Mechanisms of Alkali Metal Release During Biomass Combustion

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Introduction

The conversion of biomass materials into electricity via combustion poses several technical and economic challenges. One of the more pressing technical challenges associated with biomass combustion is fouling and slagging in combustors. Accelerated fouling and slagging in current biomass combustion facilities has been linked to the alkali metal content of the fuel. Alkali metal release during biomass combustion causes significant problems in terms of severe fouling and slagging of heat transfer surfaces in boilers thus reducing efficiency, and in the worst case leads to unscheduled plant downtime[1]. Future biomass to electricity facilities that will incorporate integrated combined cycle systems that use biomass combustion gases directly to drive an aeroderivative turbine[2] will have even lower tolerances for alkali metal vapor release because accelerated erosion and corrosion of turbine blades results in shorter turbine lifetimes.

Hot gas cleanup methods are sought that reduce the amount of alkali vapor in biomass combustion gases to acceptable levels, thus minimizing fouling and slagging. This would be facilitated by a detailed understanding of the mechanisms of alkali release during biomass combustion as well as identifying these alkali vapor species and how these vapors lead to fouling and slagging. Our experimental approach to these issues is to identify the form of alkali metal vapors from directly sampled hot gases liberated from the combustion of small biomass samples in a variable temperature quartz tube reactor employing a molecular beam mass spectrometer (MBMS) system to monitor the combustion event. The baseline condition chosen for studying alkali metal release during biomass combustion was 1100°C in 20% O_2 in helium (simulated air). This temperature is approaching the maximum turbine inlet temperatures used for the next generation of direct biomass-fired turbines for power production. Under these conditions, the large excess of oxygen assured complete combustion and the furnace temperature was high enough to insure the partial volatilization of alkali metal containing species. By screening a large variety of biomass samples for alkali metal release, it may be possible to determine combustion conditions that minimize alkali metal release. These results may also be used to identify methods for reducing the alkali metal vapor content of the hot combustion gases.

Experimental

The release of alkali metal vapor species during biomass combustion was monitored and studied using a direct sampling, molecular beam mass spectrometer (MBMS) system. The MBMS system is ideally suited for studying the high temperature, ambient pressure environments encountered during the present alkali metal screening studies. The integrity of the sampled, high temperature combustion gases is preserved by the free-jet expansion because chemical reactions are effectively quenched and condensation is inhibited. The nature of the free jet expansion and the subsequent formation of a molecular beam allows reactive and condensable species, such as alkali metal containing vapors, to remain in the gas phase at temperatures far below their condensation point for long periods of time in comparison to reaction rates. The details of the apparatus and its application to studying alkali metal release during switchgrass combustion are described in the literature[3-5].

Small (20-60 mg) samples were combusted in a tubular quartz reactor that was placed in a standard two-zone, electric clam-shell furnace[5] set at either 1100°C or 800°C. Biomass samples were loaded into hemi-capsular quartz boats of such a size that approximately 40 mg of ground, loosely packed, material filled the boat, depending on the feedstock. The actual boat temperature and flame temperature were not measured, however, the hot gas temperature in the vicinity of the sample boat could be monitored with a type-K (chromel-alumel) thermocouple. A mixture of oxygen (20%, 10%, or 5%) in helium flowed through the reactor from back to front at a total gas flow rate of 4.4 standard liters per minute. Combustion gases had a residence time of about 0.1 seconds in the reactor before reaching the sampling orifice. When appropriate, steam was added to the reactor atmosphere by injecting water into the rear of the furnace through a needle fed by a syringe pump. Stainless steel shot was packed around the tip of the needle to increase the surface area for water evaporation. This provided a steady flow of 20% steam by volume.

The end of the reactor was fitted around the tip of the sampling orifice positioned at the downstream end of the quartz tube reactor to sample the high temperature, ambient pressure biomass combustion gases. The orifice protruded into the furnace to keep it at an elevated temperature and thus prevent condensation on the sampling cone. The actual temperature of the orifice was not routinely measured, however, when the furnace temperature was set at 1100°C the tip of the orifice was observed to glow orange. Sampled gases underwent a free jet expansion into the first stage of the differentially pumped vacuum system. The expanded gases were skimmed by a second conical skimmer (1 mm orifice diameter) at the entrance to the second stage forming a molecular beam that was directed into the ionization region of the mass spectrometer in the third stage of the vacuum system. Ions were formed by electron impact ionization of the sampled gases with a nominal electron energy of 25 eV. The ions were filtered by a triple quadrupole mass analyzer and detected with an off axis electron multiplier. The mass spectrometer was scanned continuously at a rate of approximately 100 amu/sec. In this configuration, a complete mass spectrum was recorded once every 1.0 to 1.5 seconds. Background subtraction from the total ion signal yielded corresponding mass spectra at a given time during the combustion event or averaged over a given phase of the combustion event.

A total of 23 different biomass feedstocks have been screened for alkali metal vapor release under four different combustion conditions. Only the results from one combustion condition, 1100°C and 20% oxygen in helium, will be discussed below. The list of feedstocks is as follows: planer shavings of lodgepole pine (*Pinus contarta*); eucalyptus (*Eucalyptus saligna Sm.*); poplar (*Populus deltoides x nigra var. Caudina*); corn stover (*Zea mays L.*); switchgrass (*Panicum virgatum L.*); wheat straw (*Triticum aestivum.*); rice straw; (Sandia) switchgrass (*Panicum virgatum L.*); pistachio shells (*Pistacia vera*); almond shells (*Prunnus amygdalus*); almond hulls (*Prunnus amygdalus*); wood waste #1; wood waste #2; waste paper; Danish wheat straws (*Triticum aestivum*) from Slagelse and Haslev (Danish power plants) (SLAG001, SLAG002, and HAS001); alfalfa stems (*medicago sativa L.*) (IGT001 and IGT002); summer switchgrass (*Panicum virgatum L.*); Dakota switchgrass (*Panicum virgatum L.*); and two willows (*Salix veminalus, Salix alba*, tops only). This set of feedstocks can be divided into various classes of biomass identified as woody feedstocks, herbaceous feedstocks, grasses, agricultural residues, and waste feedstocks. It will become apparent that the varying nature of the feedstocks results in unique differences in terms of alkali metal release during combustion.

Results and Discussion

The combustion of the solid biomass samples occurs in three distinct phases: the combustion phase, the char combustion phase, and the ash cooking phase[4,5]. The details of the combustion event are available in the literature[5]. Based on these studies, it became obvious that the most important information concerning the species and amount of alkali metal released during biomass combustion was contained in the mass spectra averaged over the char combustion phase. Mass spectra averaged during the char combustion phases of all 23 feedstocks screened for alkali metal release qualitatively reflected the feedstock composition as determined from the ultimate and ash analyses. Although the ultimate analysis can be used to determine the total amount of alkali metal in a given feedstock, it does not reflect how much alkali metal is released into the gas phase nor the form of the alkali metal released.

The mass spectra averaged during the char combustion phase of the woody feedstocks (pine, eucalyptus, poplar, and willow) revealed that little alkali metal was released. As an example, the char phase mass spectrum averaged during the combustion of willow is presented in Figure 1. The mass spectral results are consistent with the ultimate and ash analyses for this willow sample that indicate low alkali metal levels. The only indication of alkali metal release is the detection of K^+, however, the parent alkali metal species which yield this fragment could not be identified. Based on previous results[4], the primary mechanism for alkali metal release during the combustion of low alkali containing woody feedstocks involves the vaporization or decomposition of potassium sulfate.

In general, the straws and grasses (switchgrass, wheat straw, alfalfa stems, and rice straw) contain high levels of potassium and chlorine. The mass spectrum averaged during the char phase of rice straw combustion is shown in Figure 2. Based on the composition of rice straw (shown in the inset) determined from the ultimate and ash analysis of the sample, this feedstock has high levels of both potassium and chlorine. As a result, strong mass spectral signals are observed at m/z=74 and 76, corresponding to the KCl parent ions. In fact, the fragment ions of the KCl dimer (K_2Cl^+ at m/z = 113 and m/z = 115) were also observed. Significant intensity was also observed at m/z=39, the K^+ fragment. The intensity of these signals is a function of the amounts of potassium and chlorine available in the feedstock. For high chlorine containing feedstocks, like rice straw, it is also possible to identify HCl released during combustion. The dominant mechanism for alkali metal release during the combustion of feedstocks with high potassium and chlorine contents is through the vaporization of potassium chloride.

The agricultural residues, pistachio shells, almond shells, and almond hulls, tend to have high potassium content but low chlorine content. In fact, the almond hulls have the highest level of potassium of all 23 feedstocks studied. The mass spectrum averaged over the char phase of almond hulls combustion is shown in Figure 3. The dominant alkali metal species observed in the char phase mass spectra averaged during almond hulls combustion were potassium hydroxide (m/z = 56) and potassium cyanate, KOCN (m/z = 81). The high nitrogen content in addition to the high potassium content of the almond hulls and the oxidizing combustion conditions contribute to the formation of KOCN. At this time it is not clear whether KOCN is directly released or KCN is released and then reacts with oxygen to form the cyanate. The relatively low chlorine level of the almond hulls forces the alkali metal release to other thermodynamically stable forms.

The waste feedstocks (wood waste #1, wood waste #2, and waste paper) are not as bad as their name implies in terms of alkali metal release. These feedstocks tend to have relatively low alkali levels, and as a result, it was difficult to identify any alkali species in the mass spectra averaged over the char combustion phases of these feedstocks. The waste feedstocks do have moderately high chlorine levels (0.13 w%). However, HCl was the only chlorine species identified in the char phase mass spectra.

Multiple alkali release mechanisms can occur simultaneously during biomass combustion depending on the feedstock composition. This is most apparent from the mass spectral results recorded during the char phase of alfalfa stems combustion shown in Figure 4. Alfalfa stems have a high potassium, chlorine, and nitrogen content. As a result, there is substantial alkali metal released in the form of KCl, KOH, and KOCN.

Once the major biomass combustion products were identified, including the major alkali metal containing species released, correlations were sought between the mass spectral data and the ultimate analysis data for the 23 feedstocks screened. The chlorine content determined in the ultimate analyses correlated well with the mass spectral intensities of identifiable chlorine containing species, HCl and KCl, monitored at m/z=36 and 74 (HCl^+ and KCl^+, respectively). Most of the available chlorine is released into the gas phase and can be accounted for during biomass combustion[6].

The potassium content of a given feedstock does not correlate as well with the parent and fragment ions (KOH^+, $KOCN^+$, KCl^+, and K^+) identified in the char phase mass spectra that result from the dominant gas phase potassium species. The overall potassium content of a given feedstock does not necessarily correspond to a high level of alkali metal vapor released during biomass combustion[6]. Almond hulls have the highest potassium content of the 23 feedstocks, yet combustion of almond hulls does not release the most potassium vapor (KCl, KOH, and/or KOCN). Rice straw has a high potassium content, however, it also has the highest chlorine content of any of the 23 feedstocks. As a result, significant alkali metal vapor is released as KCl during rice straw combustion. Alfalfa stems and switchgrass also have a high potassium and chlorine content that accounts for the above average alkali metal vapor released during combustion. It appears that those feedstocks with high potassium and the higher chlorine levels tend to release more alkali metal vapors (based on an average of the 23 feedstocks studied) than those feedstocks with high potassium and low chlorine contents.

Conclusions

The MBMS technique has proven to be a valuable and versatile tool for studying alkali vapor release during biomass combustion. The most significant parameter which affects alkali vapor release is the feedstock being combusted. While each individual feedstock appears to have it's own unique combustion properties, these feedstocks can often be grouped together into classes of feedstocks. Woody feedstocks have comparatively little alkali content and low levels of chlorine. Consequently, combustion of woody feedstocks leads to very little alkali vapor release, usually via a mechanism involving the vaporization of potassium sulfate.

Herbaceous feedstocks, grasses and straws contain very high levels of alkali and chlorine compared to the woody feedstocks. Large amounts of alkali metal, in the form of potassium chloride, are released into the gas phase during combustion of herbaceous feedstocks which results in a high fouling and slagging potential for these feedstocks. The results of these alkali screening studies implicate the chlorine content of a given feedstock as a facilitator of alkali release[6].

While chlorine content has been linked to substantial alkali vapor release, it is not essential. The agricultural residues still release significant amounts of alkali vapor during combustion, however, the alkali is in the form of the hydroxide and potassium cyanate instead of the chloride. These studies identify a new mechanism for alkali metal release that involves the formation of potassium cyanate. This mechanism of alkali transport seems to be dominant during the combustion of feedstocks that have high potassium and nitrogen contents.

Having identified these dominant gas phase species it should be possible to identify how these alkali metal containing species contribute to fouling and slagging in industrial combustion systems. Methods can now be sought to sequester or reduce the level of these species in the gas phase if they prove to be major precursors to deposit formation. Additives to the bed material in fluid bed combustors can be sought to capture these species after they are released. Alkali getter beds or separate hot gas cleanup units can be designed knowing that the major alkali species in the gas phase have been identified based on the feedstocks screened in this study.

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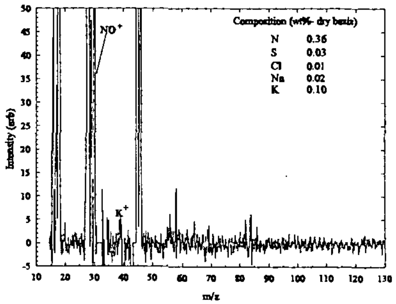

Figure 1: Mass spectrum averaged over the char phase of willow combustion at 1100°C in 20% oxygen in helium. The signals have been normalized to the $^{34}O_2^+$ signal measured before sample insertion. The composition in the inset is from the ultimate and ash analyses of the feedstock on a moisture free basis.

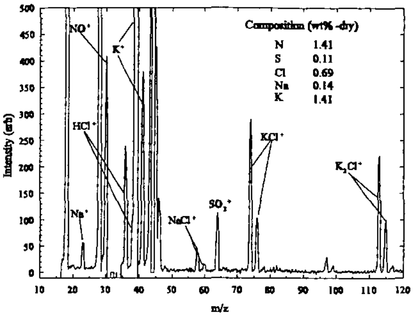

Figure 3: Mass spectrum averaged over the char phase of rice straw combustion at 1100°C in 20% oxygen in helium. The signals have been normalized to the $^{34}O_2^+$ signal measured before sample insertion. The composition in the inset is from the ultimate and ash analyses of the feedstock on a moisture free basis.

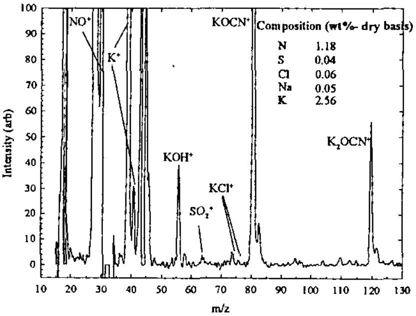

Figure 4: Mass spectrum averaged over the char phase of almond hulls combustion at 1100°C in 20% oxygen in helium. The signals have been normalized to the $^{34}O_2^+$ signal measured before sample insertion. The composition in the inset is from the ultimate and ash analyses of the feedstock on a moisture free basis.

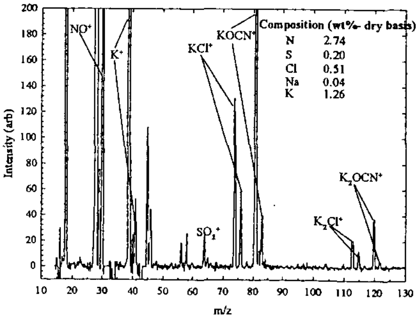

Figure 2: Mass spectrum averaged over the char phase of alfalfa stems combustion at 1100°C in 20% oxygen in helium. The signals have been normalized to the $^{34}O_2^+$ signal measured before sample insertion. The composition in the inset is from the ultimate and ash analyses of the feedstock on a moisture free basis.