QUANTIFICATION OF THE RELEASE OF Cl, K AND S TO THE GAS PHASE FROM COMBUSTION OF ANNUAL BIOMASS

Jacob N. Knudsen, Peter A. Jensen, and Kim Dam-Johansen

Department of Chemical Engineering
Building 229, Technical University of Denmark
2800 Kgs. Lyngby
Denmark

Introduction

The use of annual biomass such as straw, stalks and shells in heat and power generation is an interesting option in order to provide renewable energy and to reduce the net CO_2 emissions. In Europe and North America, straw is the most available biomass resource with a yearly production around 800 million tons[1]. In Denmark, straw is a particular interesting bio-fuel since it is an agricultural waste-product being available in surplus. However, the use of straw as a fuel in combined heat and power plants has proven to be a technical challenge. This is among other things, due to the relatively high concentrations of the elements: potassium, chlorine and sulfur. Formation of acidic pollutants and high mass loadings of aerosols together with deposition on heat transfer surfaces of potentially corrosive components are among the encountered problems[2-4].

During the conversion of annual biomass in grate-fired furnaces, Cl, K and S are partly released to the gas phase, but may also be partially retained in the bottom ash. Clearly, the extent of Cl, K and S release to the gas phase is directly related to the problems mentioned above. In order to predict the impacts of a given fuel in a combustion system, the release behavior of Cl, K and S needs to be investigated. In this work, the influence of combustion temperature and fuel composition on the gas phase release of Cl, K and S have been determined.

Experimental

Biomass fuels. Four biomass fuels with distinctive different ash composition were selected for the release investigation. As seen in Table 1, the concentration range of Cl, K, S and Si is particularly broad. Prior to use, the fuels were thoroughly homogenized in a hammer-mill and the fines were removed. The resulting particle-size fraction was 0.5-10 mm.

Table 1. Characteristics of the Biomass Fuels Applied in the Experimental Investigation.

Fuel	Wheat	Oat	Barley	Carinata
Moisture (%)	8.4	7.8	8.5	7.3
Ash (%, dry)	4.8	3.8	6.9	4.9
Ca (%, dry)	0.35	0.72	0.34	0.60
Cl %, dry)	0.27	0.05	0.79	0.05
K (%, dry)	1.2	0.55	2.3	1.4
P (%, dry)	0.05	0.11	0.06	0.14
S (%, dry)	0.17	0.14	0.20	0.26
Si (%, dry)	0.79	0.27	0.81	0.05
K/Si (mol/mol)	1.1	1.5	2.0	20
Cl/K (mol/mol)	0.25	0.10	0.38	0.04

Release quantification. An electrically heated laboratory flow-reactor was applied to combust small samples of biomass at well-controlled conditions. To simulate the heating rate of an industrial grate-fired boiler, an experimental procedure was utilized where the biomass sample was inserted into a preheated reactor. The release of Cl, K and S from the sample was subsequently quantified by a chemical analysis of the residual ash and a mass balance on the system. A series of experiments at different temperatures were conducted, in order to quantify the release as a function of combustion temperature. The influence of ash composition on the Cl, K and S release was investigated by conducting experiments with biomass fuels with different mineral content and composition.

Analytical. The residual ash samples were dissolved by pressurized digestion in a $HF/HNO_3/H_2O_2$ mixture, subsequently neutralized with boric acid and analyzed by ICP-OES.

Results and Discussion

Potassium. It is seen in **Figure 1** that potassium is released to the gas phase above 700°C and that the release increases with the applied combustion temperature for all biomass fuels regardless of the ash composition. Between 20 and 50% of the total potassium has been released at 900ºC. At temperatures above 900ºC the relative potassium release increases almost linearly with temperature until 60 to 90% is released at 1150ºC. The local temperature on the grate in grate-fired furnaces is fluctuating, but frequently above 900-1000ºC[5]. This implies that significant amounts of the fuel-potassium are released to the gas phase during grate combustion of annual biomass.

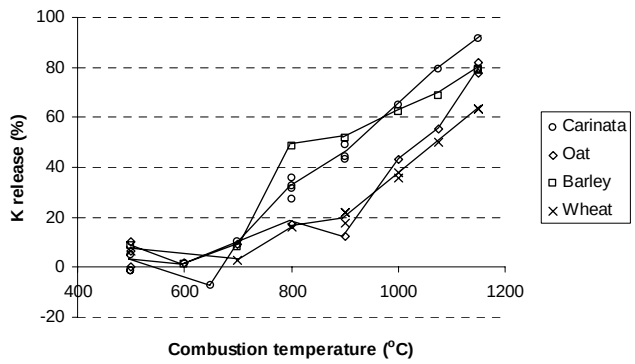

Figure 1. Release of potassium as a function of temperature.

It is furthermore seen in **Figure 1** that the release of potassium is greatly affected by the ash composition. The biomass fuels with the higher Si and lower Cl content relative to K (oat and wheat straw) display the lower potassium release. Potassium can be incorporated into silicate structures[6]. The vapor pressure of potassium fixed in silicate structures is relatively low, which implies that less potassium is released from biomass fuels having a low K/Si ratio. According to Table 1, the K/Si molar ratio of the wheat, oat and barley straw is low compared to the one of carinata and a lower potassium release is expected. However, a high concentration of chlorine relative to potassium may increase the volatility of potassium, due to the relatively high vapor pressure of KCl at combustion relevant temperatures. This indicates that chlorine promotes the release of potassium to the gas phase. A significant fraction of the potassium in the chlorine-rich barley straw is released between 700 and 800°C, the interval where KCl is found to evaporate[6]. This implies that chlorine may facilitate the release of potassium, although the biomass contains substantial amounts of silicon relative to potassium.

Thus, at grate combustion conditions it is expected that the release of potassium to the gas phase will be considerable for biomass fuels containing high amounts of chlorine and/or potassium relative to silicon. On the contrary, the potassium release is expected to be low for high-silicate fuels with low chlorine content.

Chlorine. It appears in **Figure 2** that chlorine is released in two steps for the samples which contain substantial Cl (barley and wheat). Between 30 and 60% is released in the first step below 500ºC. The remaining Cl is released in the second step between 650 and 800ºC. The observed two-step chlorine release is in agreement with observations in the literature[6]. It has been demonstrated that chlorine is released as HCl during the fuel devolatilization at 200-400ºC. The second release-step of chlorine is linked to the evaporation of KCl[6], which mainly occurs between 700 and 800ºC as seen in **Figure 2**. This is consistent with the observed step-like increase in the potassium release between 700 and 800ºC for the chlorine-rich fuels as shown in **Figure 1**.

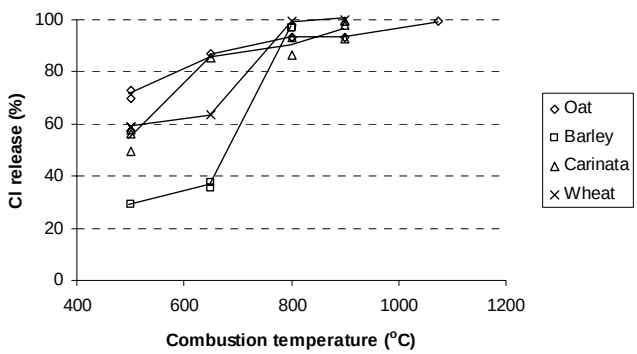

Figure 2. Release of chlorine as a function of temperature.

For the samples which have a relatively low Cl content (oat and carinata), the chlorine release is gradually increasing as a function of combustion temperature. In general a higher fraction of the fuel-chlorine appears to be released at lower temperatures for the low-chlorine fuels. This is most likely an effect of concentration rather than a true mechanistic difference. Significantly less KCl must be evaporated from the low-chlorine fuels, thus the evaporation rate becomes important at lower temperatures.

Nevertheless, the investigation indicates that combustion of annual biomass above 800ºC results in nearly complete release of Cl to the gas phase. The ash composition or the absolute Cl content of the fuel does not affect this fact. The temperature on the grate in grate-fired furnaces is typically significantly above 800ºC[5], which implies that most fuel-chlorine will be released to the gas phase during grate-combustion of annual biomass.

Sulfur. Unlike the observed release behavior of Cl and K, **Figure 3** reveals that the sulfur release appears to be more sensitive to the ash composition than the combustion temperature.

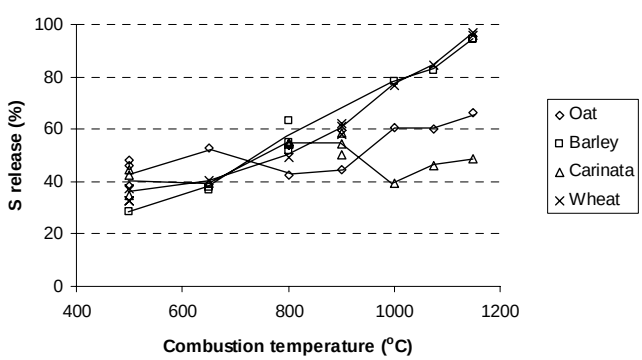

Figure 3. Release of sulfur as a function of temperature.

In case the biomass fuel contains relatively high amounts of Ca and K compared to Si, (oat and carinata), approximately 50% of the sulfur is released almost independently of the applied combustion temperature. On the other hand, if the Si concentration is high, the sulfur release increases with combustion temperature. Calcium and potassium are the elements facilitating sulfur capture in the residual ash. It appears in Table 1, that the content of Ca and K in the fuels is sufficient to retain all fuel-sulfur. However, in the high-silicate fuels, calcium and potassium are to a large extent incorporated into glassy silicate structures. The retention of sulfur in Ca-K-silicates is low, hence, the sulfur release to the gas phase is observed to be higher for high-silicate fuels.

It appears in **Figure 3** that the sulfur release is greater than 40% at all temperatures and for all of the investigated biomass fuels. This is related to the occurrence of substantial amounts of volatile organic sulfur in annual biomass. Earlier work[7] has indicated that annual biomass fuels contain both organic sulfur and inorganic sulfate. The organic sulfur is released to the gas phase during devolatilization at 200-400ºC, whereas the inorganic sulfate is retained in the char.

Altogether, the experimental work indicates that the sulfur release in grate-fired boilers is controlled by the organic-to-inorganic sulfur ratio in the fuels and the accessibility of potassium and calcium. The accessibility of potassium and calcium is largely determined by the relative concentration of silicate in the fuel.

Conclusions

The experimental investigation revealed that both the combustion temperature and the ash composition greatly affected the extent of Cl, K and S release to the gas phase at grate combustion conditions. The release of potassium was largely determined by the fuels content of chlorine and silicon along with the combustion temperature. The fuel-chlorine was found to be completely released to the gas phase at combustion temperatures above 800°C, regardless of the ash composition. The sulfur release was predominantly controlled by the association of sulfur in the fuel together with the accessibility of Ca and K.

Acknowledgement. This work is part of the CHEC (Combustion and Harmful Emission Control) research centre funded by Elsam, Elkraft, the Danish and Nordic Energy Research programs, the Technical Research Council of Denmark and the Technical University of Denmark.

References

(1) Hall, D. O.; Overend, R. P. Biomass. *Regenerable energy*, John Wiley & sons, Chichester, 1987, Chapter 4.

(2) Michelsen, H. P.; Frandsen, F. J.; Dam-Johansen, K.; Larsen, O. H. *Fuel Processing Technology*. **1998**, *54*, 95-08.

(3) Sander, B.; Henriksen, N.; Larsen, O. H.; Skriver, A.; Ramsgaard-Nielsen, C.; Jensen, J. N.; Stærkind, K.; Livbjerg, H.; Thellefsen, M.; 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*, 1st World Conference on Biomass for Energy and Industry. June 2000, Sevilla, Spain.

(4) Christensen, K. A.; Stenholm, M.; Livbjerg, H. *J. Aerosol Sci*. **1998**, *29*, 421-444.

(5) Van der Lans, R.; Pedersen, L.T.; Jensen, A.; Glarborg, P.; Dam-Johansen, K. *Biomass and Bioenergy*. **2000**, *19*, 199-208.

(6) Jensen, P.A.; Frandsen F.J.; Dam-Johansen, K.; Sander, B. *Energy & Fuels*, **2000**, *14*, 1280-1285.

(7) Knudsen, J.N.; Lin, W.; Frandsen, F.J.; Dam-Johansen, K. *Sulfur Transformations during Thermal Conversion of Biomass, Power Production in the 21st Century*, Engineering Foundation Conference, Snowbird, Utah, USA, 28 Oct. - 2 Nov. **2001**.