CONF-921034--25

DOE/MC/10637-93/C0171

Mineral Matter Transformations in a Pressurized Drop-Tube Furnace

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DE93 005197

Contractor:

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Contract Number:

DE-FC21-86MC10637

Conference Title:

Ninth Annual Coal-Fueled Heat Engines, Advanced Pressurized Fluidized Bed Combustion (PFBC) and Gas Stream Cleanup Systems Contractors Review Meeting

Conference Location: Morgantown, West Virginia

Conference Dates:

October 27-29, 1992

Conference Sponsor:

U.S. Department of Energy Morgantown Energy Technology Center

Received by OSTI DEC 31 1992

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Mineral Matter Transformations in a Pressurized Drop-Tube Furnace

CONTRACT INFORMATION

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Schedule and Milestones		FY	'92 P	rogra	am S	chedu	ıle						
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Baseline LRC Fuel Testing							_						
Ash Transformations of Beneficial LRC									<u></u>				
Additive Testing for Alkali Control			. •										
Final Report													

OBJECTIVES

Under Department of Energy (DOE) sponsorship, coal and coal-water fuels (CWF) have been investigated as fuels for gas turbine engines for several years, but major technical problems still inhibit commercialization of direct coal-fueled gas turbines. These problems include 1) deposition on the pressure and suction sides of the turbine blades which reduces the gas flow area and turbine efficiency; 2) unacceptable coal burnout, given the short residence time inherent with gas turbine engines; 3) corrosion of turbine blades by condensed alkali sulfates; 4) erosion of turbine blades and other components by ash particles entrained in the products of combustion; and 5) the control of NO_x , SO_2 , and particulate emissions. The release of certain mineral matter species found in both raw and beneficiated coals can lead to ash deposition on surfaces, regardless of the ash content of the fuel. This deposition can lead to corrosion and metal loss of critical turbine components and, ultimately, to derating, unavailability, or catastrophic failure of the power generation system. Alkali metals and sulfur, existing as impurities in coal, have been identified as key components in the initiation of deposition and the onset of corrosion.

The overall objective of this research is to continue to expand the database on the effects of low-rank coal's (LRC) unique properties on its combustion behavior in pressurized combustion systems such as gas turbine engines. Research will be directed toward understanding the properties of LRC fuels which affect ignition and burn times, combustion efficiency, vaporization and deposition of inorganics, and the erosion of critical gas turbine components.

BACKGROUND INFORMATION

To meet the objectives of the program, a pressurized combustion vessel was built to allow the operating parameters of a direct-fired gas turbine combustor to be simulated. One goal in building this equipment was to design the gas turbine simulator as small as possible to reduce the quantity of test fuel needed, while not undersizing the combustor such that wall effects had a significant effect on the measured combustion performance. Based on computer modeling, a rich-lean, two-stage, nonslagging combustor was constructed to simulate a directfired gas turbine. This design was selected to maximize the information that could be obtained on the impact of low-rank coal's unique properties on the gas turbine combustor, its turbomachinery, and the required hot-gas cleanup devices (such as high-temperature/highpressure [HTHP] cyclones).

Seventeen successful combustion tests using coal-water fuels were completed. These tests included seven tests with a commercially available Otisca Industries-produced, Taggart seam bituminous fuel and five tests each with physically and chemically cleaned Beulah-Zap lignite and a chemically cleaned Kemmerer subbituminous fuel. LRC-fueled heat engine testing conducted at the Energy and Environmental Research Center (EERC) has indicated that LRC fuels perform very well in short residence time heat engine combustion systems. Analyses of the emission and fly ash samples highlighted the superior burnout experienced by the LRC fuels as compared to the bituminous fuel even under a longer residence time profile for the bituminous fuel. The LRC fly ash shows a decrease in particle size as compared to the starting fuel, while the bituminous fuel showed an increase in particle size as compared to the starting fuel. These particle-size analyses provide some evidence of low-rank coal's nonagglomerating properties as compared to bituminous fuels.

Statistical analysis of the carbon burnout data from a series of parametric combustion tests generated simple models to predict the carbon burnout achievable under a given range of operating conditions. These models indicate that fuel type has a significant effect on the measured carbon burnout. The LRC fuels have high carbon burnouts, 97.5% to 98.7%, and appear to be relatively unaffected by other operating parameters; however, the bituminous fuel was significantly affected by combustion air temperature, atomizing air-to-fuel ratio, and fuel-firing rate. In this model, bituminous fuel carbon burnouts comparable to those of the LRC fuels can be achieved, but only under optimum conditions. As indicated by material balances, the low-rank slurries had significantly larger deposits than the Otisca slurry, primary due to its high ash content and lower ash fusion temperatures.

GM Allison Gas Turbine Division (1) and GE Transportation Systems (2) have also conducted heat engine testing with LRC coalwater fuels with great success. Carbon burnout in these systems was as high or higher than bituminous fuels in the same systems despite having a significantly larger particle size.

PROJECT DESCRIPTION

The emergence of advanced coal combustion technologies such as coal-fired gas turbines requires fundamental knowledge of the fuel combustion processes at elevated pressures. Basic combustion kinetics and the fate of coal mineral matter are critical information in the technical feasibility of such systems. To address these issues, a pressurized drop-tube furnace (PDTF) was constructed which is capable of operating under the following conditions:

> Temperature: ambient to 2732°F (1500°C) Pressure: ambient to 300 psia (20.4 atm.) Oxygen: 0 to 20 mol% Gas Flow: 0 to 7.8 scfm (220 L/min) Residence Time: 0 to 5.0 sec

A picture of the pressurized drop-tube furnace is shown in Figure 1. A multipurpose sampling probe with provision for char and fly ash collection or for collecting ash deposits on a cooled substrate. A detailed description of the PDTF system is given in Swanson and others (3).

Three scanning electron microscopy/electron microprobe analysis (SEM/EMPA) techniques: computer-controlled scanning electron microscopy (CCSEM), scanning electron microscopy point count (SEMPC), and automated image analysis (AIA) are presently used in ash behavior in combustion and gasification systems research at the EERC. These techniques permit the study of transformations of inorganic constituents from the initial stages of coal conversion through the transformations that occur during ash deposition and slag formation. Their specific applications include 1) determination of the size, composition, and association of minerals in coals; 2) determination of the size and composition of intermediate ash components and fly ash; 3) determination of the degree of interaction (sintering) in ash deposits; and 4) identification and quantification of the components of ash deposits and slags; this includes liquid-phase composition, reactivity, and crystallinity. Details of the SEM analytical techniques are also given in Swanson and others (3).

RESULTS

Tables 1 and 2 show the analyses of the fuels utilized in the PDTF combustion tests. CCSEM results for these coals are reported elsewhere (3,4), and the four major constituents for each fuel are shown in Figure 2. Chemical fractionation results for the as-received Spring Creek coal, and the hydrothermally treated Spring Creek fuel are given in Tables 3 and 4.

Producing premium fuels from low-rank coal feedstocks involves the integration of coal-



Figure 1. Photograph of the Pressurized Drop-Tube Furnace

	As-Received Spring Creek Coal (SPCRK)	HWD' Spring Creek (AFSPC)	PCA/AC/HWD ² Spring Creek (APSPC)
PDU ³ Test No.	NA ⁴	55	45
Proximate Analyses, mf Volatile Matter Fixed Carbon Ash	43.48 51.7 4.82	42.82 52.58 4.60	39.62 56.21 2.07
Ultimate Analyses, mf Hydrogen Carbon Nitrogen Sulfur Oxygen, diff. Ash	4.75 72.52 0.86 0.41 16.94 4.82	4.66 73.22 0.97 0.40 16.12 4.60	4.51 75.00 1.37 0.35 16.70 2.07
Heating Value, mf, Btu/lb Ash Fusion Temp., °F Reducing Int. Deform. Softening Hemispherical Fluid	12,260 ND' ND ND ND	12,693 ND ND ND ND	12,820 2148 2278 2310 2313
Mean Particle Size, μm Top Size (99% <), μm	54 348	13 100	15 81

Table 1. Proximate and Ultimate Analyses of Fuels Tested

¹ Hot-water dried.

² Physically cleaned/Acid cleaned/Hot-water dried.
³ Process Development Unit.
⁴ Not applicable.
⁵ Not determined.

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Sample:	Raw Spring Creek Coal	HWD Spring Creek	PC/AC/HWD Spring Creek
PDU Test No.	NA	55	45
SiO ₂	29.2	31.0	33.5
Al_2O_3	18.7	21.3	31.9
Fe ₂ O ₃	8.1	9.6	14.7
TiO	2.3	2.0	3.3
P_2O_5	· 1.2	0.6	0.9
CaO	23.0	22.0	10.1
MgO	7.6	7.8	4.3
Na	9.0	5.5	1.0
K ₂ O	0.8	0.2	0.2
Total	99.9	100.0	99.9

Table 2. X-Ray Fluorescence Analysis of LRC Fuels Tested in the Turbine ProgramHigh-Temperature Ash Results (% of ash, SO3-free)

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Figure 2. Major Mineral Species Determined by CCSEM Analyses of Beneficiated Spring Creek fuel.

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	Initial	Removed	Removed	Removed	
	(ppm)	by H ₂ O	by NH₄OAc	by HCl	Remaining
Silicon	4273	0	0	0	100*
Aluminum	3997	3	6	49	42
Iron	2442	0	16	72	12
Titanium	604	0	45	0	55
Phosphorus	315	2	73	22	3
Calcium	6688	0	59	40	0
Magnesium	2024	1	79	17	2
Sodium	3058	34	65	1	1
Potassium	790	65	25	2	8

Table 3. Chemical Fractionation Results of As-received Spring Creek Coal (wt%)

* Results are expressed with silicon loss normalized to zero.

	Initial (ppm)	Removed by H ₂ O	Removed by NH₄OAc	Removed by HCl	Remaining
Silicon	7702	0	0	0	100*
Aluminum	4634	0	0	0	100
Iron	2712	6	4	45	44
Titanium	427	0	3	0	97
Phosphorus	108	0	12	64	24
Calcium	6902	0	30	55	15
Magnesium	2725	0	42	51	7
Sodium	489	6	82	3	9
Potassium	161	0	20	0	80

Table 4. Chemical Fractionation Results of HWD Spring Creek Coal (wt%)

* Results are expressed with silicon loss normalized to zero.

cleaning and drying technologies. The EERC has developed methods to produce clean, energy-dense coal product, suitable for solid or CWF utilization. For this particular study,the deep-cleaned CWF was produced using physical cleaning by dense media separation, acid leaching using 4 wt% NO₃ acid solution, and hydrothermally treating the cleaned coal at 300° C.

The treated coal was then wet-milled to the desired $15-\mu m$ average particle size. Various samples were taken for testing to examine the coal and ash characteristics after each cleaning and/or drying method. In addition to studying these fuels, a sample of the CWF which was used for the General Motors Allison Coal-Fueled Gas Turbine project was also characterized.

Each of the fuels analyzed as part of this project was run as an air-dried sample, not in the slurry form. Future plans will include the integration of a pump system to feed slurry into the test furnace. Details of the CWF preparation procedures, slurry fuel characteristics, and test burn information are given elsewhere (3,4,5).

The fly ash combustion tests using the coals listed in Table 1 were conducted in the PDTF at 1300°C, 120 psia, and with a calculated residence time of 2.5 seconds. These high-pressure tests utilized Cyclones 2 and 5 from a multicyclone set and a final filter to collect the fine aerosols. The multicyclones were calculated to have cut points of 3.0 and 0.45 μ m, respectively. Percent ash of the fly ash was determined using a modified thermogravimetric analysis (TGA) technique. Residence times are calculated based on centerline velocities equal to two times the plug-flow velocities.

Figures 3 and 4 show the major species as determined by SEMPC analyses of the fly ash samples collected in the three size fractions. Figure 3 shows the measured chemical composition while Figure 4 shows the distribution of the same species between the three size fractions. Both the PC/AC/HWD/micronized and the Allison HWD/micronized Spring Creek fuels had lower sodium levels in the final filter fraction than the raw Spring Creek fuel. This is expected since acid cleaning and hot-water drying processes have been shown to reduce the sodium levels of the coal ash. However, Figure 4 shows that for the hydrothermally treated fuel approximately the same percentage of the sodium was collected in the smallest-size fraction as with the asreceived Spring Creek fuel. As shown in Figure 4, acid cleaning of the fuel resulted in a significant decrease in the percentage of the sodium collected in the smallest-size fraction.

Particle size analysis of the three sized fractions was also conducted by SEM. These analyses indicate that the filter cake consists of very fine (<1 μ m) particles while Cyclone 5 consisted of particles in the 1- to 4- μ m size range and Cyclone 2 consisted of the larger particle sizes.

Figure 5 shows the distribution of the major species in each size fraction for the asreceived Spring Creek and the same fuel doped with sized kaolinite added to the fuel such that the ash content was increased by 50 weight percent. These tests indicated that the addition of the kaolinite decreased the amount of sodium species which reported to the smallest size fractions as fine sodium aerosols by approximately 50%. It can be seen that the sodium is shifted into the Cyclone 5 size fraction which is the size fraction of the added kaolinite. Presumably, this reduction in the amount of sodium is due to the reaction of the vapor-phase sodium species with the kaolinite to form sodium aluminosilicates.

FUTURE WORK

Preliminary results suggest that by employing beneficiation techniques, the sodium content of a potentially high-fouling/slagging coal such as Spring Creek can be substantially reduced. This reduction decreases the amount of vapor-phase sodium available to participate in alkali sulfate-induced deposition and corrosion of turbine blade materials in a direct coal-fired gas turbine. Future work will examine the effect of beneficiation on the deposition potential of these fuels in addition to expanding the fuel types and the types of beneficiation techniques utilized on the baseline Spring Creek coal.

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Figure 3. SEMPC Analyses of Major Species in Size-Fractioned Fly Ash Samples from Spring Creek Combustion Tests



Cluster order is Cyclone 2, Cyclone 5, filter.

Figure 4. Distribution of Major Species Between Size Fractions for Spring Creek Combustion Tests



Cluster order is Cyclone 2, Cyclone 5, filter.

Figure 5. Distribution of Major Species Between Size Fractions for Alkali-Gettering Combustion Tests with As-Received Spring Creek Fuel

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FILMED 3/17/93

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