Quarterly Progress Report
Covering Period July 1, 2010 to September 30, 2010
Date of Report – October 21, 2010

Award Number:	DE-FC36-04GO17884
Project Title:	Improving Heat Recovery in Biomass-Fired Boilers
Project Period:	October 1, 2009 to September 30, 2012
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DOE Contract Specialist: N/A

1. **Project Objective:** The goal of this project is to improve heat recovery in biomass-fired boilers by enabling these boilers to operate with higher superheater tube temperatures thus improving the energy efficiency in the many industries that use biomass as fuel including the chemical, petrochemical, steel, and forest products industries. The challenge to obtaining increased energy efficiency is to clearly identify all operative corrosion mechanisms in the superheaters when operating at temperatures above the first melting point of the deposits, and then address solutions to each of these mechanisms in turn. This will be achieved by a program that combines theoretical thermodynamic analyses, laboratory studies and in situ probes to explore and expand the operating envelope of future biomass-fueled steam generating systems.

2. **Background:** High energy prices are an increasingly critical component of manufacturing costs in North American process industries and are likely to become even more significant as traditional fossil fuels become more scarce and more contaminated. The effect of these increased costs, combined with the new emphasis on greenhouse gas reduction, is presenting a challenge to energy intensive industries that currently consume large amounts of fossil fuels. In response, companies are looking to non-traditional fuels based on biomass to help address these critical issues and allow them to remain competitive in a global marketplace.

   Relative to most fossil fuels, biomass-based fuels are extremely inhomogeneous and contain significant impurities, such as chlorides, alkali metals and heavy metals that deposit on heat transfer surfaces. While these deposits may reduce the overall energy efficiency of the boiler, their principal effect is to cause rapid corrosion of heat transfer surfaces that approach, or exceed, the first melting point of the deposits. As a consequence, boilers burning biomass have largely been limited to operating with superheater steam temperatures of less than 510°C (950°F) and steam pressures of less than 11 MPa (1600 psi). Most existing biomass boilers in North America operate at substantially lower steam temperatures and pressures, particularly those utilized as waste utility boilers.

   While small, incremental gains in energy efficiency can be met by improving operation of existing biomass-fired boilers, much larger gains could be obtained by designing and building biomass boilers that operate with substantially higher pressures and superheater steam temperatures than is the current practice. To gain this enhanced energy efficiency and retain operational reliability, challenging materials problems in the areas of high temperature strength and environmental degradation must be overcome, particularly at temperatures near or above the first melting point of the superheater tube deposits.

3. **Accomplishments:** The first draft of a report titled "Superheater Corrosion in Biomass Boilers: today's science and technology" was completed. Two visits were made to the Southern Company's power plant in Gadsden, Alabama to discuss the possibility of exposing a corrosion probe in their power boiler that co-fires coal and biomass. Arrangements were made for a visit to the Howe Sound Pulp and Paper Company's mill in Port Mellon, British Columbia where there is a power boiler that burns wood from logs that have been floated in seawater and consequently have a relatively high concentration of chloride.

4. Progress and Status:

Task 1. Conduct critical review of technology status

The participants in the project continue to collect reprints of papers and reports of relevance to the project. The first draft of the report titled "Superheater Corrosion in Biomass Boilers: today's science and technology" was completed. The Executive Summary of this 96 page report reads as follows:

This report broadens a previous review of published literature on corrosion of recovery boiler superheater tube materials to consider the performance of candidate materials at temperatures near the deposit melting temperature in advanced boilers firing coal, wood-based fuels, and waste materials as well as in gas turbine environments. Discussions of corrosion mechanisms focus on the reactions in fly ash deposits and combustion gases that can give corrosive materials access to the surface of a superheater tube.

Setting the steam temperature of a biomass boiler is a compromise between wasting fuel energy, risking pluggage that will shut the unit down and creating conditions that will cause rapid corrosion on the superheater tubes and replacement expenses.

The most important corrosive species in biomass superheater corrosion are chlorine compounds and the most corrosion resistant alloys are typically FeCrNi alloys containing 20 to 28%Cr. Although most of these materials contain many other additional additions, there is no coherent theory of the alloying required to resist the combination of high temperature salt deposits and flue gases that is found in biomass boiler superheaters.

After the depletion of Cr2O3 by chromate formation or chromic acid volatilization exceeds a critical amount, the protective scale gives way to a thick layer of Fe2O3 over an unprotective (FeCrNi)3O4 spinel. This oxide is not protective and can be penetrated by chlorine species that cause further acceleration of the corrosion rate by a mechanism called active oxidation. Active oxidation, cited as the cause of most biomass superheater corrosion under chloride ash deposits, does not occur in the absence of these alkali salts when the chloride is supplied as HCl gas.

Although a deposit is more corrosive at temperatures where it is molten than at temperatures where it is frozen, increasing superheater tube temperatures through the measured first melting point of fly ash deposits does not necessarily produce a step increase in corrosion rate. The corrosion rate typically accelerates at temperatures below the first melting temperature and mixed deposits may have a broad melting temperature range. Although the environment at a superheater tube surface is initially that of the ash deposits, this chemistry typically changes as the deposits mature. The corrosion rate is controlled by the environment and temperature at the tube surface, which can only be measured indirectly. Some results are counter-intuitive. For example, Vattenfall's experience with the "chlorine trap" in the Schweinfurt waste boiler suggests that superheater deposits that grow thick enough to be molten at the ash/flue gas interface appear to provide protection to the underlying tube because transport rates through the molten deposits are slow.

Two boiler manufacturers and a consortium have developed models to predict fouling and corrosion in biomass boilers in order to specify tube materials for particular operating conditions. It would be very useful to compare the predictions of these models regarding corrosion rates and recommended alloys in the boiler environments where field tests will be performed in the current program.

Manufacturers of biomass boilers have concluded that it is more cost-effective to restrict steam temperatures, to co-fire biofuels with high sulfur fuels and to use fuel additives rather than trying to

increase fuel efficiency by operating with superheater tube temperatures above melting temperature of fly ash deposits. Similar strategies have been developed for coal fired and waste-fired boilers. Additives are primarily used to replace alkali metal chloride deposits with higher melting temperature and less corrosive alkali metal sulfate or alkali aluminum silicate deposits.
Design modifications that have been shown to control superheater corrosion include adding a radiant pass (empty chamber) between the furnace and the superheater, installing cool tubes immediately upstream of the superheater to trap high chloride deposits, designing superheater banks for quick replacement, using an external superheater that burns a less corrosive biomass fuel, moving CFB superheaters from the convective pass into the hot recirculated fluidizing medium and adding an insulating layer to superheater tubes to raise their surface temperature above the dew point temperature of alkali chlorides. All these design changes offer advantages but introduce other challenges. For example, operating with superheater temperatures above the dew point of alkali chlorides could require the use of creep-resistant tube alloys and does not eliminate chloride corrosion.

Improved test methods that can be applied within this project include automated dimensional metrology to make a statistical analysis of depth of penetration and corrosion product thickness, and simultaneous thermal analysis measurements to quantify the melting of complex ashes and avoid the unreliability of the standard ash fusion test.

Other important developments in testing include the installation of individually-temperature-controlled superheater loops for corrosion testing in operating boilers and temperature gradient testing. Several laboratories have shown that increases in temperature gradient increase corrosion rates at a given tube temperature. Although constant temperature laboratory tests can be useful for identifying candidate alloys, field testing or thermal gradient laboratory testing may be more appropriate for simulating conditions in operating boilers.

Task 2. Quantify financial benefits of increased superheater tube temperatures

It has been determined that suitable software is available through a consultant, and efforts are underway to determine the best arrangement for working with the consultant to have access to this software.

Task 3. Conduct laboratory corrosion studies in environments simulating superheater conditions in biomass fired boilers

The experimental procedure was finalized during this quarter, based on discussions between the three principal investigators and insight gained from the site visits and discussions with boiler manufacturers and other laboratories in the first quarter of this project. Cylindrical, upright specimens will be stood vertically in alumina crucibles, and surrounded by a mixed salt with fixed (and pre-determined) first melting point. The crucibles will be filled to the half-way mark with the salt, and the objective at the end of the test will be to section each specimen at a point above and below the "tide line" for the salt. In this way corrosion information will be obtained from exposure to the atmosphere in the furnace in the presence of thin film salts that creep up the sides of the specimen, and underneath a molten pool of salt at the bottom of the crucible.

Two standard salt compositions will be used; one representative of kraft recovery boilers that contains NaCl, KCl, Na_2CO_3 and Na_2SO_4 with a first melting temperature of 522°C. The composition of the second salt is still under discussion, but will model deposits found in biomass-fired boilers. Duplicate samples of 6 to 8 materials will be placed in each furnace for the duration of the test. The initial atmosphere to be used for the tests will include 5%O_2, 10% CO_2, and 20% H_2O, with the balance N_2.

The other activities for the quarter including ordering necessary crucibles and other supplies for the tests, as well as configuring and preparing three horizontal furnaces for the work. A number of test runs were completed in the furnaces to calibrate them for temperature control, and to sort out final details about procedures and specimen configurations. One important task was to determine the necessary accuracy for machining the specimens so that scale and thickness loss due to corrosion can be accurately assessed from the original diameter of the specimens.

Task 4. Measure corrosion rates of alternate materials in superheater environments below, at, and above the deposit melting point temperature

The basic design of the corrosion probes has been determined, and most of the components that will be common to all the probes have been purchased. This includes the computers that will be used in the data collection, the LabView software that will be used for temperature measurement and control of the flow of cooling air, the instrument modules that will serve as the interface for collection of temperature data, and the pipe components that will form the external portion of each corrosion probe.

The compositions of sample materials for the corrosion probes have been identified, and alloy manufacturers have been contacted to determine which materials can be acquired as 1.5 inch schedule 40 pipe (1.90 inch OD, 0.145 inch wall). The list of preferred alloys and possible alternatives is shown in Table 1. The alloys listed range from relatively common austenitic stainless steels to high chromium content alloys intended for highly corrosive applications to alloys that develop a surface layer of alumina (instead of the more common chromia).

Alloys originally selected	Special features	Status	Alternative
310H stainless	High Cr stainless steel	Available	
Sandvik 28	Popular alloy in Europe	Available	
Inconel 690	Ni base, 29% Cr	Available	
Alloy 33	Highest Cr (33%)	Available	
602 CA	Alumina forming alloy	Available	
AFA 20	Alumina forming alloy	Developmental	
Haynes 224	Alumina forming alloy	Not available as pipe	Haynes 214
AC66	Fe base, 32% Ni, 27% Cr	Available	
Esshete 1250	Popular in Europe	Available as bar	
HR160	Ni base, 25% Cr, 30% Co	Not available as pipe	HR120
Alloy 59	Ni base, 23% Cr, 16% Mo	Available	

In addition to these alloys, 347HFG is being added to the list because it is frequently used in Europe.

Efforts are continuing to identify locations for exposing corrosion probes. The Southern Company's boiler in Gadsden, Alabama fires coal mixed with biomass. Generally at least 5% wood is added, but they have used switchgrass. They have agreed to operate for a period with 15% wood while we expose a corrosion probe, and they are looking into the possibility of operating for a limited period with switchgrass. Plans are being made to prepare a probe for insertion in early December for an exposure of about 2000 hours. A second probe will be provided if they choose to co-fire with switchgrass in a subsequent period.

The Howe Sound Pulp and Paper Company previously operated their power boiler with chips from logs that had been floated in seawater, so this was viewed as a location where samples could be exposed in a very high chloride environment. However, they are now using pine beetle-killed wood as part of their feed so this is lower in chloride content, but they are adding some construction waste which could have glues and adhesives which could increase the corrosiveness of the boiler environment. This boiler is going to be rebuilt in the spring, so there is some interest in determining how the different operating conditions will affect the corrosiveness of the environment. Studies are underway to determine if this is a suitable location for exposing a probe.

The MeadWestvaco mill in Covington, Virginia, operates with only hardwood feed, so the superheater environment is expected to be relatively high in potassium content. An early November meeting is planned with the mill operators to discuss the possibility of exposing a corrosion probe in one of their boilers.

Task 5. Report on project activities and prepare final report summarizing project results
Quarterly reports have been prepared as required, and plans are being formulated for a second meeting with the project participants, possibly in early or mid-January.

5. Scope Issues:
None

6. Patents:
None

7. Publications/Presentations:
Presentations have been made during visits at the industrial sites being considered for exposure of corrosion probes.

8. Plans for Next Quarter:
- Complete plans for laboratory corrosion studies and initiate testing
- Acquire materials for fabrication of corrosion samples and corrosion probes
- Assemble corrosion probe for exposure in Southern Company’s power boiler
- Continue evaluation of existing software for calculation of energy benefits

9. Commercialization Status:
Commercialization efforts will be conducted in collaboration with boiler manufacturers and boiler operators. Those discussions will be initiated after results of laboratory and field testing are available and initial energy benefits calculations have been made.

Task/ Milestone Number	Title or Brief Description	Task/Milestone Completion Date				Progress Notes
		Original Planned	Revised Planned	Actual	Percent Complete	
1	Initiate critical review of technology status	11/1/09		10/1/09	100%	Collecting reports and papers, met with European researchers
2	Complete determination of laboratory test plan	9/30/10	10/31/10		50%	Work delayed by problems setting up FPInnovations subcontract
3	Complete determination of corrosion probe test plan	9/30/10	10/31/10		45%	
4	Initiate laboratory corrosion testing	10/31/10	11/30/10		30%	
5	Initiate corrosion probe testing	12/31/10			30%	
6	Complete oxide solubility tests in molten salt solutions	1/31/11				
7	Initiate energy benefits calculations	6/30/11				
8	Complete at least 4 meetings with participants including kick-off meeting and annual meeting	9/30/12			25%	Kick-off meeting conducted December 10th and 11th, 2009
9	Complete final report	9/30/12				

Project Spend Plan

Quarter	From	To	Estimated Federal Share of Outlays	Actual Federal Share of Outlays	Estimated Recipient Share (Cost Share) of Outlays	Actual Recipient Share (Cost Share) of Outlays	Cumulative Actual Outlays (Federal + Recipient)
	Start	12/31/09		42.3K		36.0K	78.3K
2Q10	1/1/10	3/31/10		63.3K		1.5K	64.8K
3Q10	4/1/10	6/30/10		136.9K		13.7K*	150.6K
4Q10	7/1/10	9/30/10		154.1K		20.0K**	174.1K
1Q11	10/1/10	12/31/10	153.5K		95.0K		
2Q11	1/1/11	3/31/11	153.5K		100.0K		
3Q11	4/1/11	6/30/11	153.5K		100.0K		
4Q11	7/1/11	9/30/11	153.5K		100.0K		
1Q12	10/1/11	12/31/11	143.5K		100.0K		
2Q12	1/1/12	3/31/12	143.5K		85.0K		
3Q12	4/1/12	6/30/12	143.5K		65.0K		
4Q12	7/1/12	9/30/12	143.5K		65.0K		
Totals			**1,327.5K**	**396.6K**	**755.0K**	**71.2K**	**467.8K**

* Estimate based on attendance at meetings during this quarter

** Estimate based on efforts to collect boiler operating information