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Mercury Emissions during Cofiring of Sub-bituminous Coal and Biomass (Chicken Waste, Wood, Coffee Residue, and Tobacco Stalk) in a Laboratory-Scale Fluidized Bed Combustor

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Four types of biomass (chicken waste, wood pellets, coffee residue, and tobacco stalks) were cofired at 30 wt % with a U.S. sub-bituminous coal (Powder River Basin Coal) in a laboratory-scale fluidized bed combustor. A cyclone, followed by a quartz filter, was used for fly ash removal during tests. The temperatures of the cyclone and filter were controlled at 250 and 150 °C, respectively. Mercury speciation and emissions during cofiring were investigated using a semicontinuous mercury monitor, which was certified using ASTM standard Ontario Hydra Method. Test results indicated mercury emissions were strongly correlative to the gaseous chlorine concentrations, but not necessarily correlative to the chlorine contents in cofiring fuels. Mercury emissions could be reduced by 35% during firing of sub-bituminous coal using only a quartz filter. Cofiring high-chlorine fuel, such as chicken waste (Cl = 22340 wppm), could largely reduce mercury emissions by over 80%. When low-chlorine biomass, such as wood pellets (Cl = 132 wppm) and coffee residue (Cl = 134 wppm), is cofired, mercury emissions could only be reduced by about 50%. Cofiring tobacco stalks with higher chlorine content (Cl = 4237 wppm) did not significantly reduce mercury emissions. This was also true when limestone was added while cofiring coal and chicken waste because the gaseous chlorine was reduced in the freeboard of the fluidized bed combustor, where the temperature was generally below

650 °C without addition of the secondary air. Gaseous speciated mercury in flue gas after a quartz filter indicated the occurrence of about 50% of total gaseous mercury to be the elemental mercury for cofiring chicken waste, but occurrence of above 90% of the elemental mercury for all other cases. Both the higher content of alkali metal oxides or alkali earth metal oxides in tested biomass and the occurrence of temperatures lower than 650 °C in the upper part of the fluidized bed combustor seemed to be responsible for the reduction of gaseous chlorine and, consequently, limited mercury emissions reduction during cofiring. This study identified the important impacts of temperature profile and oxides of alkali metal (alkali earth metal) on mercury emissions during cofiring in the fluidized bed combustor.

1. Introduction

Biomass and solid wastes are potential renewable fuels that can be blended with coal to replace oil and natural gas to help the mitigation of carbon dioxide (CO_2). For example, the U.S. Department of Energy (DOE) is proposing strategies on the use of biomass-derived ethanol and biodiesel to be combined with coal-derived liquid fuels (CDTL) for displacement of petroleum fuels in transportation, and advanced cofiring technologies of coal and biomass for power generation (*1, 2*). The Directive of the European Parliament and Council (*3*) targets a 12% share of electricity production based on renewable sources in the European electricity market by 2010. However, there are disadvantages using biomass, relating to its supply, transportation, and composition. These can be reduced if the biomass is cofired with coal (*3*). Cofiring does not involve the high capital cost of building a new biomass plant, but allows for significantly lower retrofitting costs at an existing plant. Retrofitted boilers can use biomass when biomass supplies are plentiful, but switch to coal when biomass supplies are cut (*4*). Biomass can be a good source of renewable energy and fuel. The amount of biomass produced annually in the United States, beyond its current use for food, animal feed, and forest products, is expected to be between 500 and 600 million dry tons per year for the period 2010−2020 (*5*). The two largest biomass productions are generated in wood manufacture and on agricultural land (*6*). Recent enthusiasm regarding biomass utilization for energy also has promoted the increased production of fast-growing grasses in larger nonagriculture areas of the U.S. These include perennials, such as switchgrass (*7*). With regard to animal manure, chicken litter production makes up the largest portion in the United States (*8*).

Biomass-derived methane emissions are one of the major anthropogenic sources of greenhouse gases when biomass-derived solid wastes are landfilled (*8*). Animal manure, such as chicken litter, poses a significant threat to the soil and air because of the release of methane and ammonia to the atmosphere. The overfertilization of phosphorus (*9−11*) during application of animal manure on crops causes environmental problems as well. Animal manure releases nitrogen and phosphorus, which results in eutrophication that destroys the ecological balance, and threatens fauna, as well as drinking water quality. Biomass waste from agriculture is responsible for an estimated 48% of the water-quality problems in rivers and streams in the U.S. (*12*). In the last three decades, phosphate research has shifted its emphasis from agricultural productivity to environmental protection (*13*). Increasing occurrences of these outbreaks of environmental issues, caused by biomass waste production, would

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TABLE 1. Proximate, Ultimate Analysis, and Major Oxides of Coal and Biomass Samples (On a Dry Basis)

	As Deter				Dry Basis, by weight								
	ADL	Moisture	Ash	Vol. Mat	Sulfur	Btu	Carbon	Hydrogen	Nitrogen	Oxygen	Chloride	Mercury	Fluoride	Bromide
SampleName		%	%	%	%	BTU/lb	%	%	%	%	ppm	ppm	ppm	ppm
PRB coal		15.01	7.64	43.32	0.54	11818	69.02	4.72	0.80	17.28	82	0.12	54	ND
Chicken waste		9.31	34.91	54.18	1.06	5097	33.32	3.91	4.87	21.91	22340	0.01	51	ND
Wood biomass		6.57	0.56	80.27	0.01	8488	46.65	5.90	ND	46.89	132	< 0.01	15	ND
Coffee residue		6.19	1.08	42.31	0.06	5559	27.86	8.63	0.87	61.49	134	< 0.01	17	ND
Tobacoo stalk		6.31	11.34	74.11	0.34	7079	44.08	5.18	3.77	35.28	4237	0.01	28	ND
Limestone											ND	< 0.01		

	Minor oxides, dry basis, by weight												
SampleName	Na_2O	MgO	Al_2O_3	SiO_2	CaO	K_2O	SO_3	P_2O_5	BaO	SrO	Fe_2O_3	MnO	TiO_2
	%	%	%	%	%	%	%	%	%	%	%	%	%
PRB coal	0.40	3.79	13.10	23.69	23.20	0.27	27.84	0.82	0.44	0.34	4.89	0.02	1.19
Chicken waste	4.77	5.89	3.33	31.95	16.09	12.32	4.88	18.8	0.02	0.02	1.44	0.18	0.32
Wood biomass	0.16	4.01	9.49	24.3	28.98	20.28	6.7	1.02	0.4	0.12	3.4	0.44	0.69
Coffee residue	0.08	17.04	0.93	2.14	9.16	49.41	3.12	16.79	0.06	0.06	0.58	0.15	0.49
Tobacoo stalk	< 0.01	4.2	1.78	17.13	16.86	45.37	6.41	7.2	0.08	0.04	0.73	0.04	0.16
Limestone	ND	4.33	3.73	0.3	91.31	0.15	0.12	0.04	ND	ND	ND	ND	0.37

compel the U.S. Environmental Protection Agency (EPA) to regulate the amount of chicken waste used per acre on agricultural land. Biomass cofiring can be an efficient and economical alternative route to utilize biomass. It is the most economical near-term option for introducing new biomass resources into today's energy mix. However, evaluating thermal utilization of biomass is necessary to assess its environmental repercussions during cofiring. Opportunities for the reduction of sulfur oxides (SO_x) and nitrogen oxides (NO_x) by cofiring have been extensively investigated, (14−21) but emissions of mercury and other trace metals during cofiring have not been extensively addressed.

The U.S. EPA promulgated the Clear Air Mercury (Hg) Rule (U.S. EPA CAMR on March 15, 2005) to permanently cap and reduce mercury emissions from coal-fired electric utilities boilers. However, on February 8, 2008, the U.S. Court of Appeals for the District of Columbia Circuit issued an unanimous decision objecting to the U.S. Environmental Protection Agency's Clean Air Mercury Rule (CAMR) and the rule "de-listing" electric generating units (EGUs) from the list of sources required to be regulated under the Clean Air Act Section 112. The new regulation will become effective on January 1, 2009 (22, 23). There are less than detectable amounts of mercury in biomass, which results in low mercury emission rates during cofiring of coal and biomass. Moreover, some biomass resources contain higher halogen content, which may impact mercury speciation during cofiring, and thus fate of mercury in available air pollutant control devices in power generation (24−29). This is especially attractive for cofiring with low rank coals such as sub-bituminous coals, where a low occurrence of chlorine is generally found. Therefore, benefits of cofiring coal and biomass for CO_2, SO_x, and NO_x abatement may be a new economic strategy for mercury emission control in coal-fired power generation. Mercury reduction by cofiring technologies today may be able to get credits toward development of any future mercury mandates by the EPA, which is similar to what is being considered for carbon dioxide (30).

In this study, several types of biomass were cofired with a sub-bituminous coal (Powder River Basin coal (PRB)) in a laboratory-scale bubbling fluidized bed combustor. Mixture ratio of biomass/coal will be generally as high as 30 wt % of the total fed fuels, sometimes up to 50 wt %. Issues related to mercury speciation and emission control during cofiring were addressed in this study. The relevant factors of mercury speciation and emission, such as chlorine levels in cofired biomass, occurrence of chlorine in the gas phase and solid phase, and the effect of additional limestone, were identi-fied, by investigation of physical and chemical characteristics of flue gas constituents and solid residues.

2. Experimental Section

Coal and Ash Analysis. One sub-bituminous coal and four types of biomass, (chicken waste (CW), wood pellet (WP), coffee residue (CR), and tobacco stalk (TS)), were studied. Raw coals were purchased from a coal-fired power plant. CW and TS were collected from a local farm. WP was purchased from a local wood residue factory. CR was collected from a local Starbucks. Biomass has a much lower bulk density, is generally moist, and has lower heating values and lower particle density than coal. Therefore, all raw fuels were first pulverized and sieved. The particle size of the coal samples is 500−1000 μm, and those of the biomass are between 1000 and 2000 μm. The purpose of using slightly larger biomass particles is to satisfy their fluidization conditions and residence time. The selected coal and biomass were premixed before being fed into the combustor. All samples were dried in an oven at 100 °C overnight before testing.

Analysis of all fuel samples in this study follows ASTM standard procedures. A detailed description on these ASTM methods was provided in a previous study (31). Analysis results of all tested fuels and limestone are presented in Table 1 on a dry basis. All tested fuels have a high volatile content. Sub-bituminous coal, CW, and CR have comparable volatile content, which varies between 43.3 and 54.2 wt % on a dry basis. Much higher volatile content is found in WP and TS, which are both above 75 wt %. CW has the highest ash content at 34.9 wt %, TS has 11.3 wt % ash, and sub-bituminous coal has an ash content below 10 wt %. The ash content in WP and CR is generally close to or below 1 wt %. The sulfur content in all fuels is low, at about 1 wt % for CW, followed by 0.54 wt % for sub-bituminous coal, and 0.34 wt % for TS. Sulfur in CR and WP are even low, which can be ignored. Chlorine content in all fuels is below 150 wppm, except for CW and TS. CW has a very high chlorine content (about 22300 wppm). TS has medium chlorine content (about 4500 wppm). Only coal has measurable mercury, at about 0.12 wppm. Mercury in all other fuels is insignificant. The major metal oxides in the tested fuels are also shown in the Table 1. This study indicates that sub-bituminous coal and CW and WP have a relatively high content of CaO and MgO, which are about 25 wt % in the total ash. All biomasses have a higher occurrence of alkali metal oxides, such as Na_2O and K_2O. Among them, CR and TS have more K_2O, but no Na_2O. However, the total amount of alkali earth metal oxides and

alkali metal oxides should be ignored for WP and CR because of their ignorant ash contents. One may notice that CW and CR also has a higher content of P_2O_5, which is about 17.5 wt %.

Laboratory-Scale Fluidized Bed Combustor and Measurements. The fluidized bed cofiring combustor, used in this study, has seven major components, as shown in Figure S1 (see Supporting Information). It includes an electrically heated main body of the fluidized bed combustor, one fuel hopper and one fuel screw feeder, a compressed air delivery line and its metering flow meter, and a flue gas cleanup unit, including a cyclone and a high temperature quartz filter assembly, as well as a wet scrubber. Under an oxygen-firing mode, an oxygen cylinder and flow meter provides oxygen supply and flow control. Simultaneously, a CO_2 cylinder is available to deliver a CO_2 stream for dilution purposes. In this study, results for the oxygen-firing mode were not included. The outside diameter (OD) of the combustor is 6.4 and 0.8 cm in thickness. The total height of the combustor is 110 cm. There is a gas distributor mounted at the bottom of the combustor with a 1% opening to prevent maldistribution of the gas passing through bed material.

The combustor temperatures are monitored by a platinum−rhodium thermocouple, which is sealed in a stainless steel tube in the combustor. The thermocouple could be moved inside the tube to monitor the temperature profile along the height of the combustor, as indicated in Figure S1 (see Supporting Information).

The bed temperature was 850−900 °C in the main portion of the combustor at the bottom, and gradually decreased to 450 °C starting at 2/3 of the distance from the combustor's bottom. The fuel mixtures for cofiring were fed into the combustor through a coal feeder at the top of the combustor. The maximum mixing ratios was 50 wt%. The fluidized bed combustor was generally operated at a velocity 3−5 times that of U_{mf} (the minimum fluidization velocity). The excess air ratio was maintained at about 1.2, while the oxygen concentration at the combustor outlet was about 6.0−8.0%. The flue gas produced with the char residue at the top outlet of the combustor was collected by combining a cyclone and a porous quartz metal filter. The cleaned flue gas was delivered to either gas analyzers (O_2, SO_2, and mercury) or collection impingers to determine the presence and amount of mercury and halogens. Mercury and chlorine contents in tested limestone were determined to be low, which could be negligible.

Initially, the fluidized bed combustor was electrically heated to 650 °C. Then coal was fed into the combustor to increase the temperature of the combustor. Initial ash produced was left in the combustor as bed material. One hour later after the temperatures began to approach 850 °C, air and coal fed into the combustor were adjusted to stabilize the temperature across the combustor for a few hours. The mercury variation was monitored continuously by the PS Analytical (PSA10.680) Semicontinuous Mercury Emission Monitoring (SCEM) system. A PSA Cavkit is used for calibration and high spiking correction of the PSA SCEM to ensure the accuracy of mercury measurement. Because low-sulfur fuels were tested and there were very low gaseous sulfur concentrations in this study, the wet-impinger-derived bias should be ignorant. American Standard Test Method (ASTM) Ontario Hydra Method (OHM) measurements (ASTM 6784-02) were used to confirm the SCEM sampling results during test periods. The detailed description of two mercury test methods and QA/QC procedures may be found in refs *31 and 32*. For every test condition, at least two tests were conducted. If no abnormal results (the deviation between data from SCEM and OHM, and results form two repeat tests of SCEM and OHM are greater than 20%) were found, the average data was accepted. Gaseous hydrogen chloride (HCl)

and chlorine (Cl_2) were determined by Environmental Protection Agency (EPA) standard method 26A. All gaseous mercury and gaseous chlorine concentrations were measurement at the outlet of filter.

3. Results and Discussion

Mercury emission rates (in a dry basis) and removal efficiencies for the test fuels are summarized in Figure 1, and mercury speciation in offgas is shown in Figure 2. To accurately estimate the mercury emission rates and removal efficiencies during cofiring, a commonly acceptable unit of mercury emission rates (lb/TBtu) was used. The calculation of mercury emission rates was based on the calculation of a *F*-factor in eq (1) and elemental analysis of fuels, which was introduced in EPA Part 75, Appendix A, Method 19. The mercury emission rate, during firing of sub-bituminous coal only, was about 6.25 lb/TBtu. When cofiring CW and sub-bituminous coal (weight ratio of CW introduction at 30%), the mercury emission rate was largely reduced to about 1.27 lb/TBtu on average. Increasing the introduction ratio of CW to 50% during cofiring with sub-bituminous coal, the mercury emission rate was further reduced to 1.02 lb/TBtu. It seems that mercury emissions were not significantly reduced after increasing CW into the combustor. Regardless of originally occurring alkali metal oxides and alkali earth metal oxides in coal and CW, additional alkali metal oxides (limestone), at a Ca/S mole ratio of about 2.5 for SO_x capture were fed into the combustor during cofiring of 30 wt % CW and 70 wt % sub-bituminous coal. In this case, the mercury emission rate was about 3.48 lb/TBtu, which was much higher than the case without limestone introduction into the combustor. It seemed that the introduction of limestone (an ignorant mercury content in limestone) resulted in the increase of mercury emissions, although it was still lower than burning sub-bituminous coal alone.

Switching cofiring fuels from CW to WP, CR, or TS at the same mixing ratio, resulted in mercury emissions similar to that under cofiring CW and sub-bituminous coal with of the introduction of limestone. Mercury emission rates from cofiring WP, CR, and TS with sub-bituminous coal were about 3.32, 2.67, and 3.21 lb/TBtu, respectively. In all cases, the cofiring reduced mercury emission rates compared to burning sub-bituminous coal alone. On the basis of the same thermal output in per trillion Btu, mercury emissions for cofiring CW with a high chlorine content produced the lowest mercury emissions.

Cofiring with different biomass and limestone addition seems to affect mercury emission rates and mercury removal efficiencies. In this study with a fluidized bed combustor, 37.9% mercury removal efficiency ($100*(Hg_{fuel} − Hg_{fluegas})/Hg_{fuel}$) was achieved for burning of sub-bituminous coal alone. Cofiring with CW at 30 and 50 wt % made mercury removal efficiency greatly improved to 83.6% and 84%, respectively. Limestone introduction reduced mercury removal efficiency to 55.7% when cofiring CW at a ratio of 30 wt%. Cofiring of WP, CR, and TS with sub-bituminous coal (at ratio of 30 wt % biomass to 70 wt % coal) had similar mercury removal efficiencies, which were at 52.9%, 62.1%, and 59.1%, respectively.

Because a filter was used in this study to remove mercury by deposited fly ash on the filter during cofiring of biomass and sub-bituminous coal, reductions in mercury emissions likely suggest an increase of the particle-bound mercury. Cofiring of CW with a higher chlorine indicates that more particle-bound mercury was obtained, but not much improvement was achieved with the introduction of CW to a weight ratio (increasing from 30−50 wt %). The higher chlorine content in CW may have helped to enhance the mercury capture by the generated fly ash. However, this effect was eliminated by the introduction of limestone. Limestone
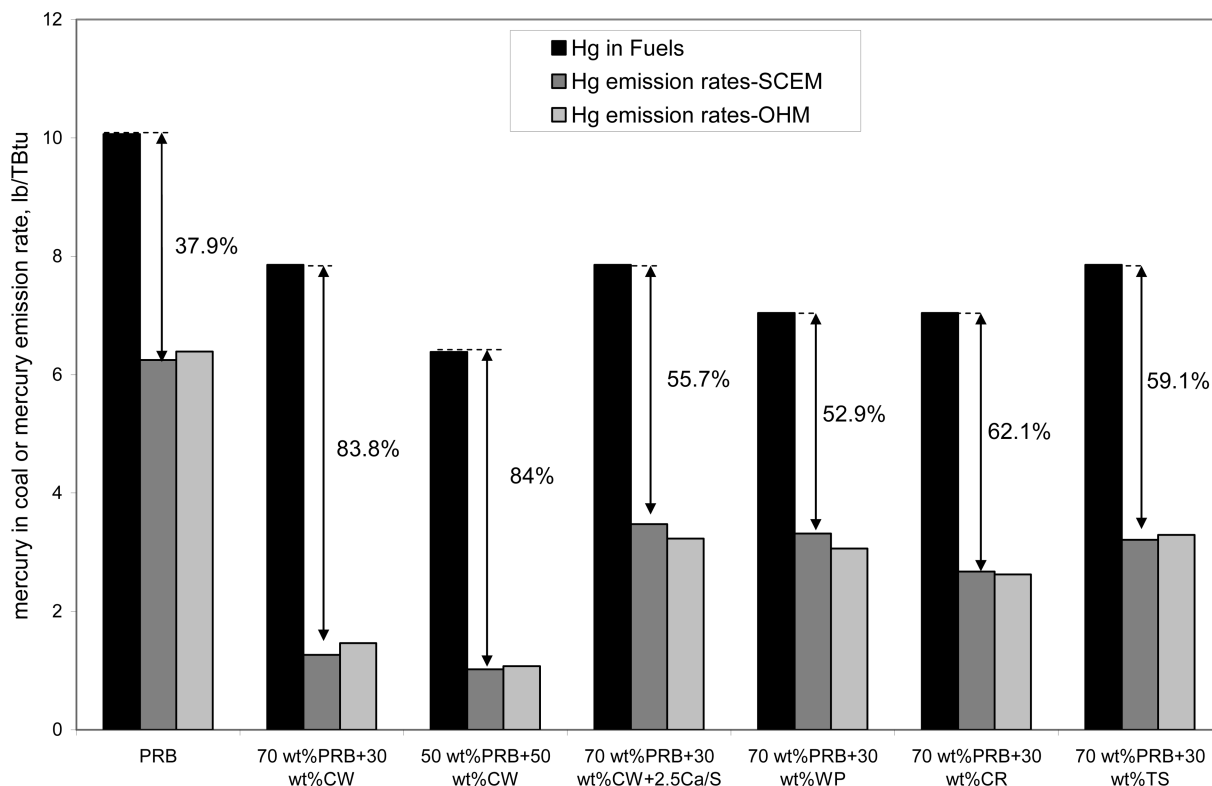
FIGURE 1. Variation of mercury emission during cofiring of sub-bituminous coal and biomass.
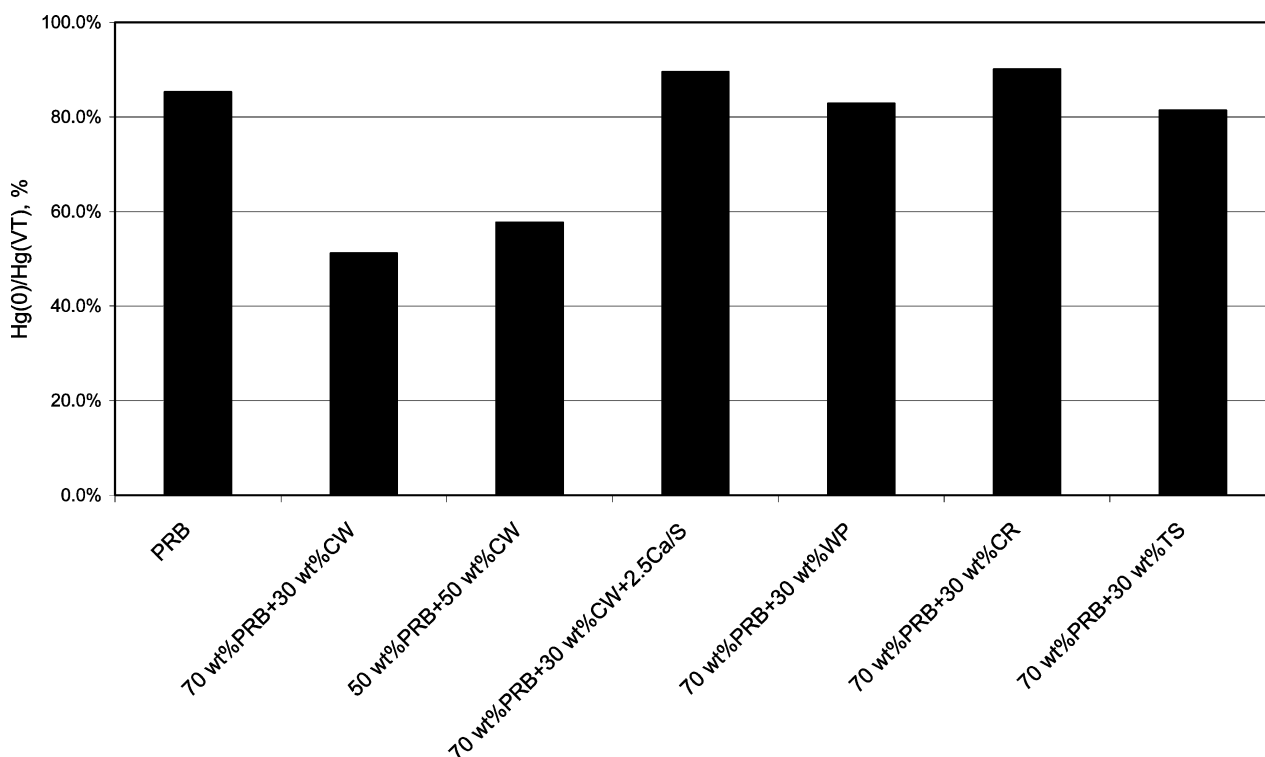

FIGURE 2. Mercury speciation during cofiring of sub-bituminous coal and biomass.

introduction may have decreased the availability of chlorine on mercury oxidation and consequently may have decreased the mercury capture by fly ash. Cofiring of biomass with lower chlorine content, such as WP and CR, did not significantly reduce mercury emission rates as compared to those during cofiring with CW. The chlorine content in the cofiring fuels seems to be essential on mercury emission rates. However, this was not true for TS. Although TS has an appreciable amount of chlorine in it, its mercury emission

rate was comparable to those of fuel mixtures with low chlorine content.

$$F = \text{F-factor (dscf/mmBtu)}$$

$$F = 10^6[3.64(\text{wt \% H}) + 1.53(\text{wt \% C}) + 0.57(\text{wt \% S}) + 0.14(\text{wt \% N}) - 0.46(\text{wt \% O})]/\text{GCV} \quad (1)$$

where wt % H, wt % C, wt % S, wt % N, and wt % O represent the weight percent (dry basis) of each element as obtained

from the elemental fuel analysis as indicated in Table 1 and GVC represents the gross calorific value of fuel (Btu/lb, dry basis). If blended fuels are used, the H, C, S, N, O, and GCV of blended fuels are calculated on the basis of their blending ratio.

The mercury speciation at the fluidized bed combustor outlet (after the filter), is shown in Figure 2. Almost 90% of the total gaseous mercury (Hg(VT)) was elemental mercury (Hg(0)) after flue gas passed through the filter, when sub-bituminous coal or a combination of sub-bituminous coal and WP, CR, and TS was burned. When the cofired fuel was CW and sub-bituminous coal, the mercury speciation analysis indicated about 50% of the total gaseous mercury was elemental mercury. Therefore, almost 50% of the oxidized mercury was still in the flue gas after the fly ash filtration, and the oxidized mercury was not fully captured by the fly ash generated when CW was cofired. With the introduction of limestone, the elemental mercury was 90% even when cofiring with CW.

The elemental mercury is difficult to capture by fly ash because it is extremely volatile (33) under either 250 °C in the cyclone or under 150 °C in the filter. That means the capture of the elemental mercury by fly ash needs an additional oxidization step on the fly ash surface prior to its adsorption. On the other hand, effectiveness of the oxidized mercury capture by fly ash is dependent on its contact efficiency with fly ash and residence time. In the case of cofiring CW, inefficient capture (nearly 50%) of the oxidized mercury by fly ash on the filter may also suggest less residence time available for its capture by fly ash in this study. This assumption seems reasonable because higher contacting efficiency was generally found for mercury and fly ash on the filter. In those cases of firing fuels with less chlorine content, occurrences of almost 90% of the elemental mercury may suggest either that not much oxidized mercury in flue gas before the filtration step or that little elemental mercury can be oxidized by generated fly ash on the filter after flue gas passes through the fly ash cake on the filter. Therefore, it is difficult to conclude that the mercury adsorption on the fly ash was strongly correlated to the occurrence of the oxidized mercury in the flue gas. It has been reported that oxidized mercury has more affinity to the surface of fly ash than elemental mercury (33). Comparably, it was also reported that the elemental mercury was showed a higher affinity to the fly ash (34). These conflicted investigations indicated intensive future works are needed.

Mercury oxidation is strongly dependent on chlorine content in the flue gas. This was corroborated during the investigation of chlorine content in flue gas, which is shown in Figure S2 (see Supporting Information). When sub-bituminous coal was burned, hydrogen chloride (HCl) and chlorine (Cl_2) concentrations in the flue gas were 1.42 and 1 vppm, respectively. When it was cofired with CW at 30%, HCl and Cl_2 concentrations dramatically increased to 28.2 and 1.85 vppm, respectively. Increasing the cofiring ratio of CW to 50 wt% aslo increased the HCl and Cl_2 concentrations to 36.5 and 1.91 vppm, respectively.

It seems that the introduction of limestone largely controlled the occurrence of chlorine species in the flue gas, which made the HCl and Cl_2 concentrations drop to 1.81 and 1.01 vppm, respectively. This was similar to burning sub-bituminous coal only. Cofiring WP and CR had similar HCl and Cl_2 profiles, which were 1.23 and 1.25 vppm during cofiring of WP and 1.46 and 106 vppm during the cofiring of CR. Hydrogen chloride (HCl) and Cl_2 were about 7.32 and 2.05 vppm for cofiring TS, which corresponds to the higher chlorine content in feeding TS. The mercury emission rates and mercury speciation strongly correlates to chlorine in the flue gas. Introduction of CW greatly increased the occurrence of the total availability of chlorine species in the flue gas,

which is supposed to contribute to the oxidation of elemental mercury. Introduction of limestone in cofiring CW greatly eliminated the occurrence of chlorine in the flue gas, which results in reduction of mercury oxidation. This is very similar to cases when cofiring biomass with low chlorine content, such as WP and CR. Comparably, high chlorine content was found in both CW and TS, but the majority of chlorine in these two cofiring fuels did not occur in the gas phase but in the fly ash, based on the assumption of mass balance closure of chlorine. This could explain why the increasing cofiring ratio of CW and cofiring of high chlorine TS did not significantly increase the partition of particle-bound mercury and further reduction of gaseous mercury emission rates. This also agrees with a previous study that stated that an increase of chlorine inputs not necessarily lead to increased oxidized mercury (24, 25).

The presence of less chlorine in the gas phase was better explained by the investigation of higher content of alkali metal oxides (Na_2O and K_2O) and alkali earth metal oxides (CaO and MgO) in the tested fuels. The mole ratio of the total CaO, MgO, Na_2O, and K_2O to chlorine (ROMC) in the tested fuels is shown in Figure S3 (see Supporting Information). This ratio was as high as approximately 250 for sub-bituminous coal, mainly, because of the higher content of CaO and less chlorine in the sub-bituminous coal. The ROMC greatly decreased to approximately 8 when cofiring CW with sub-bituminous coal because of the very high chlorine content found in the CW. This ratio was again close to that of burning sub-bituminous coal at approximately 190 (Ca + Mg + Na + K/Cl) during tests with limestone introduction during the cofiring of CW and sub-bituminous coal. During the cofiring of 30 wt % WP and CR, The ROMCs were still higher because of less chlorine in these fuels. A considerable amount of ash with higher content of CaO and K_2O in TS made TS to have higher ROMC.

It was reported that alkali metal and alkali earth metal oxides can capture Cl in the flue gas more efficiently at a temperature below 650 °C (27). This typical temperature zone was found in the fluidized bed combustor in this study. The major reactions between oxides of alkali metals and alkali earth metals with sulfur in the flue gas occurred at temperatures about 800 °C. However, this could not totally consume all oxides of alkali metals and alkali earth metals. During these test, ratios of alkali metal oxides and alkali earth metals to sulfur were higher than 3 for the tested fuels, which were far more than sufficient for sulfur capture. If one assumes that just part of the sulfur was generally captured by the metal oxides in this study, the utilization of available metal oxides for sulfur capture was below 1, as indicated in Figure S4 (see Supporting Information). The remaining metal oxides will be better reactants and also sufficient for Cl capture.

Previous studies by both thermodynamics equilibrium calculations (19) and cofiring tests (24, 35, 36) indicated that the presence of HCl and Cl_2 in the flue gas became lower, especially, when burning low-sulfur coal at temperatures was below 800 °C. The availability of alkali metal oxides should retain Cl species in the solid phase, which decreases gaseous Cl. Statistical analysis correlating the amount of oxides of alkali metals and alkali earth metals (Ca + Mg + Na + K), and the total gaseous chlorine are shown in Figure 3. This correlation was negative (increasing metal oxides decreased the occurrence of gaseous Cl) and strong with the linear R^2 value of 0.98. Similarly, the correlation between gaseous chlorine and the mercury emission rates is shown in Figure 3. It was found that the linear R^2 value was 0.75 for the gaseous chlorine and the mercury emission rate correlation. Therefore, the lower occurrence of Cl in the gas phase, which was attributed to a lower mercury oxidation rate, is a major reason for less mercury capture by fly ash for all fuels except for CW.
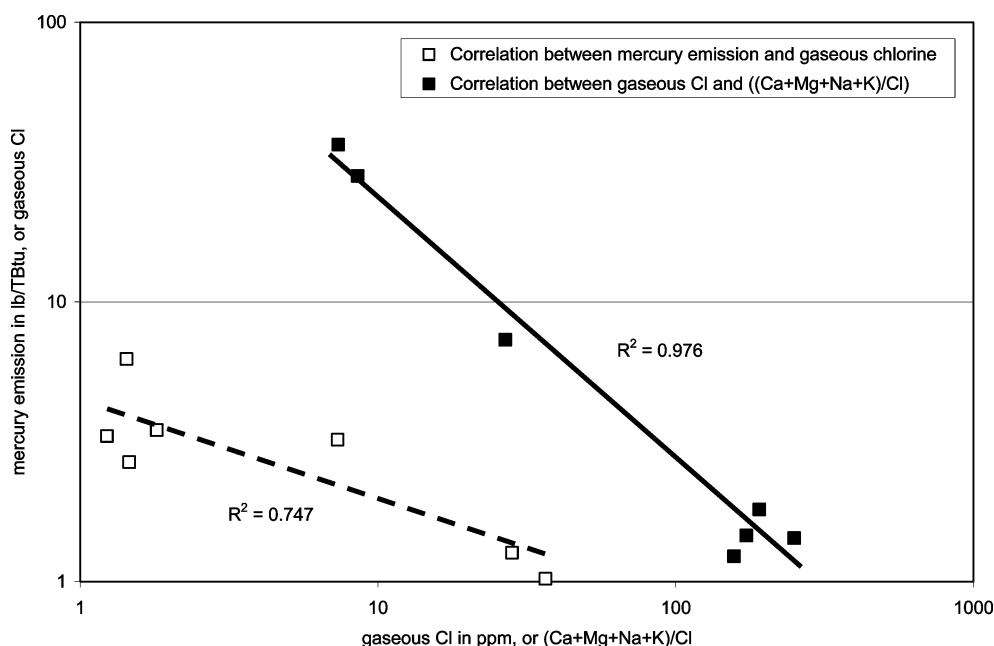
FIGURE 3. Correlation of mercury emission rate and gaseous Cl, the correlation of gaseous Cl and (Ca + Mg + Na + K)/Cl.

A previous study (*26*) by Institute for Combustion Science and Environmental Technology (ICSET) of Western Kentucky University (WKU) in a 0.1 MW fluidized bed combustor (FBC) facility found different trends on mercury speciation and mercury adsorption by fly ash during cofiring of high chlorine or coal with high chlorine polyvinyl chloride (PVC). Results indicated that using high-chlorine coal in an FBC system, the gas-phase mercury, which was around 45% of the total mercury input, was primarily in the oxidized state (40% of the total mercury input), while only a small portion (4.5% of total mercury input) still existed as elemental mercury in the flue gas. Close to 55% of the total mercury input was found in the solid phase.

In this previous study, it was that higher oxidized gaseous mercury and particle-bound mercury may have contributed to the use of secondary air and lower oxide content of alkali metal and alkali earth metal in a tested bituminous coal. Higher sulfur content was found in the bituminous coal. Therefore, a lower ROMC ratio should be true, when bituminous coal was burned with limestone was introduced. In addition, the secondary air likely produced higher carbon-content fly ash, which was critical for mercury adsorption (*28*). Furthermore, the secondary air also increased the temperature in the upper portion of the fluidized bed compared to the case without the secondary air injection. It was assumed that higher temperatures at the upper portion of the combustor made captured Cl by limestone inefficient, and thus, more Cl remained in the gas phase to oxidize the elemental mercury. Therefore, both higher content of alkali metal oxides or alkali earth metal oxides in tested biomass and the occurrence of temperatures lower than 650 °C in the upper part of the fluidized bed combustor seemed to be responsible for the reduction of gaseous chlorine and, consequently, for limited mercury emissions reduction during cofiring. This study identified the important impacts of temperature profile and oxides of alkali metal (alkali earth metal) on mercury emissions during cofiring in the fluidized bed combustor.

Acknowledgments

Supporting Information Available

Four figures showing the lab-scale fluidized bed coal combustor, gas phase chlorine concentration in the flue gas during cofiring in the fluidized bed combustor, ratios of (Ca + Mg + Na + K)/Cl in tested fuels during cofiring in the fluidized bed combustor, and sulfur removal efficiency or (Ca + Mg + Na + K)/S during cofiring in the fluidized bed combustor. This material is available free of charge via the Internet at http://pubs.acs.org.

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