Fireside Corrosion in Oxy Fuel Combustion of Coal/Biomass

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Abstract - **This research work is focused on the fireside corrosion in oxy fuel combustion of coal/biomass. An experiment was conducted in a laboratory, simulating an environment similar to that in power station boilers. Four stainless steel specimen coated separately with biomass ash and coal ash were inserted on a cooling bomb in a 2.4KW furnace and five gases; N_2, O_2, CO_2, HCl and SO_2 were passed through mass flow controllers into the corrosion furnace at set temperature $800^oC\pm5^oC$ and metal specimen at set temperatures of 529^oC to 546^oC for the cold side and hot side of the stainless steel respectively. An SEM/EDX analysis carried out on the metal specimen shows the extent of corrosion that has occurred on their surface. Which shows the rate of corrosion of the biomass coated stainless steel is greater than the rate of corrosion of the 50/50 mixture biomass/coal coated stainless steel which is also greater than the rate of corrosion of the uncoated stainless steel. Thermo-gravimetric analysis was conducted on the biomass/coal sample. Ultimate analysis was completed for the biomass/coal sample. An ash fusion test was conducted on the biomass/coal ash sample, which generated the four ash fusion temperatures. SEM/EDX analysis was conducted on the biomass ash and coal Ash.**

Key words: Carbon Capture Storage, Fireside Corrosion, Energy Dispersive X-ray, Oxy-fuel Combustion, Scanning Electron Microscope, Stainless Steel, Thermo-gravimetric Analysis ©2013

I. INTRODUCTION

The global demand for energy grows nearly double as fast as its entire energy consumption, therefore the challenge to meet this demand is heightened by the investment necessary to change ageing power sector infrastructure [2]. It is expected that roughly one third of the confirmed reserves of fossil fuel can be exhausted prior to 2050 that is if the world is to attain the 2^oC goal, except carbon capture and storage (CCS) technology is generally deployed. This observation is recognised on the assessment of world-wide "carbon reserves", measured as the main CO_2 emissions from confirmed fossil fuel reserves. About two thirds of these carbon reserved are linked to coal, 22% to oil and 15% to gas (Outlook, 2012). Across the globe, about two thirds are held by North America, the Middle East, China and Russia. Hence this indicates that there is great need to embrace the CCS technology as a main option to mitigate CO2 emissions [6]. Global energy consumption has almost doubled over the past three decades of the last century. 77.8% of primary consumption was got from fossil fuels in 2004. (32.4% oil, 21.2% natural gas and 24.1% coal), 5.4% from nuclear fuels and renewable resources consists of 16.5% [3].

Carbon capture technologies are suggested as possible solutions to carbon dioxide emissions from coal fired power plants. Thus there are three main processes which are: post combustion capture, Pre combustion capture and oxy fuel combustion capture.

Having technologies that capture and remove CO_2 from the power plants is not enough as the next big question is what is this captured CO_2 used for? The CO_2 can be stored either beneath the ocean, in coal beds or exhausted oil wells.

Fireside corrosion is among the leading causes of boiler tube failure. Apart from corrosion, boiler tubes are also susceptible to ash deposition. Hence the development of advanced techniques (such as oxy fuel combustion) for future power plants and the implementation of retrofit technologies to existing ones in order to reduce pollutant emission has raised among other concerns, the effect of these measures on corrosion and deposition of the boiler heat transfer surfaces [5].

From this research work which shows the extent of corrosion of metal specimens from the results of the experiment conducted, hence ascertain the extent of corrosion of stainless steel specimen to prove that it (AISI 310) is the most suitable, durable and affordable to be used as a boiler material.

II. METHODOLOGY

A. Sample Preparation

The metal specimen goes through preparatory process of smoothing the top surface with silicon carbide grinding paper and diamond micron compound till a mirror like clean dry surface is obtained. The coal is obtained from Drax located in Selby, UK. This is a high ash coal that is normally blended with a better quality coal such as Colombian El Cerejon which has about 3% ash; coal is converted to ash at 850^oC, while biomass is converted to ash at 550^oC over a set period of time. The metal specimen are coated with the ash of the biomass and coal separately.

B. Experimental Setups and Methods

Auxiliary equipment used for the experiment include; furnace, control panel for the furnace mass flow controllers, bubbler, cooling bomb, temperature controllers, scrubber (NaOH), Eductor, computer with a lab-view software for logging data.

The purpose of the corrosion rig is to study the effect of various parameters on the corrosion of different steel specimens. ; N_2, O_2, CO_2, HCl and SO_2 are passed through mass flow controllers, although N_2 flows from the mass flow

controller to the bubbler together with steam to enter the furnace with the other gases. The exit gas stream leaving the furnace is scrubbed with a very dilute NaOH solution to get rid of the acid gases before leaving the system through the exhaust fume hood. Fig 2.1 shows a description of the setup of the equipment used to conduct experiment.

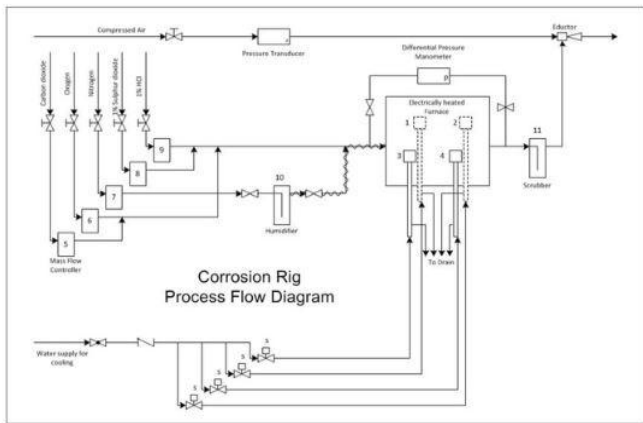Fig 2.1 Electric heater furnace, Control furnace panel, Bubbler and Mass flow controllers

Fig 2.2 Corrosion Rig

Fig 2.2 is the corrosion rig process flow diagram, the part labelled (s) are the solenoid valves which are activated by temperature controllers at a set temperature. 1 to 4 are the metal specimen securely placed on the cooling bomb, 5 to 9 indicate the mass flow controllers for the various gases. 10 is the bubbler, 11 is the scrubber, and there is an Eductor and also a differential pressure manometer. After the metal specimen is removed from the furnace it undergoes some preparatory process of encapsulating, cutting and polishing then it is analysized by a Carl Zeiss EVOMA 15VP SEM. Other experiments conducted include: Thermo-gravimetric TGA, Ultimate analysis, Ash fusion test, SEM/EDX of biomass/coal ash and SEM/EDX of corroded stainless steel specimens.

III. RESULTS AND DISCUSSIONS

For the Thermo-gravimetric experiment conducted on biomass (miscanthus), three stages where involved; the first stage was the loss of moisture, followed by the second stage which is the loss of volatiles and finally the loss of carbon leaving only the ash content. This is shown in Fig 3.0 below.
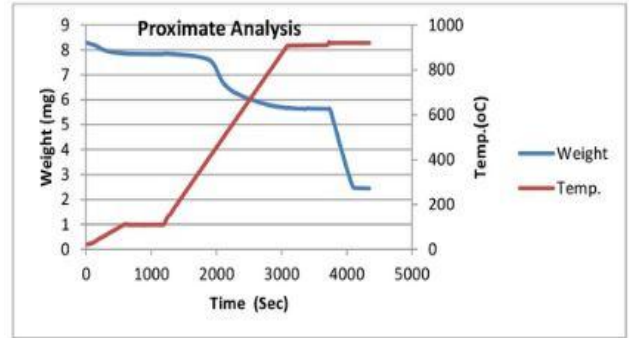

Fig 3.0 Proximate Analysis of Biomass

For the Thermo-gravimetric experiment conducted on coal UK 15 it also passes three stages before it is converted to ash, there is little loss of moisture as indicated in the beginning of the blue slope in Fig 3.1, then there is also variable loss of volatiles as the slope curves downwards and finally a steep slope dropping downwards that indicates the loss of carbon. Comparing the TGA proximate analysis of coal using the STA 8000 with the actual TGA results of coal 15 there is great similarity [4].
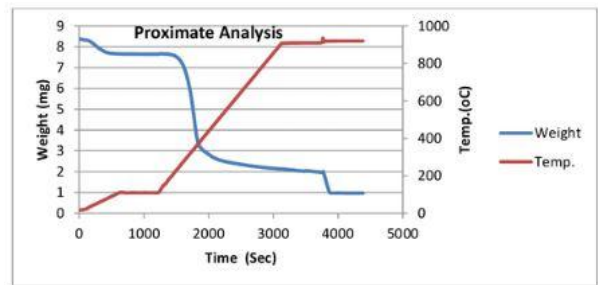

Fig 3.1 Proximate Analysis of Coal UK 15

Hence comparing both TGA results of biomass and coal it can be said that biomass contains much volatiles content than coal while coal has more carbon content than biomass [8].

An ash furnace test was also conducted and the results in table 3.0 shows coal ash wt% 27.1, while biomass ash wt% is 8.95.

Table 3.1 Ash furnace Test Result

	Coal (g)	Biomass (g)
Weight of Empty Crucible	10.2041	11.3593
Weight of Crucible + Sample	11.2047	12.3591
Weight of Crucible + Sample (Out of Oven)	11.1498	12.2719
Weight of Crucible + Ash	10.4604	11.4410
Weight of Ash	0.2563	0.0817
Ash wt %	27.1	8.95

Combining both proximate analysis data and ultimate analysis data the oxygen content for biomass miscanthus and coal UK 15 was calculated to be 29.23% and 4.04% respectively. The high oxygen content in the Ultimate analysis results of biomass (miscanthus) is as expected although for coal it is quite low below the coal expected oxygen percentage and this is due to experimental errors. Of course oxygen is calculated by difference method. This is indicated in table 3.1 below.

Table 3.1 Proximate Analysis and Ultimate Analysis Results

Proximate Analysis

	Biomass (miscanthus)	Coal (UK15)
Moisture %	8.688	5.48
Volatiles %	67.099	26.43
Carbon %	12.868	38.51
Ash %	11.5	29.56

Ultimate Analysis

	Biomass (miscanthus)	Coal (UK15)
Nitrogen %	2.48	1.98
Carbon %	43.2	53.5
Hydrogen %	7.42	6.86
Sulfur %	0	2.51
Oxygen %	29.23	4.04

Biomass ash discretion percentage for miscanthus biomass ash which is approximately 9.6% according to Garcia et al (2013) in a paper on biomass proximate analysis using TGA [8].

The four deformation temperatures were generated from the ash fusion test and are presented in a table 3.2 below. The Hemispherical temperature was inaccurate for both temperatures due to inconsistency of the shapes that it formed.

Table 3.2 Ash Fusion Test Results

	IDT	ST	HT	FT
Biomass (Miscanthus) Ash	820oC	895oC	1020oC	1040oC
Coal	1165oC	1305oC	1475oC	1495oC

IDT – Initial Deformation Temperature

ST – Softening Temperature

HT – Hemispherical Temperature

FT – Final Temperature

SEM/EDX analysis was also performed on the coal ash, biomass ash and 50/50 thermal mixture of biomass ash and coal ash. This is indicated below in Fig 3.2, 3.3, and 3.4 respectively. In Fig 3.2 it produced as semi quantitative analysis which indicated high wt% of Si (19.62%), Al (14.9%), and O (53.09%). In Fig 3.3 semi quantitative analysis also gave results high wt% of Si (16.09%), O (51.69%), and K (17.97%). In Fig 3.4 semi quantitative analysis indicated high concentrations of O (52.51%), Si (19.97%), and Al (13.62%). With the knowledge of this characteristics of this ash types this will go a long way in redesigning boilers to withstand corrosion as a result of molten ash deposits. The EDX profile results correlates with the values of wt% found from the semi quantitative analysis.
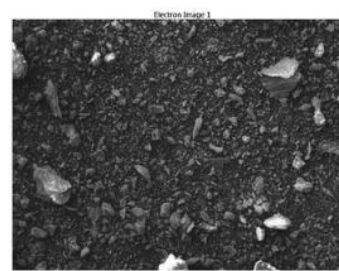
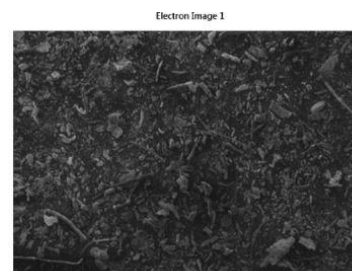Fig 3.2 SEM image of coal

Fig 3.3 SEM image of biomass

Fig 3.4 SEM image of 50/50 mixture

SEM/EDX analysis were conducted on the corroded stainless steel specimen that were coated with biomass ash, 50/50 mixture of coal/biomass and uncoated stainless steel specimen that have been in the corrosion furnace at temperature of 800oC±5oC over a period of 14 days. Fig 3.5 shows the stainless steel coated with biomass which showed the highest rate of corrosion at 20.83nm/day. In Fig 3.6 the 50/50 biomass/coal mixture coated stainless steel with corrosion rate of 18.45nm/day. Then Fig 3.7 which is the uncoated stainless steel that displayed the lowest corrosion rate of 17.261nm/day as a result of an oxide layer formed by chromium oxide and iron oxide which acts as a protective layer preventing corrosion even under oxy fuel combustion environment and at high temperatures. From the SEM image below it shows that the cloud like formation in Fig 3.6 is as a result of the mixture of ash which has embedded on the surface of the metal. The semi quantitative analysis showed that for the biomass coated stainless steel the high compositions are iron (42.32wt%), chromium (19.44wt%) and oxygen (14.30wt%). For the 50/50 mixture coated steel it has high compositions of oxygen (32.12wt%), iron (16.89wt%) and (13.99wt%) of sulphur. For the uncoated steel chromium content was 24.94wt%, iron 22.49wt% and sulphur 16.44wt%. This correlated to EDX profile results.
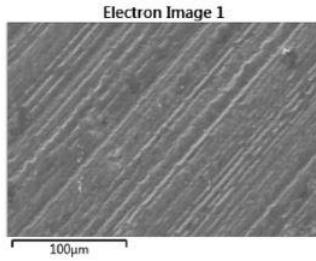
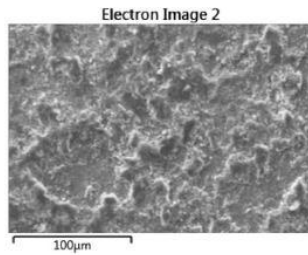Fig 3.5 SEM Biomass coated
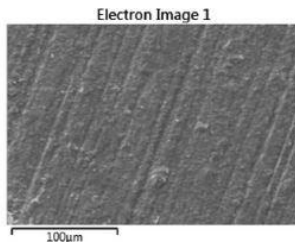

Fig 3.6 SEM 50/50 mixture coated

Fig 3.7 SEM Uncoated

"AISI 310 is a high chromium alloy, thus increased corrosion resistance can be achieved by enrichment of the surface of the specimen to be protected with elements such as chromium or aluminium" [1].

A mechanism was recommended for external fireside corrosion that started with the formation of alkali metal sulphate layer on the tube surface of the boilers (normally 3mol K2SO4/1mol Na2SO4). Pekka Pohjame et al (2010) postulated in the paper on fireside corrosion of super-heater material in oxy fuel combustion that as the alkali sulphates layer thickened, there would be corresponding increase in the surface temperature until the ash begins to stick to the surface. Finally the ash would subsequently sinter and result into molten slag [6].

The good corrosion resistance of stainless steel can be attributed to formation of very thin layer of oxides (chromium oxides and iron oxides) notwithstanding the fact that with the thickness of very little nanometres formed by this oxide layer; the oxide layer is very strong that it meritoriously isolates the steel from the environment [8].

Below is table 3.3 showing the rate of corrosion of AISI 310 stainless steel and also the metal loss experienced by the various stainless steel after they have been in the corrosion furnace for a period of 14 days. The corrosion loss was calculated from the subtraction of the final width of the stainless from its initial weight then it was converted from millimetres to micrometres and the corrosion rate was calculated over a 14 day period, because that is how long the steel specimen was in the corrosion furnace. These values are indicted in the table

Table 3.3 Corrosion rate of AISI 310 stainless steel

	Initial width (mm)	Final width (mm)	Corrosion loss (μm)	Corrosion rate (nm/day)
Coated with biomass ash	11.0197	11.0127	7	20.83
50/50 mixture coal/biomass ash	11.0769	11.0707	6.2	18.45
Plane specimen	11.0736	11.0678	5.8	17.26

The heat flux was calculated from the formula;

$$Q = KA (\triangle T/x)$$

After calculation the heat flux = 74.8kW/m2 while the heat transfer = 39.71W

Temperature plays an important role in study of heat transfer. Hence the thicker the wall of the stainless steel material the higher the resistance, and also the lower the thermal conductivity the higher the resistance. The heat transfer is from the hot side to the cold side of the steel specimen (T.Prosek, 2005).

IV. CONCLUSION

From the results generated for the experiment carried out to determine the extent of corrosion that occurred on stainless steel coated with biomass ash, stainless steel coated with 50/50 mixture of coal/biomass ash and uncoated stainless steel in an oxy fuel combustion environment similar to that in power station boilers. It showed that the rate of corrosion of stainless steel coated with biomass ash (20.83nm/day) is greater than the rate of stainless steel coated with 50/50 mixture of coal/biomass (18.45nm/day) and is also greater than the rate of corrosion of uncoated stainless steel (17.26nm/day). Chromium oxides and iron oxides form a thin layer that protects the stainless steel from corrosion even at high temperatures and under oxy fuel combustion environments but when there is ash deposit on the surface of the metal it forms molten slag at high temperatures and this can lead to corrosion. Through SEM/EDX analysis of ash types; a good knowledge of this can be used to redesign boiler materials.

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