ANALYSIS OF COMBUSTION PRODUCTS FROM THE COFIRING OF COAL WITH BIOMASS FUELS

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INTRODUCTION

The threat of increased global warming has subjected fossil fuels to increasing scrutiny in terms of greenhouse gas and pollutant emissions. As a result, using renewable and sustainable energy resources, such as biomass, for electricity production has become increasingly attractive. The use of dedicated biomass feedstocks for electricity generation could help reduce the accumulation of greenhouse gases because carbon dioxide is consumed during plant growth. The agricultural and wood products industries generate large quantities of biomass residues that could also provide fuel for electricity production. Increasing the use of these waste biomass fuels could alleviate the burdens of waste disposal in the agricultural and wood products industries.

Coal-fired power plants produce the most electricity in the United States. If biomass were cofired at low percentages in a small number of coal-fired power plants, the use of biomass for power production could dramatically increase. Cofiring biomass and coal increases the use of sustainable fuels without large capital investments, and takes advantage of the high efficiencies obtainable in coal-fired power plants. Fuel diversity is another advantage of biomass/coal cofiring. Cofiring reduces the need for a constant supply of biomass required as in a biomass power plant, and is a viable way to decrease the emissions of greenhouse gases and other pollutants from power-generating facilities.

Biomass and coal have fundamentally different fuel properties. Biomass is more volatile than coal and has a higher oxygen content. Coal, on the other hand, has more fixed carbon than biomass. In general, biomass contains less sulfur than coal, which translates into lower sulfur emissions in higher blending ratios of biomass. Wood fuels generally contain very little ash (~1% or less), so increasing the ratio of wood in biomass/coal blends can reduce the amount of ash that must be disposed. A negative aspect of biomass is that it can contain more potassium and chlorine than coal. This is particularly true for some grasses and straws.

Several utilities have tested biomass/coal cofiring in utility boilers.[1,2] Several issues still remain regarding how blending biomass and coal will affect combustion performance, emissions, fouling and slagging propensities, corrosion, and ash saleability.[3] In an effort to further address some issues that biomass/coal cofiring faces, representatives from the National Renewable Energy Laboratory, Sandia National Laboratories Combustion Research Facility, and the Federal Energy Technology Center have embarked on a collaborative effort to study many of the fireside issues pertaining to biomass/coal cocombustion such as ash behavior, particle capture efficiency, carbon burnout, NO_x and SO_x emissions, and reactivity. This paper describes bench-scale biomass/coal cofiring experiments that support this effort.

EXPERIMENTAL APPROACH

The combustion behavior, gaseous emissions, and alkali metals released during the combustion of several biomass/coal blends were investigated with a direct sampling, molecular beam mass spectrometer (MBMS) system[4] in conjunction with a high temperature quartz-tube reactor that has been described in detail in the literature.[5,6]

The biomass and coal samples, including the blends, were provided by L. Baxter of the Sandia Combustion Research Facility. In this study, results are presented for blends of Pittsburgh #8 coal with red oak wood chips, Danish wheat straw, and Imperial wheat straw (from California). Blends are reported as a percentage on an energy input basis, based on the higher heating value of the feedstock. The blends investigated during this study consisted of 15% biomass, on an energy input basis, with Pittsburgh #8 coal.

Twenty to thirty milligrams of the blended samples were loaded into hemi-capsular quartz boats that were placed in a platinum mesh basket attached to the end of a ¼- inch diameter quartz rod. This quartz rod can be translated into a heated quartz-tube reactor enclosed in a two-zone variable temperature furnace. Furnace temperatures were maintained at 1100°C, and a mixture of 20% O_2 in He was flowed through the reactor at a total flow rate of 3.0 standard liters per minute. Gas temperatures near the quartz boat were measured with a type-K thermocouple inserted through the quartz rod. The actual boat temperature and the flame temperature were not measured.

Triplicate samples were studied to establish experimental reproducibility. The MBMS results for the pure fuels and the blends were similar to previous results for biomass and coal combustion.[5,6] All of the samples exhibited multiple phases of combustion, including the devolatilization and char combustion phases. The char combustion phase for coal was generally longer than for biomass. The blends showed a similarly longer char combustion phase compared to the pure biomass.

RESULTS AND DISCUSSION

Pittsburgh #8/Biomass Blends

MBMS results were obtained for combustion of Pittsburgh #8 coal, the pure biomass fuels, and blends of 15% of the biomass with Pittsburgh #8, in 20% O_2 in He at 1100°C. The relative amounts of individual combustion products were determined by integrating the individual time versus intensity profiles for the given ions measured during the combustion event. Only results for four of the detected combustion products, NO, HCl, SO_2, and KCl, are presented. For example, Figure 1 presents the relative intensities of the ions with $m/z = 30$ (NO^+), $m/z = 36$ (HCl^+), $m/z = 64$ (SO_2^+), and $m/z = 74$ (KCl^+) as measured during the combustion of Pittsburgh #8 coal, Imperial wheat straw, Danish wheat straw, red oak, and the biomass/coal blends. The results represent the averages of the triplicate samples studied and the intensities were normalized to the background $^{34}O_2^+$ signal intensity and the sample weight. The error bars represent one standard deviation.

The Pittsburgh #8 sample contains 1.53% nitrogen. The most NO was observed during combustion of this coal sample. The wheat straws contain 1% nitrogen and the red oak contains only 0.09% nitrogen; hence, less NO was detected during combustion of the biomass samples. The amount of NO detected during combustion of the blends was less than that observed during combustion of the pure coal which suggests that the NO_x released during combustion of the blends (compared to the pure fuels) was diluted. The Imperial wheat straw contains the most chlorine (2.46%) of the four samples; as a result, the most HCl was observed during combustion of this sample. Less HCl was detected during the combustion of the coal/wheat straw blends compared to combustion of the pure wheat straws.

Pittsburgh #8 coal contains almost 4% sulfur, 10 times more than found in any of the biomass fuels. Not surprisingly, the largest amount of SO_2 was released during combustion of Pittsburgh #8 coal. The amount of SO_2 released during combustion of the biomass fuels was significantly less compared to the Pittsburgh #8 coal combustion. During combustion of the blends, the amount of SO_2 released was less than the pure coal but substantially more than detected during combustion of the biomass fuels.

As stated, the Imperial wheat straw sample has the highest chlorine content of the four pure fuels and has the highest potassium content (2.5%). Consequently, the most KCl^+ was detected during combustion of this biomass sample. The alkali metal released during the coal combustion was quite low, and blending the high alkali metal-containing biomass with the coal reduced the amount of alkali metal vapors detected during combustion compared to the pure biomass.

The remaining figures display the relative amounts of products detected during combustion of a Pittsburgh #8/biomass blend compared to what would be expected based on the combustion results for the pure fuels. For example, Figure 2 shows the relative amounts of SO_2 released during combustion of the three blends compared to a calculated amount of SO_2 expected for each blend. The calculated values were determined by taking the appropriate ratios of the amount of SO_2 detected during the combustion of the pure coal and pure biomass fuel that comprised the blend of interest. Within experimental error, the amount of SO_2 detected during combustion of the Pittsburgh #8/biomass blends was expected based on the combustion results for the pure fuels and any reduction in the amount of SO_2 observed during combustion of the blends was a result of dilution. The same conclusion can be drawn from Figure 3 for the amount of NO released during combustion of the blends.

The relative amounts of HCl^+ detected during combustion of the Pittsburgh #8/biomass blends are shown in Figure 4. The measured amount of HCl^+ detected during the combustion of the Pittsburgh #8/red oak blend appears to be close to that expected based on the combustion results for the pure fuels. In fact, both fuels have very low levels of chlorine, and not much HCl^+ was expected. Conversely, the wheat straws have much higher chlorine contents than either the red oak or the coal, and higher levels of HCl^+ were detected during combustion of the pure wheat straws and the blends of the coal with wheat straw. During combustion of the Imperial wheat straw blend, more HCl^+ was detected than expected based on the combustion results for the pure fuels. This difference is not statistically significant for the Danish wheat straw blend. Blending the coal with the high chlorine-containing wheat straws seems to affect the amount of HCl produced during combustion. This may be a function of the chlorine content of the biomass fuel. The Imperial wheat straw was 2.46% chlorine; the Danish wheat straw was 0.61% chlorine. The error bars on these measurements are quite large; however, if this conclusion proves to be valid this could have important implications concerning high temperature corrosion in coal-fired boilers that cofire high chlorine-containing fuels such as herbaceous biomass, plastics, and municipal solid waste.

Figure 5 shows the relative amounts of KCl^+ detected during combustion of the Pittsburgh #8/biomass blends compared to the levels of KCl^+ expected based on the combustion results for the pure fuels. The amount of KCl^+ detected during combustion of the Pittsburgh #8/red oak blend was as expected. The amount of KCl^+ observed during combustion of the coal/wheat straw blends was less than expected based on the combustion results for the pure fuels. Based on the results in Figures 4 and 5, the partitioning of chlorine in the gas phase seems to have been affected by blending the high alkali metal- and chlorine-containing wheat straws with coal.

Thermochemical Equilibrium Calculations

An equilibrium analysis of the biomass/coal blend combustion was undertaken in an attempt to explain some of the observations made during the batch combustion experiments. The calculations were performed with a modified version of STANJAN,[7] a thermodynamic equilibrium computer code that minimizes the Gibbs free energy of the system via the method of element potentials with atom population constraints. Information about the mechanics and mathematics of the program is available in the literature.[8] The main program has been modified to accept as many as 600 species and 50 phases.[9] A comprehensive database of species and related thermodynamic data was used to predict the equilibrium gas- and condensed-phase compositions given an initial temperature and pressure as well as the populations of Al, Ba, C, Ca, Cl, Fe, H, He, K, Mg, Mn, N, Na, O, P, S, and Si. Gas-phase species were treated as ideal gases and the condensed-phases were assumed to be ideal solid solutions. This simplified treatment of the condensed phases may not be an accurate representation of reality, and caution should be exercised in overinterpreting the calculated condensed-phase species mole fractions.

Table 1 shows a small subset of the many gas- and condensed-phase species predicted by calculating the equilibrium concentrations of available products with the input elemental compositions of the various fuels and blends studied experimentally. Equilibrium product compositions were calculated for the Pittsburgh #8 coal, the three biomass fuels, and the three coal/biomass blends that were studied experimentally. The calculated values for the blends represent the equilibrium concentrations that would be expected based on the appropriate ratios of those species as predicted from the calculations for the pure fuels. The equilibrium mole fractions of NO and SO_2 are consistent with the expected mole fractions based on the calculations for the pure fuels. This signifies that any difference in the amounts of SO_2 and NO measured during combustion of Pittsburgh #8/biomass blends is caused by dilution. This is consistent with the experimental results.

The equilibrium amounts of HCl and KCl vapors show similar trends observed experimentally. There is more HCl in the gas phase based on the equilibrium calculations on the compositions of the blends compared to the amount of HCl calculated from the compositions of mixtures of the pure fuels. Conversely, less gas-phase KCl is predicted from the compositions of the blends versus the amount of KCl calculated from the ratios of the equilibrium results for the pure fuels.

Within the limitations of how realistically the equilibrium calculations treat the condensed phase, the effect of blending coal and biomass on the composition of the ash as determined from the equilibrium calculations can be interpolated. For instance, the amounts of condensed-phase KCl calculated for the blends are lower than expected based on the amounts of KCl determined for the pure fuels. The results of the calculations suggest that the concentrations of the alkali aluminosilicates are enhanced when the coal and biomass fuels are blended compared to a simple ratio based on the equilibrium results for the pure fuels.

CONCLUSIONS

The MBMS results for the relative amounts of NO and SO_2 detected during the combustion of the coal/biomass blends suggested that any decrease in the amount of NO or SO_2 observed because of blending coal and biomass was the result of diluting the nitrogen and sulfur present in the fuel blend. The chlorine released during the combustion of the coal/biomass blends, however, may have been affected by blending the two fuels beyond a dilution effect. Improving the experimental reproducibility in future studies would confirm this hypothesis. Particularly that the amount of HCl detected during the combustion of the coal/wheat straw blends was higher than expected based on the combustion results for the pure fuels and that the amount of KCl detected during the combustion of the coal/wheat straw blends was lower than expected.

Blending coal and high chlorine and alkali containing fuels seems to affect the chlorine equilibrium in such a way that cannot be explained based on just mixing of the pure fuels. Other chemical interactions between the two blended fuels affect the partitioning of chlorine in the gas phase between alkali and hydrogen chlorides.

The results of the equilibrium calculations qualitatively help to explain the repartitioning of the gas phase chlorine inferred from the MBMS results. The amount of HCl in the gas phase is enhanced compared to the amount expected from a simple blending of the pure fuels at the expense of gas phase KCl. The potassium, however, is sequestered in the ash in the form of potassium aluminosilicates. The high concentrations of aluminum and silica in the coal tend to interact with the large amount of potassium in the wheat straws.

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REFERENCES

1. Boylan, D.M. (1993). "Southern Company Tests of Wood/Coal Cofiring in Pulverized Coal Units." Proceedings from the conference on Strategic Benefits of Biomass and Waste Fuels, March 30-April 1, 1993 in Washington, DC. EPRI Technical Report (TR-103146), pp. 4-33 - 4-45.
2. Gold, B.A. and Tillman, D.A. (1993). "Wood Cofiring Evaluation at TVA Power Plants EPRI Project RP 3704-1." Proceedings from the Conference on Strategic Benefits of Biomass and Waste Fuels, March 30-April 1, 1993 in Washington, DC. EPRI Technical Report (TR-103146), pp. 4-47 - 4-60.
3. Tillman, D.A. and Prinzing, D.E. (1995). "Fundamental Biofuel Characteristics Impacting Coal-Biomass Cofiring." Proceedings from the Fourth International Conference on the Effects of Coal Quality on Power Plants, August 17-19, 1994 in Charleston, SC. EPRI Technical Report (TR-104982), pp. 2-19.
4. Evans, R.J. and T.A. Milne, *Energy and Fuels* 1, 311-319 (1987).
5. Dayton, D.C.; French, R.J.; Milne, T.A., *Energy and Fuels*, 9(5), 855-865 (1995).
6. Dayton, D.C. and T.A. Milne, (1995). "Laboratory Measurements of Alkali Metal Containing Vapors Released during Biomass Combustion," in Application of Advanced Technologies to Ash-Related Problems in Boilers, edited by L. Baxter and R. DeSollar, Plenum Press, New York, pp. 161-185.
7. Reynolds, W.C., (1986). "The Element Potential Method for Chemical Equilibrium Analysis: Implementation in the Interactive Program STANJAN," Department of Mechanical Engineering, Stanford University. January 1986.
8. Van Zeggemon, F.; Storey, S.H. The Computation of Chemical Equilibria, Cambridge, England, 1970, Chapter 2.
9. Hildenbrand, D.L.; Lau, K.H., (1993). "Thermodynamic Predictions of Speciation of Alkalis in Biomass Gasification and Combustion." SRI International, Inc. Final Report for NREL Subcontract XD-2-11223-1, Menlo Park, CA, February 1993.

Table 1. Diluted and equilibrium mole fractions calculated for biomass/coal blends at 1100°C, multiplied by a factor of 10^4.

Species (phase: g = gas, c = condensed)	Pittsburgh #8/Imperial wheat straw blend		Pittsburgh #8/Danish wheat straw blend		Pittsburgh #8/Red oak blend	
	Diluted mole fraction	Equilibrium mole fraction	Diluted mole fraction	Equilibrium mole fraction	Diluted mole fraction	Equilibrium mole fraction
NO (g)	3.17	3.14	2.54	3.20	3.18	3.20
SO_2 (g)	15.6	17.9	16.0	18.2	16.1	17.8
HCl (g)	1.05	1.63	0.497	0.879	0.364	0.412
KCl (g)	3.27	1.01	1.12	0.212	0.0179	4.63×10^{-3}
KCl (c)	71.1	22.7	23.6	4.63	0.389	0.101
$NaAlSiO_4$ (c)	260	1320	250	400	320	310
$KalSiO_4$ (c)	25.5	250	25.7	230	110	19.7
$KAlSi_3O_8$ (c)	160	690	160	810	280	150

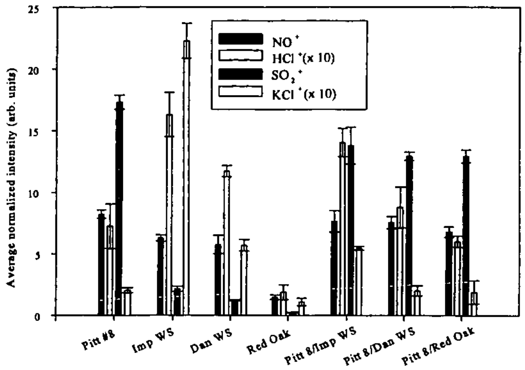

FIGURE 1. Measured amounts of NO, HCl, SO_2, and KCl released during the combustion of pure and blended fuels.

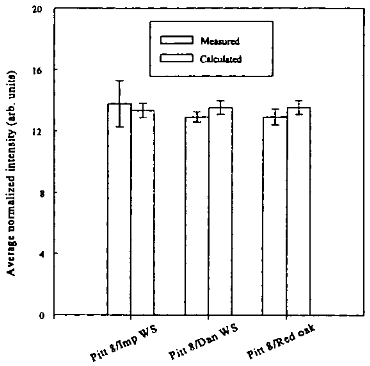

FIGURE 2. Measured and predicted amounts of SO_2 released from Pittsburgh #8/biomass blends.

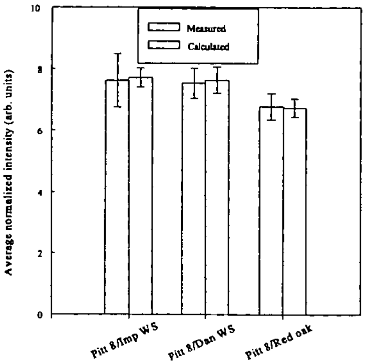

FIGURE 3. Measured and predicted amounts of NO released from Pittsburgh #8/biomass blends.

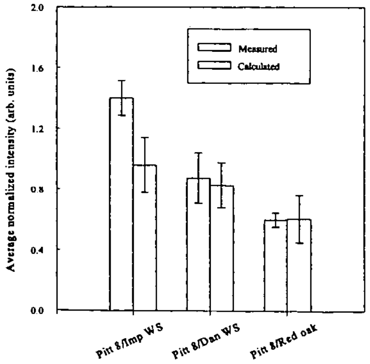

FIGURE 4. Measured and predicted amounts of HCl released from Pittsburgh #8/biomass blends.

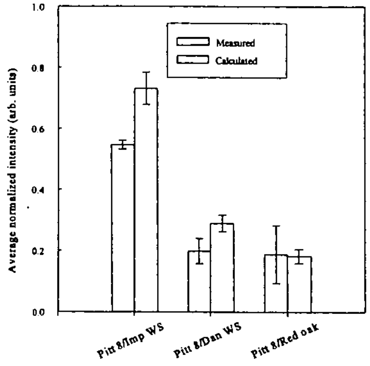

FIGURE 5. Measured and predicted amounts of KCl released from Pittsburgh #8/biomass blends.