Investigations on the Influence of Additives for SO_2 Reduction during High Alkaline Biomass Combustion

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Straw and other biomasses can cause severe problems when used as fuel in combustion systems. Some of the major problems include high emission of alkalis, HCl, and especially SO_2 to the gas phase. The development of low-cost primary measures for achieving a SO_2 emission below the European Union (EU) emission limit of 200 mg/Nm^3 without the need for the installation of a flue gas desulfurization unit requires an increased understanding of the chemistry of biomass combustion. For this reason, laboratory combustion experiments with two different high alkaline (HIAL) biomasses doped with additives have been conducted in the temperature range of 800−1100 °C. The use of a high-pressure mass spectrometry (HPMS) sampling technique allows the on-line specification of combustion byproducts such as K, Na, S, and Cl species in the combustion flue gases. The results of the measurements show that the SO_2 emission may be related to the K/S and K/Si ratios in the initial samples. The release of potassium is mostly dependent on the chlorine content of the samples. Calcium- and potassium-based additives are able to reduce the release of SO_2 into the gas phase.

Introduction

An increased use of renewable energy sources for energy production is used to achieve the 8% reduction in CO_2 emissions of the European Union (EU) by 2012 (the Kyoto Objective). In this context, electricity from biomass and biomass-derived fuels is considered to be a possible energy source for the future. Straw and other high alkaline (HIAL) biomasses are important fuel resources, and ~800 Mt of straw are actually usable for energy production in the EU und North America.[1]

Grate firing is the only combustion technique that allows the use of 100% straw as fuel. The grate firing of straw is characterized by a high propensity for slagging and fouling, limited steam temperatures, and relatively high emissions.[2] Full-scale testing programs with existing straw-fired combined heat and power (CHP) plants show that the alkali chemistry in the grate combustion process has a strong influence on the emission of pollutants and corrosion behavior.[3] Emissions of SO_2 and HCl from grate combustion of straw are highly variable on an hourly basis and do not correlate directly with the content of sulfur and chlorine in the fuel, but are somehow related to the chemistry of the combustion process.[4]

Measurements at some straw-fired power plants in Denmark have revealed that the SO_2 emissions often significantly exceed the value of 200 mg/Nm^3 (dry, 6% O_2), which is the emission limit in the proposal for a revised EU directive on emissions from large combustion plants.[3,5] The technical objective is to develop low-cost primary measures for achieving SO_2 emissions below the limit of 200 mg/Nm^3 without the installation of a desulfurization unit.[3]

Calcium and potassium are known for their ability to capture sulfur at elevated temperatures, via the formation of calcium and potassium sulfates under oxidizing conditions.[6] The sulfur can be retained by being bound to bottom ash or slag, via the formation of $CaSO_4$ or K_2SO_4 with the calcium and potassium in the fuel in the temperature range of 600−800 °C.[7] At higher temperatures, calcium and potassium may be incorporated into silicate structures and no longer be available for sulfate formation. Therefore, the maximum achievable sulfur retention in straw ash is dependent on the Ca/Si and K/Si ratios in the fuel.

Today, the SO_2 emission of fluidized-bed combustors is controlled by adding dolomite or other calcium-

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(1) *Production Yearbook 2002*, Vol. 56; FAO Statistics Series; Rome, 2002.

(2) Jensen, P. A.; Frandsen, F. J.; Dam-Johansen, K. HCl and SO_2 Emissions from Full-Scale Biomass-Fired Boilers. In *Power Production in the 21st Century: Impacts of Fuel Quality and Operations*, Snowbird, UT, 2001; United Engineering Foundation: New York, 2001.

(3) Sander, B.; Henriksen, N.; Larsen, O. H.; Skriver, A.; Ramsgaard-Nielsen, C.; Dam-Johansen, K.; Frandsen, F. J.; van der Lans, R.; Hansen, J. Emissions, Corrosion and Alkali Chemistry in Straw-Fired Combined Heat and Power Plants. In *1st World Conference on Biomass for Energy and Industry*, Sevilla, Spain, 2000.

(4) Jensen, P. A.; Frandsen, F. J.; Dam-Johansen, K.; Sander, B. Experimental Investigation of the Transformation and Release to Gas Phase of Potassium and Chlorine during Straw Pyrolysis. *Energy Fuels* **2000**, *14*, 1280−1285.

(5) Directive 2001/80/EC of the European Parliament and of the Council of 23rd October 2001 on the Limitation of Emissions of Certain Pollutants into the Air from Large Combustion Plants. *Off. J. Eur. Communities: Legis.* **2001**, *44* (November), L307.

(6) Cheng, J.; Zhou, J.; Liu, J.; Zhou, Z.; Huang, Z.; Cao, X.; Zhao, X.; Cen, K. Sulfur Removal at High Temperature during Coal Combustion in Furnaces: A Review. *Prog. Energy Combust. Sci.* **2003**, *29*, 381−405.

(7) Knudsen, J. N.; Jensen, A. P.; Lin, W.; Frandsen, F. J.; Dam-Johansen, K. Sulfur Transformations during Thermal Conversion of Herbaceous Biomass. *Energy Fuels* **2004**, *18*, 810−819.

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Table 1. Ultimate Analysis of the Biomass Samples

	Composition (wt %, dry)	
element	HIAL 5 winter barley	HIAL 10 wheat 2000
Al	0.008	0.040
C	45	46
Ca	0.39	0.34
Cl	1.1	0.3
Fe	0.005	0.02
K	2.5	1.3
Mg	0.1	0.07
Na	0.3	0.02
P	0.05	0.08
S	0.19	0.15
Si	0.82	1.5

containing substances to the bed material.[8,9] The sulfur then undergoes a gas−solid reaction when in contact with a Ca species, such as $Ca(OH)_2$, CaO, or $CaCO_3$. The turbulent regime in fluidized beds leads to sufficient contact of the S species with the bed material to fulfill the necessary reactions. The sulfur retention of modern pressurized fluidized-bed combustion (PFBC) systems approaches values of >90%.[9]

Future biomass power plants will be grate-fired at temperatures of ~1100 °C. However, for the latter type of combustion system, the problem of SO_2 emission has yet to be solved. The use of a downstream desulfurization unit should be avoided under all circumstances, because of its high capital costs. One way to minimize the SO_2 emission of biomass fired boilers is to blend the biomass with sorbents before firing it on the grate.

For this reason, laboratory combustion experiments have been performed for two different HIAL biomasses. The combustion products were investigated on-line by a high-pressure mass spectrometer. Six calcium- and potassium-based additives were added to the biomasses in different quantities to investigate their influence on the SO_2 release. The results of this work, among others, will be the basis for a further development of grate-fired biomass power plants.

Experimental Section

Fuel Preparation. Samples of the high alkali biomass fuels—HIAL 5 (winter barley) and HIAL 10 (wheat)—were collected and prepared for analysis. All fuels were milled through a 1-mm screen for the present studies. The biomass fuels were air-dried at room temperature and archived under dry conditions until the time of the study. The ultimate analysis for the investigated fuels is presented in Table 1. The biomasses were chosen bceause of their different K/Si and K/S ratios, which are predicted to have a major influence on the sulfur release, because of the competing formation reactions of potassium silicate or potassium sulfate. CaO, $Ca(OH)_2$, $CaCO_3$, Ca-stearate, K_2CO_3, and potassium sorbate were used as additives. In one experiment, kaolinite was added, to investigate the influence of potassium retention. All additives were air-dried, ground (to a particle size of <50 μm), and mixed into the biomasses before the experiments. CaO, $Ca(OH)_2$, $CaCO_3$, K_2CO_3, and potassium sorbate were added to attain an overall ratio of Ca/S and K/S of 20 each. Ca-stearate was added in a Ca/S ratio of 5.

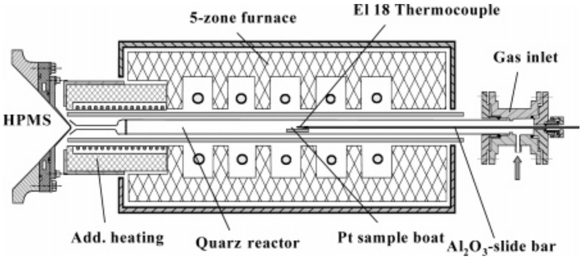

Figure 1. Setup used for the combustion experiments.

Experimental Setup. Hot gas analysis in this study was conducted using high-pressure mass spectrometry (HPMS). HPMS has been proven to be a reliable method for studying high-temperature, ambient pressure environments, which has been established in the present studies.[10−12] For all measurements in this study, the HPMS system has been coupled to a high-temperature reactor. Figure 1 shows the reactor setup used for the combustion experiments. A detailed description of the system used in this study has been given by Wolf.[13]

A platinum sample boat containing 50 mg of biomass material was attached to the end of a 6-mm-diameter alumina rod. The rod was inserted into a 21-mm-inner-diameter tubular quartz reactor that was housed in a high-temperature furnace. The temperature of the furnace was maintained at a constant temperature of either 800 or 1100 °C in the combustion zone. However, during combustion, the temperature probably increased. A gas mixture of 20% O_2 in helium flowed through the reactor at a flow rate of 3.0 slm (standard liters per minute). Therefore, the residence time of combustion products in the reactor before sampling was in the range of 0.15−0.3 s, depending on the furnace temperature.

The end of the quartz reactor was coupled to the sampling orifice of the HPMS device, to sample the high-temperature combustion products. The orifice protruded into the furnace, to maintain an elevated temperature to prevent condensation of gas-phase species on the tip of the orifice. The furnace provided an extra heating zone near the exit of the furnace, to prevent the combustion products from condensing on the reactor tube walls.

Figure 2 shows a schematic of the HPMS system used for the experiments in this study. The HPMS system consists of three differentially pumped vacuum chambers. Gases entering the 300-μm orifice undergo a supersonic free jet expansion into the first chamber, and intermolecular collisions between molecules are decreased drastically ~10 orifice diameters downstream from the orifice. At that point, the expansion has attained free molecular flow. The condensation of the gas-phase species is inhibited and intermolecular reactions are quenched. Therefore, high-temperature combustion products can be sampled directly, without being altered on their way to the HPMS detector. After being collimated by a conical skimmer with a diameter of 1 mm, the sampled gases form a molecular beam that is directed into the third stage of the vacuum system. In this stage, ions are formed by electron impact ionization with a nominal electron energy of 30 eV. After passing a deflector system, the ions are filtered in a

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[8] Schemenau, W. Druckwirbelschichtfeuerung—Fortschrittliche Kohleverstromung mit Betriebserfahrung. *Brennst.−Waerme−Kraft* **1993**, *45*, 23−26.

[9] Mitchell, S. *Hot Gas Cleaning for Advanced Coal-Based Power Systems*; IEA Coal Research: London, 1998.

[10] Dayton, D. C.; French, R. J.; Milne, T. A. Direct Observation of Alkali Vapor Release during Biomass Combustion and Gasification. 1. Application of Molecular Beam/Mass Spectrometry to Switchgrass Combustion. *Energy Fuels* **1995**, *9*, 855−865.

[11] Dayton, D. C.; Frederick, W. J., Jr. Direct Observation of Alkali Vapor Release during Biomass Combustion and Gasification. 2. Black Liquor Combustion at 1100 °C. *Energy Fuels* **1996**, *10*, 284−292.

[12] Dayton, D. C.; Jenkins, B. M.; Turn, S. Q.; Bakker, R. R.; Williams, R. B.; Belle-Oudry, D.; Hill, L. M. Release of Inorganic Constituents from Leached Biomass during Thermal Conversion. *Energy Fuels* **1999**, *13*, 860−870.

[13] Wolf, K. J. *Untersuchungen zur Freisetzung und Einbindung von Alkalien bei der Reduzierenden Druckwirbelschichtverbrennung*; Forschungszentrum Jülich: Jülich, Germany, 2003; pp 30−62. (ISSN 0944-2952.)

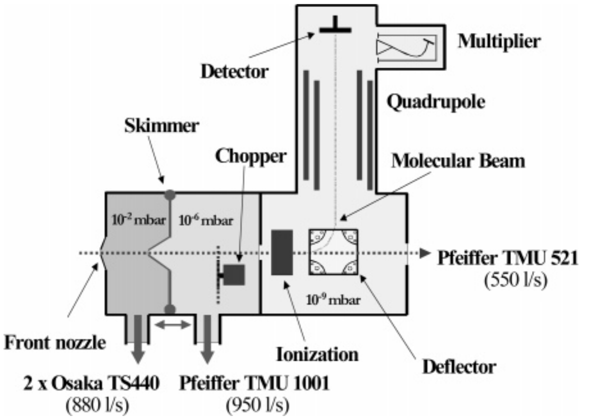

Figure 2. Schematic of the high-pressure mass spectrometry (HPMS) system.

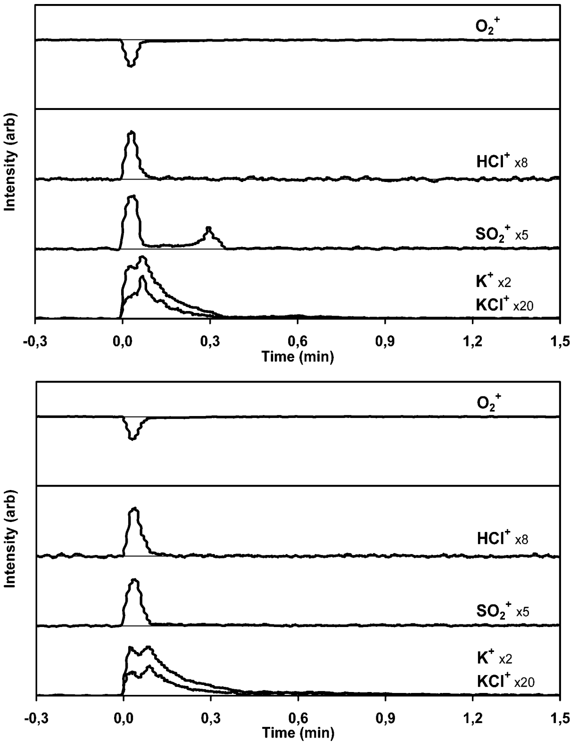

Figure 3. Chro trace of important species during HIAL 10 combustion at 1100 °C in He/20% O_2 without and with $CaCO_3$ (Ca/S = 20).

quadrupole mass analyzer and detected by an off-axis electron multiplier with a conversion dynode applied. A complete computer and software package was used to control all mass scanning parameters and collect the preamplified multiplier signal, as a function of time and the mass-to-charge (*m/z*) ratio.

At the beginning of each experiment, the platinum sample boat was held in the cooled zone of the reactor and a background spectrum was acquired for ~30 s. While the HPMS system was kept in a constantly scanning mode, the sample boat was inserted into the heated region of the reactor and the combustion process was monitored over time. The species sampled were O_2^+, CO^+, CO_2^+, Na^+, $NaCl^+$, K^+, KCl^+, SO_2^+, and HCl^+. Figure 3a shows an example of a Chro trace of the HIAL 10 combustion at 1100 °C in He/20% O_2. For the quantification of the release of the sampled species, the ion signals were integrated over time.

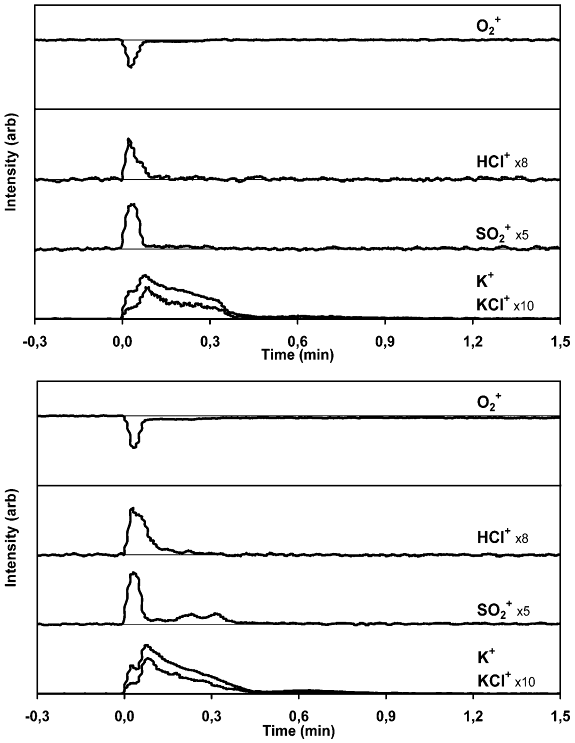

Figure 4. Chro trace of important species during HIAL 5 combustion at 1100 °C in He/20% O_2 without and with kaolinite (K/Si = 0.5).

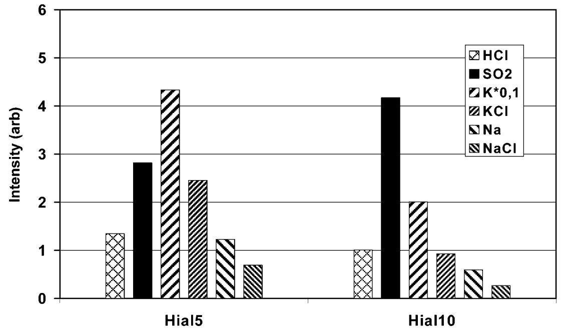

Figure 5. Measured intensities of species released during HIAL combustion at 1100 °C in He/O_2 20%.

The duration of the entire combustion process, including ash cooking, was dependent on the furnace temperature: 2 min were required at 800 °C, whereas 20 s were needed at 1100 °C. Ten identical samples were measured, and the results were averaged to ensure reproducibility. During one series of measurements, all settings were kept constant, to ensure comparability.

Results and Discussion

Combustion of HIAL 5 and 10 Samples at 1100 °C. In a first step, the two HIAL biomass samples were combusted without addition of additives in He/20% O_2. In the case of HIAL 10, the sulfur is released in two steps, as shown in Figure 3a. The first phase is the combustion or devolatilization phase, the second phase is the char combustion phase.[10] In the case of HIAL 5, the sulfur is almost exclusively released during the devolatilization phase, as shown in Figure 4a. The integrated intensities of some important species are shown in Figure 5. A comparison of Figure 4 and Table 1 reveals that the amount of SO_2 released during the combustion experiments does not correspond to the amount of sulfur found in the ultimate analysis. The higher amount of potassium and sodium, in relation to sulfur, in the HIAL 5 sample leads to a retention of

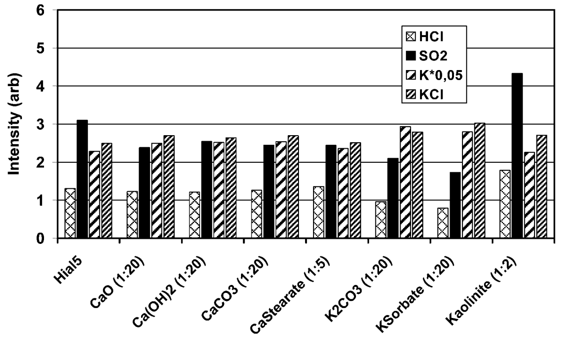

Figure 6. Relative intensities of species released from HIAL 5 samples doped with additives during combustion at 1100 °C in He/20% O_2.

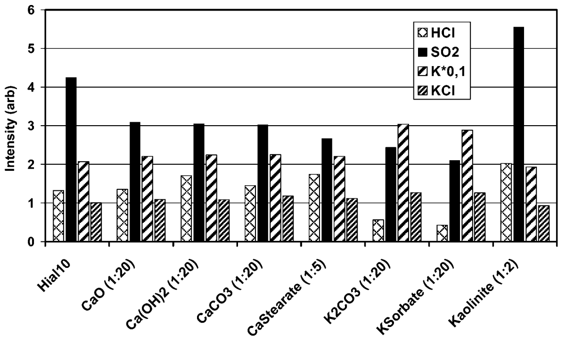

Figure 7. Relative intensities of species released from HIAL 10 samples doped with additives during combustion at 1100 °C in He/20% O_2.

sulfur via the formation of K_2SO_4 and Na_2SO_4, primarily reducing the SO_2 release during the char combustion phase. This correlation has been found by other authors previously.[7] The release of KCl, NaCl, and HCl seem to be mainly influenced by the amount of chlorine in the initial samples and, therefore, are higher for the HIAL 5 sample. The K^+ and Na^+ signals measured by HPMS are mostly fragment ions from KCl^+, $NaCl^+$, $K_2SO_4{}^+$, and $Na_2SO_4{}^+$, which are the main alkali-containing species. Alkalis released as free metals are not likely to contribute to these intensities.[10] The simple comparison of these two samples reveal that the release of inorganic constituents is strongly dependent on other inorganic constituents in the samples.

Combustion of HIAL Samples + Additives at 1100 °C. Figure 3b shows that sulfur binding additives slightly decrease the release of more-volatile sulfur, which is released during devolatilization. The release of less-volatile sulfur, released during char combustion, is decreased to zero. In Figures 6 and 7, the results for the combustion of HIAL samples 5 and 10 doped with different additives are shown. For the HIAL 5 sample, a reduction of 20% of the SO_2 release could be achieved using calcium-based additives. For the HIAL 10 sample, the retention increased to >25%. The better performance of the calcium-based additives for HIAL 10 can be explained by the higher amount of SO_2 released during char combustion by the undoped sample.

Although potassium-based additives will not likely be used in commercial boilers in the laboratory experiments, potassium was added in several forms, to examine their retention behavior on sulfur. For both HIAL fuels, the performance of the potassium-based additives was even better than the performance of the calcium-based additives. The reason for this must be observed in the greater affinity of sulfur for alkalis than for calcium. As thermodynamic equilibrium calculations reveal, K_2SO_4 is much more stable at 1100 °C than $CaSO_4$. The best results for the retention could be gained using organic calcium- and potassium-based additives. Organic-bound calcium and potassium show a higher reactivity than inorganic-bound calcium and potassium. Adding kaolinite to the biomass samples increased the sulfur release for both biomasses. Kaolinite forms potassium silicate with the potassium in the sample, which is no longer available for the formation of K_2SO_4, leading to a decrease in the overall sulfur retention. Moreover, during char combustion, kaolinite reacts with K_2SO_4, resulting in an increased sulfur release, as can be observed in Figure 4b.

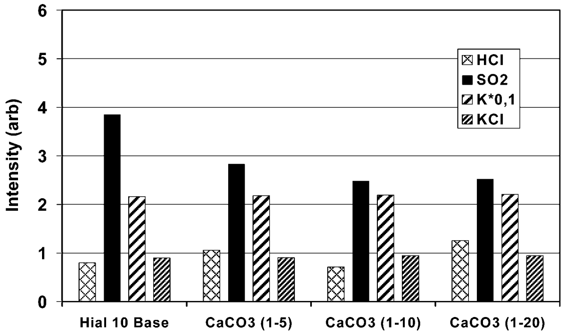

Figure 8. HIAL 10 combusted at 1100 °C in He/20% O_2 with $CaCO_3$ added in different ratios (S/Ca).

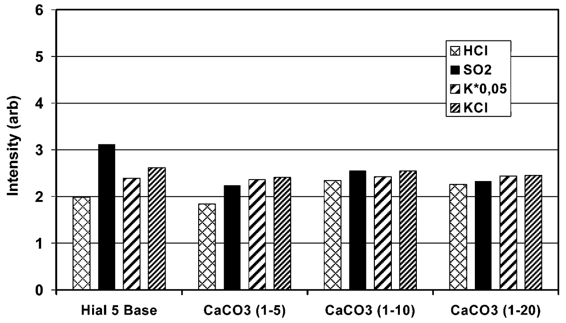

Figure 9. HIAL 5 combusted at 1100 °C in He/20% O_2 with $CaCO_3$ added in different ratios (S/Ca).

Some more experiments have been conducted at 1100 °C to determine the amount of additives needed for maximum sulfur retention. In Figure 8, the results of the combustion of HIAL 10 doped with $CaCO_3$ in three different ratios of Ca/S (Ca/S = 5, 10, 20) are shown. The sulfur retention increases up to a Ca/S ratio of 10; a further increase of the amount of $CaCO_3$ has no influence on the sulfur release from the sample. However, the better performance gained by adding a higher amount of additives is primarily due to a better contact between the additive and the sample. In the case of a very low amount of additive, most of the sulfur released from the sample does not come into contact with the calcium from the additive. For the HIAL 5 samples, practically no difference in sulfur retention could be observed, depending on the amount of additive used (Figure 9).

Combustion of HIAL 5 and 10 Samples at 800 °C. Additional measurements have been performed at a temperature of 800 °C, using the same biomasses and additives. Figures 10 and 11 show the results of the

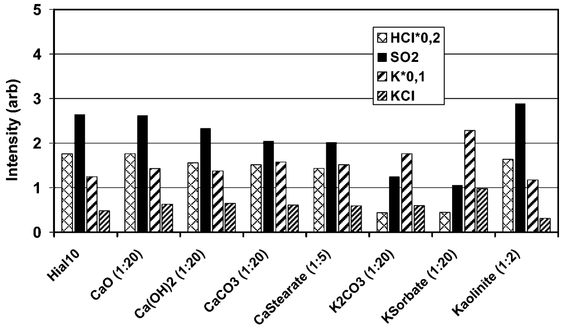

Figure 10. Relative intensities of species released from HIAL 10 samples doped with additives during combustion at 800 °C in He/20% O_2.

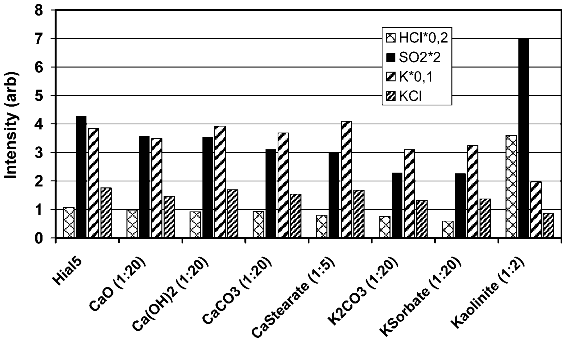

Figure 11. Relative intensities of species released from HIAL 5 samples doped with additives during combustion at 800 °C in He/20% O_2.

combustion of HIAL 5 and HIAL 10 with different additives. The overall release of sulfur at 800 °C is less than that at 1100 °C. Because devolatilization happens at relative low temperatures during heating of the sample, the main reducing effect likely happens during char combustion. As the experiments reveal, for CaO and $CaCO_3$, the potential for a sufficient sulfur retention is less than that at 1100 °C. The reason for this must be observed in the lower sulfur release during char combustion, where the calcium components mainly react. On the other hand, potassium-based additives show an even better performance in sulfur retention at 800 °C than at 1100 °C. The higher reactivity of potassium at elevated temperatures leads to a sorption of potassium by the silica in the biomass, and the potassium captured this way is not any longer available for sulfur retention.

Finally, the influence of kaolinite on the sulfur release at 800 °C is even higher than that at 1100 °C. Because the overall sulfur release is less at 800 °C than at 1100 °C, the total amount of sulfur bound as K_2SO_4 in the residual ash is higher. Therefore, more sulfur is released when kaolin is added.

Conclusions

In this work, laboratory combustion experiments with two different high-alkaline biomasses blended with additives have been performed in the temperature range of 800−1100 °C under oxidizing conditions to examine the influence of the additives on the SO_2 emission. CaO, $Ca(OH)_2$, $CaCO_3$, calcium stearate, K_2CO_3, potassium sorbate, and kaolinite have been used as additives. Hot gas analysis was performed, via high-pressure mass spectrometry (HPMS).

Preliminary measurements of unblended biomass samples show that the release of inorganic constituents such as sodium, potassium, and sulfur from the fuel during combustion is strongly dependent on other inorganic constituents, such as silicon and chlorine.

At 1100 °C, a reduction of up to 25% of the sulfur dioxide (SO_2) release could be achieved using calcium-based additives. The additives mainly decrease the sulfur release during char combustion. The best retention could be achieved for a biomass with a low initial potassium content. Because of the greater affinity for sulfur, the performance of potassium-based additives was better than that for calcium-based additives. The best results were achieved using organic calcium- and potassium-based additives. Adding kaolinite to the biomass increased the sulfur release, because of the formation of potassium silicate. Potassium retained this way is no longer available for K_2SO_4 formation.

At 800 °C, the sulfur retention is lower for all calcium-based additives than at higher temperatures. Organic calcium-based additives seem to do better than inorganic calcium-based additives in this context. Potassium-based additives show an even better performance at 800 °C than at 1100 °C. The reason for this can be observed in the lower reaction kinetics of the potassium silicate formation at lower temperatures.

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