP ash. Nitrogen oxide (NO_x) emissions also were up to 55% lower than the NSPS regulations, without selective noncatalytic or catalytic reduction. Low NO_x emissions were achieved through improved uniformity of the slurry

TABLE 14

Average Flue Gas Emissions from Combustion of the Carbonized RDF Slurry Fuel

	Slurry Fuel no additives	Slurry Fuel 1.5% ALS	Slurry Fuel 1.5 % ALS and 7.5% Diesel	NSPS
Flue Gas Emissions				
CO_2, ppmv	11.3	11.3	14.1	---
CO, ppmv	16.3	17.0	5.3	50-150
NO_x, ppmv	82.2	99.7	211.1	180
HC1, ppmv	17	17	17	25
Hg, mg/dscm	0.003	0.003	0.003	0.080
SO_2, ppmv	40.4	121.3	158.4	30
Particulate Matter, mg/dscm	471	471	471	15
Dioxins/Furans, ng/dscm	ND[2]	ND	ND	13
Cd, mg/dscm	ND	ND	ND	0.010
Pb, mg/dscm	ND	ND	ND	0.100
Carbon Burnout, %	99.9	99.9	99.9	---

' Flue gas emissions are corrected to 7 % O_2, dry.
[2] Not determined.

fuel and km-rich combustion air staging. As expected, NO_x emissions were proportional to combustion temperature and were higher than expected for the slurry fuel with diesel because of its higher flame temperature. In future combustion tests, NO_x emissions will be lower for carbonized RDF slurry fuels when compared to slurry fuels blended with diesel because of lower flame temperatures at similar combustion temperatures. In addition, NO_x emissions possibly could be lowered further by blending the slurry fuel with a small amount of NH_3, or obviously by injecting NH_3 directly into the flue gases.

Since slurry carbonization extracted over 85% of the RDF chlorine, HC1 emissions, determined by EPA Reference Method 26, were 32% lower than the NSPS regulations without acid gas scrubbing. HC1 emissions were sampled and averaged across all three combustion tests. EERC and EnerTech are aware of the concern with the acute toxicity of dioxins and furans. It was impractical to measure these toxins during the subject combustion test program because of the short duration of experimental combustion runs, expense of those tests, and budget limitations. If additional research funds are awarded, EERC and EnerTech plan to characterize these pollutants using EPA Reference Method 23.

Mercury emissions were measured at 0.003 mg/dscm by EPA Reference Method 29 and were 95% lower than the NSPS regulation limit. Cadmium and lead were not determined and will be characterized in a follow-up research project. For the slurry fuel with no additives, sulfur dioxide emissions were comparable to the NSPS regulation limit but were higher for the slurry fuel with ALS and ALS-diesel mix. ALS is a sulfated viscosity agent and diesel contains approximately 0.6 wt% sulfur. As can be seen from Table 12, sulfur contents of the slurry fuel with ALS and ALS-diesel

were higher than the slurry fuel without additives. Blending the carbonized RDF slurry fuel with ALS and diesel was done only for this combustion test because of the low solids loading slurry fuel, and feed pump limitations. However, SO_2 emissions could be reduced, if necessary, by blending the slurry fuel with a small quantity of limestone or lime or injecting limestone or lime into the flue gases.

For these combustion tests, particulate matter (PM) was the only emission to exceed NSPS limits. During the combustion test, flue gases are split between an ESP and cyclone. Because of an improper valve setting, flue gas volumes through the ESP, and hence velocities, were higher than the design specification. This condition was not realized until the end of the third combustion test, when the valve for the orifice plate upstream of the ESP was properly adjusted. This resulted in an ash collection efficiency of 26.3% by weight, averaged across all three combustion tests. However, as can be seen by Figure 16, the resistivity profile of the fly ash indicates an excellent potential for efficient collection by an ESP. A commercial ESP or baghouse would have collection efficiencies higher than those obtained in this combustion test. Note that the quantity of combustion ash associated with the carbonized slurry fuel is substantially lower than that from a mass bum facility.

Table 15 summarizes the ash balance and composition for all three combustion tests. In general, ash did not accumulate abnormally in any section of the test facility and had a very low tendency to adhere or stick to boiler surfaces, as indicated by the mass of ash on the horizontal slag probe and high-temperature fouling probe bank. An x-ray powder diffraction analysis of the high-temperature fouling probe ash indicated a large amorphous phase, with decreasing minor phases of rutile, anatase, quartz, plagioclase, melilite, and mullite, respectively.
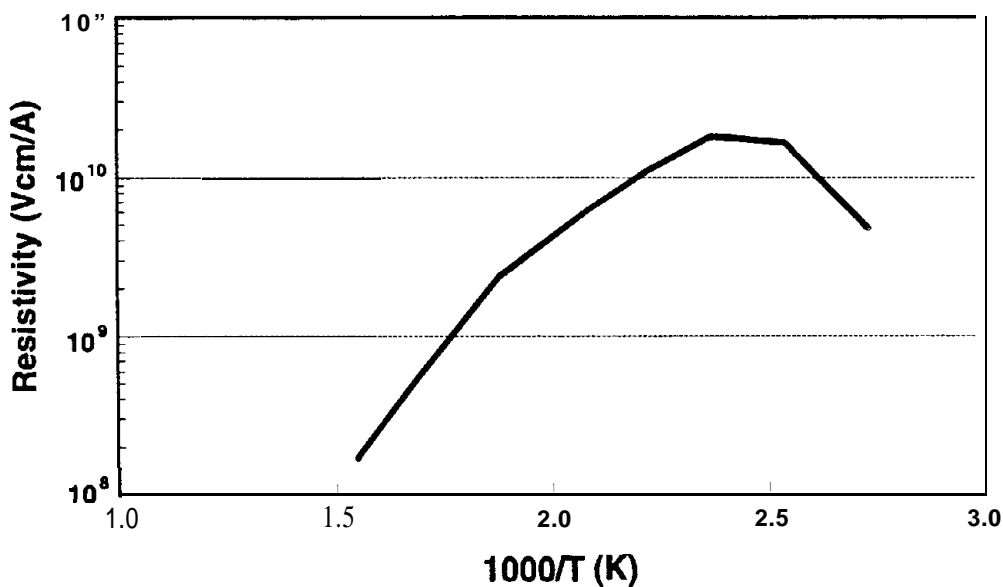

Figure 16. Effect of temperature on resistivity of combustion fly ash.

TABLE 15

Ash Mass Balance and Composition For combustion Tests

	Slurry Fuel Ash	Combustor Ash	Slag Probe Ash	Duct Ash	High Temp Probe Ash	Heat Exg. Ash	Cyclone Ash	ESP Ash	Fly Ash
Total Mass, lb	33.76	3.46	<0.01	1.18	0.02	4.00	0.21	6.54	18.35
Ash XRFA, wt%									
Silicon	41.25	40.36	42.09	41.57	42.23	41.71	41.64	42.26	---
Aluminum	35.59	36.40	34.93	33.33	36.22	35.74	36.17	35.77	---
Iron	3.19	4.19	4.32	3.80	3.46	4.41	4.00	3.50	---
Titanium	8.96	8.77	8.55	10.72	8.08	7.88	7.57	8.55	---
Phosphorus	0.50	0.50	0.48	0.51	0.54	0.49	0.56	0.52	---
Calcium	1.94	2.49	2.35	3.09	1.73	2.00	2.40	2.02	---
Magnesium	3.85	3.95	3.79	3.80	3.86	4.03	3.90	3.99	---
Sodium	3.32	2.75	2.64	2.37	2.73	2.39	2.37	2.48	---
Potassium	0.38	0.44	0.44	0.47	0.42	0.40	0.42	0.41	---
Sulfur	1.02	0.16	0.40	0.34	0.73	0.94	0.98	0.49	---
Ultimate Analysis, wt%									
Carbon	---	0.19	ND[1]	0.41	ND	0.88	1.27	0.46	---
Hydrogen	---	0.06	ND	0.01	ND	0.16	0.21	0.06	---
Nitrogen	---	0.03	ND	0.01	ND	0.05	0.01	0.04	---

[1] Not determined.

Table 16 summarizes the trace metal balance around the ESP and is based upon the total ash from all three combustion tests. In Table 16, % balance closure was calculated by (fly ash exit ESP + collected ESP ash) * 100/ fly ash enter ESP; and % removal efficiency by collected ESP ash/ fly ash enter ESP. As can be seen in Table 16, mass balance closure was low for arsenic, chlorine, mercury, manganese, nickel, and selenium. Removal efficiencies were lower than average for cadmium, copper, mercury, lead, and zinc. Low removal efficiencies for cadmium, mercury, and lead may be due to their higher vapor pressures. Removal efficiency was higher than average for arsenic, beryllium, chromium, nickel, antimony, and selenium. However, these results may be affected by the low mass balance closure and should be interpreted cautiously.

One representative sample of ash, collected by the ESP, was analyzed for leaching characteristics. Three leaching tests were performed: EPA's toxicity characteristic leaching procedure (TCLP), synthetic groundwater leaching procedure (SGLP) for 18 hours, and SGLP for 30 days. A SGLP for 60 days also is being performed, but results were not available at the time of this report. Synthetic groundwater was prepared to resemble that for Grand Forks, North Dakota, which is unique because of its alkaline pH. Table 17 summarizes the results from each leaching test and compares it to the Resource Conservation and Recovery Act (RCRA) maximum concentration limit (MCL) regulation. As can be seen in Table 17, no RCRA metal exceeds the MCL for the TCLP or SGLP. This combustion ash would be classified as nonhazardous and could be disposed of in Subtitle D landfills. Even when compared to primary drinking water standards, which are 100 times lower, only cadmium and chromium exceed the limit. For the SGLP test, no metal exceeded the primary drinking water standards. Higher combustion temperatures should produce an ash with even better leaching characteristics.

TABLE 16

Trace Metal Analysis Results of Collected ESP and Fly Ash'

	Fly Ash Enter ESP	Fly Ash Exit ESP	collected ESP Ash	% Balance Closure	% Removal Efficiency
Element, mg					
As	71.7	64.0	23.1	121.5	32.2
Be	19.0	14.2	5.6	104.2	29.5
Cd	256.2	188.0	59.9	96.8	23.4
c l	7278.7	6962.8	2010.9	123.3	27.6
c o	345.3	258.7	89.9	100.9	26.0
Cr	4491.4	2978.1	1471.1	99.1	32.8
Cu	6240.5	4641.9	1583.8	99.8	25.4
Hg	8.2	6.6	0.4	85.4	4.9
Mn	6319.5	4026.3	1260.6	83.7	19.9
Ni	1647.6	1231.2	679.2	116.0	41.2
Pb	5518.3	4167.7	1257.6	98.3	22.8
Sb	1805.6	1289.4	516.1	100.0	28.6
Se	28.2	29.9	8.6	136.5	30.5
Zn	25165.1	17802.2	5813.4	93.8	23.1

[1] Total ash collection efficiency was 26.3%

TABLE 17

TCLP and SGLP Analysis Results of Combustion Ash

	TCLP	SGLP 18 hrs	SGLP 30 day	RCRA MCL
Element, mg/L				
Ag	ND	ND	ND	5.(K)
As	<0.010	<0.010	<0.010	5.00
Ba	ND[1]	ND	ND	100.00
Be	<0.001	<0.001	<0.001	---
Cd	0.111	<0.005	<0.005	1.00
c l	---	39.1	45.0	…
c o	0.066	<0.010	<0.010	---
Cr	0.241	0.070	<0.050	5.00
Cu	0.102	c 0.050	<0.050	---
Hg	<0.001	<0.001	<0.001	0.20
Mn	1.610	<0.050	<0.050	---
Ni	1.400	<0.050	<0.050	---
Pb	0.028	<0.010	<0.010	5.00
Sb	0.397	0.344	0.712	---
Se	0.017	0.037	0.083	1.00
Zn	2.680	<0.050	<0.050	---

[1] Not determined.

6.0 SUMMARY AND CONCLUSIONS

Carbonized RDF slurry fuels were produced with the EERC'S 7.5-tpd pilot plant facility. Process temperatures were varied over 585 °–626°F in optimization tests to determine the effect of temperature on slurry quality. During operation of the pilot plant, samples of the feed RDF slurry, carbonization gas, condensate, carbonized solids, and filtrate were taken and analyzed.

Pilot-scale slurry carbonization experiments with RDF produced a homogeneous pumpable slurry fuel with a HHV of 3,000-6,600 Btu/lb (as-received basis), at a viscosity of 500 cP, at 100 Hz decreasing, and ambient temperature. Greater-heating-value slurry fuels were produced at higher slurry carbonization temperatures. During slurry carbonization, PVC plastics in the feed RDF also decompose to form hydrochloric acid and salts. Pilot-scale slurry carbonization experiments extracted 82%-94 % of the feed RDF chlorine content as chloride salts. Higher carbonization temperatures and higher alkali additions to the feed slurry produced a higher chlorine extraction.

The carbonized slurry fuel was combusted in a 650,000-Btu/hr atmospheric pulverized-coal boiler simulator. From a storage tank, the carbonized RDF slurry was pumped through the burner gun to the atomizer, where it was mixed with atomizing air. Heated primary air carried the atomized

slurry out of the burner gun, while heated secondary air was introduced in an annular section surrounding the burner gun. Heated tertiary air was added through two tangential ports located about 12 inches above the burner gun. The combustion flue gases were **analyzed** on line for major pollutants, and **extractive samples** were taken for analysis of trace pollutants. In addition, **samples** of the combustion ash were taken and analyzed.

During the combustion test of the carbonized RDF slurry fuel, three combustion temperatures were investigated (1600°F, **1800°F,** and 2000°F). Excess air averaged 15%-61%, depending on the combustion temperature, and was split approximately 11%, 83%, and 6% among primary and atomizing air, secondary swirl air, and tertiary overtire air. Percentages of excess air were adjusted manually based upon levels of carbon monoxide in the flue gases. As expected, higher combustion temperatures required less excess air to produce excellent combustion performance. In future combustion tests, excess air initially would be set no higher than 35%.

Compared to proposed NSPS, CO emissions were 65 %-90% lower at 5-17 ppmv at 7% O_2 dry, with carbon burnout exceeding 99.9 %. NO$_{\_}$emissions also were up to 55% lower than the NSPS at 82 ppmv without selective **noncatalytic** or catalytic reduction. Since **slurry carbonization** extracts chlorine from the RDF, **HCl** emissions were 17 ppmv, or 32% lower than the NSPS, without any acid gas **scrubbing.** Mercury emissions also were analyzed at 0.003 **mg/dscm,** or 96% lower than the NSPS. Cadmium, lead, and **dioxin/furan** emissions were not characterized during these combustion tests. Flue gas emissions from the combustion of the carbonized RDF slurry **fuel** were exceptional. Because of a limited quantity of fuel, ESP performance was not optimized. However, fly ash resistivity of the particulate collected in the ESP indicated that this fly ash would be **easily** collected in an adequately sized precipitator. Deposits collected on fouling probes in the furnace, proper, and simulated convective pass duct indicated a very low fouling potential for the carbonized RDF slurry. Deposits were present as a dusty coating on the probea and were only lightly attached to these surfaces.

Three leaching tests were performed with a representative sample of the combustion ash: EPA's TCLP, SGLP for 18 hours, and SGLP for 30 days. Synthetic groundwater was prepared to resemble groundwater for Grand Forks, North Dakota, which is unique because of its alkaline pH. For each leaching procedure, no RCRA MCL was exceeded, and this combustion ash would be classified as nonhazardous. All SGLP leaching concentrations were lower than those of the TCLP. In general, the ash **exhibited** very low leaching characteristics, and was 89%-99% below the RCRA MCL.