



## **RELEASE OF ASH-FORMING ELEMENTS FROM BIOMASS DURING OXIDATION AND PYROLYSIS**

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### **ABSTRACT**

In this work, the release of several ash-forming elements from four biomass fuels has been quantified as function of temperature and residence time in a single particle reactor. The fuels are spruce bark, torrefied softwood, wheat straw and miscanthus. For the experiments, the fuels were pelletized. In the experiments, three different temperatures were used 800, 900, and 1050 °C. In addition, two different gas atmospheres were used, one containing 3% O<sub>2</sub> and one oxygen free. The release of the ash forming elements was determined as a function of conversion. For the pyrolysis experiments the same holding times were used in order to see the influence of the gas atmosphere. The release was calculated using the elemental composition of the chars analyzed using ICP-MS and ICP-AES.

*Keywords: Release; biomass conversion*

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### **1 Introduction**

Understanding the behaviour of ash-forming elements is the key to predict operational problems such as agglomeration, slagging, fouling, particulate formation and corrosion related problems. Many of these aspects are discussed in the review paper of Werther et al. [1]. Understanding the release of the ash-forming elements can also be valuable when it comes to operating the combustion facility in such a way that the ash can be further utilized, for example in cement manufacturing or as a fertilizer.

The release of ash-forming elements during thermal conversion of biomass has been investigated in a number of studies. Most attention has been put on the K, S and Cl. A number of techniques have been applied, the probably most common one though is a fixed bed reactors setup [2-4], but also flow reactor [5,6] and grid heater setup has been utilized [7,8].

In the present study the release of ash forming elements during thermal conversion of single pellets are studied. The release is studied both at combustion as well as at pyrolysis conditions. The aim of this study is to reveal the influence of temperature, atmosphere composition and char conversion on the release of a number of ash forming elements.



## **2 Experimental**

### **2.1 Laboratory experiments**

Pellets were prepared from pulverized/grinded fuel. Four different fuels were studied: spruce bark, torrefied softwood, wheat straw and miscanthus. The pellets had a diameter of 8 mm. The height of the pellets varied, since the controlling parameters were the amount of fuel, in this case 200 mg, and the applied pressure.

The pellets were placed on a sample holder of quartz glass. Before being inserted into the hot gas atmosphere the samples were kept in a protective N<sub>2</sub> atmosphere. Then the samples were quickly inserted. After a certain holding time the sample was removed from the hot environment into the cold protected N<sub>2</sub> atmosphere. Here the sample was allowed to cool down to room temperature before being removed from the quartz holder.

The test matrix included a total of 96 experiments: four fuels, two gas atmospheres, three temperatures and four different holding times. The gas atmospheres were 1) 3% O<sub>2</sub> + 97% N<sub>2</sub> and 2) 100% N<sub>2</sub>. The temperatures were 800 °C, 900 °C and 1050 °C. The holding times were 1) end of pyrolysis, 2) 50% char burnout time, 3) char burnout and 4) burnout + 5 min cooking time. The experiments were performed such that first the longest holding times were studied. During these runs the devolatilization time was established based on flame out, the burn out time was established using CO and CO<sub>2</sub> analyzers. The 50% burnout time is taken as the mid-point between end of pyrolysis and end of char oxidation. For the experiments performed in N<sub>2</sub> the holding times established in the runs with O<sub>2</sub> in the atmosphere were utilized.

### **2.2 Fuel and char analysis**

The inorganic content of fuel, and char and ash samples were analyzed by two different methods: ICP-AES and ICP-MS. ICP-AES stands for inductively coupled plasma atomic emission spectroscopy. The analyzer consists of two parts: the plasma generating part and the optical unit where the intensity of the lines in the atomic emission spectra is analyzed. The ICP-MS differs from the ICP-AES in that a mass spectrometer is used for quantification. The detection limit of the ICP-MS is lower than that of the ICP-AES. On the other hand, the ICP-AES is a robust method for analyzing non-metals like Si, S and P.

For digestion of the solid samples, micro-wave assisted digestion was utilized. The samples they were first digested in a mixture of HNO<sub>3</sub> (4ml), HClO<sub>4</sub> (2ml) and HF (0.5ml). For some of the samples also 2ml of H<sub>2</sub>O<sub>2</sub> were added. The amount of digested sample varied from approximately 200 mg for the untreated fuel samples to less than 1 mg from the torrefied fuel char residue. In order to digest the samples fully they were then kept 60 minutes in the acids at elevated temperatures.



### 3 Results

The results from the elemental analysis were recalculated to mass element/mass of untreated fuel. The analysis results obtained with the two different methods agreed well. Figure 1 shows results for two elements, but similar trends were observed for all elements both methods could analyze. Since the ICP-MS could analyze a larger number of elements, results obtained using this method will be focused on in this paper.

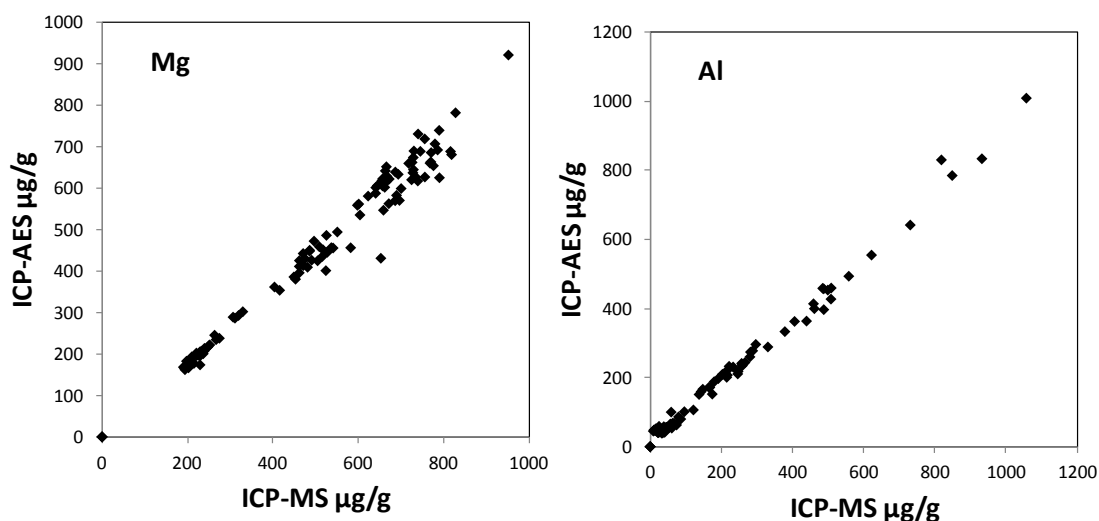


Figure 1. Element analysis results from ICP-AES vs. ICP-MS.

The results from the analysis showed that most elements were retained in the char residue/ash regardless of the conditions. This was the result for the following elements: Ca, Fe, Mn, Cr, CO, Ni, Cu, Na, Mg, Al, Pb, Li, Rb, Sr, Cd, Ba and As. Many of these elements were present in concentrations less than 100 µg/g untreated fuel: Cr, Co, Ni, Cu, Pb, Li, Rb, Sr, Ca and As. For some of the elements the analysis showed considerable variations, e.g. for Fe and Na the variations were considerable.

The most interesting trends were observed for K and Zn. Figure 2 shows the potassium content on fuel bases for the four fuels at different conversion stages. The figure shows that for bark and torrefied wood there is a release of K at the highest temperature for the case of complete char burnout plus 5 min cooking time. This is partly in contrast to the findings of Johansen et al. [3] that found that the release of K took place primarily in connection to the sublimation of KCl at temperatures exceeding around 700 °C. The differences in the results can most likely be explained by differences in the experimental setup and conditions. For the herbal fuels no release of K seems to occur. These fuels clearly also have the highest potassium content. It is interesting to note that the straw has clearly the highest content of Si, approximately 12000 µg/g untreated fuel, whereas the content of Si in the torrefied wood is only around 300 µg/g untreated fuel. The bark and the miscanthus both have similar content of Si, around 4000 µg/g untreated fuel, but for the bark the scatter is rather large. This may indicate that released potassium is trapped in a silicate phase in the ash of the straw and miscanthus as discussed by others [3].

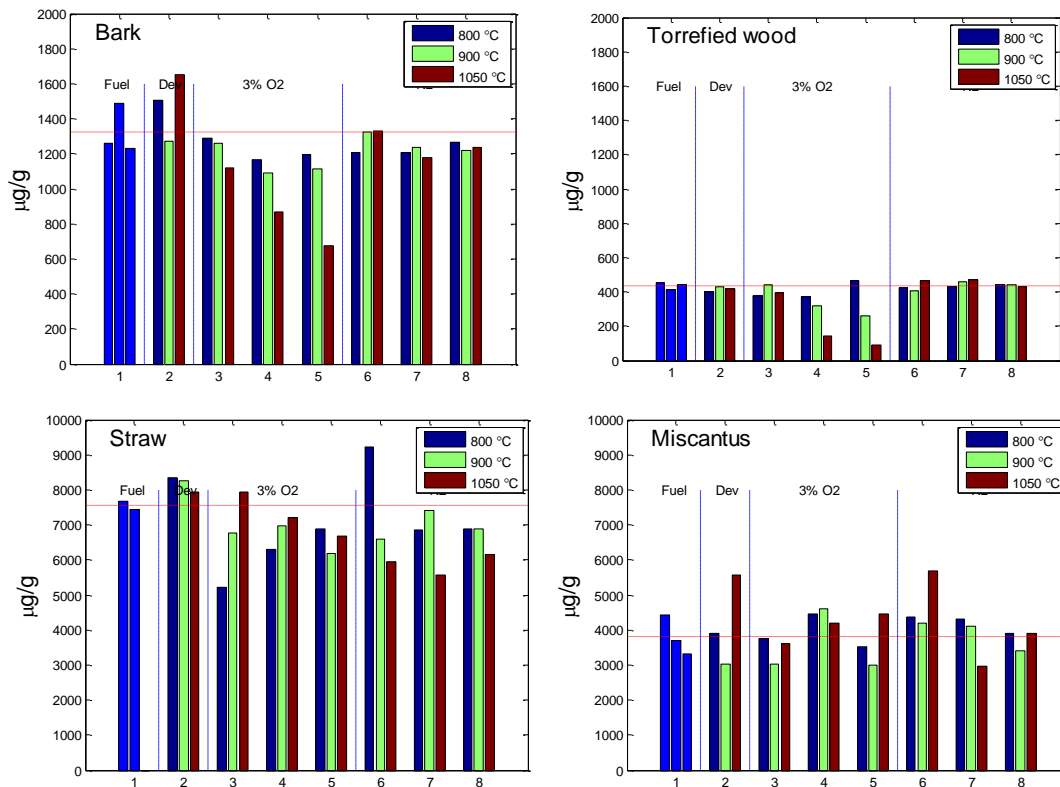


Figure 2. Potassium content of the four fuels as  $\mu\text{g/g}$  untreated fuel. In each plot, Group “1” are results for the untreated samples, “2” are the devolatilized samples, “3” and “6” the 50% burn out, “4” and “7” the 100% burn out and “5” and “8” 100% burnout + 5 min cooking time. In the figure the atmosphere is also indicated. The red line indicates the average content in the untreated fuel samples.

Figure 3 shows the zinc content on fuel bases for the four fuels at different conversion stages. Here the trend for the bark and the torrefied wood is very clear: zinc is effectively released at reducing conditions. At oxidizing conditions the zinc release increases with temperature. The results for the devolatilization tests are surprising and require further investigation. One possible explanation for the results is that zinc is released after the sample has been retracted into the protective  $\text{N}_2$  atmosphere. For miscanthus and straw the trend is difficult to interpret because of scatter in the analysis. All but one analyzed miscanthus sample has low zinc content. Also the zinc content of the straw samples are generally low according to the analysis results, except for two samples prepared at 800 °C and in an oxidizing atmosphere.

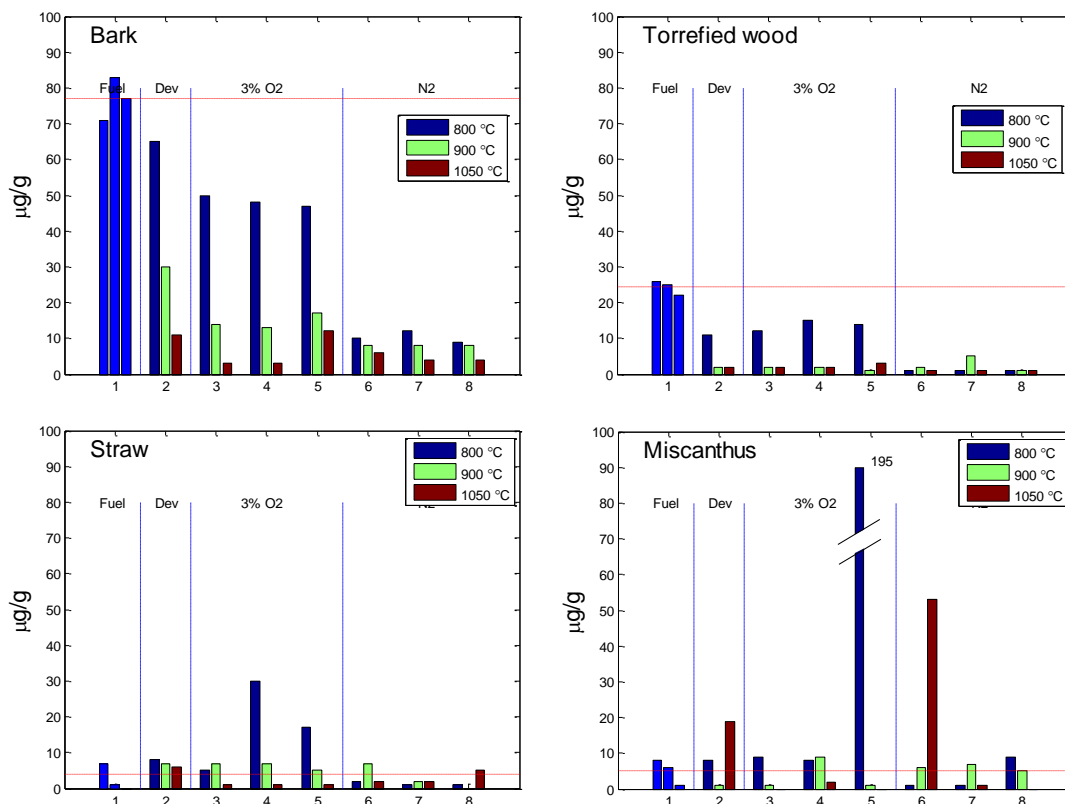


Figure 3. Zinc content of the four fuels as  $\mu\text{g/g}$  untreated fuel. In each plot, Group “1” are results for the untreated samples, “2” are the devolatilized samples, “3” and “6” the 50% burn out, “4” and “7” the 100% burn out and “5” and “9” 100% burnout + 5 min cooking time. In the figure the atmosphere is also indicated.

## 4 Conclusions

The fate of ash-forming elements in four biomass fuels during conversion has been studied in two different atmospheres in the temperature range 800 °C to 1050 °C. The results shows that most of the metallic elements only present in trace amount are retained in the fuel sample. Also some of the elements present in slightly higher amounts, such as Ca and Mg, are also retained in the fuels. Potassium on the other hand is released from the bark and the torrefied wood. The release increases with temperature and holding time. This behavior is not observed for the miscanthus and the straw samples. Zinc is released from the bark and the torrefied wood at reducing conditions. At oxidizing conditions zinc release could also be observed at high temperatures.

## 5 Acknowledgements

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## REFERENCES

1. Werther, J., Saenger, M., Hartge, E.-U., Ogada, T., Siagi, Z., Combustion of agricultural residues, *Progress in Energy and Combustion Science* 26 (2000) 1–27.
2. Knudsen, J.N., Jensen, P.A., Kim Dam-Johansen K., Transformation and Release to the Gas Phase of Cl, K, and S during Combustion of Annual Biomass, *Energy & Fuels* 2004, 18, 1385-1399.
3. Johansen, J.M., Jakobsen, J.G., Frandsen, F.J., Glarborg, P., Release of K, Cl, and S during Pyrolysis and Combustion of High-Chlorine Biomass, *Energy Fuels* 2011, 25, 4961–4971.
4. Davidsson, K.O., Korsgren, J.G., Pettersson, J.B.C., Jäglid, U., The effect of fuel washing techniques on alkali release from biomass, *Fuel* 81 (2002), 137-142.
5. Sippula O., Lind, T., Jokiniemi, J., Effects of chlorine and sulphur on particle formation in wood combustion performed in a laboratory scale reactor, *Fuel* 87 (2008) 2425–2436.
6. Shah, K.V., Cieplik, M.K., Bertrand, C.I., van de Kamp, W.L., Vuthaluru, H.B., Correlating the effects of ash elements and their association in the fuel matrix with the ash release during pulverized fuel combustion, *Fuel Processing Technology* 91 (2010) 531–545.
7. Kymäläinen, M., Janka, K., Keskinen, J., Moisio, M., Backman, R., Hupa, M., Measurement of time-dependent fume release rate during black liquor pyrolysis, *Journal of Pul and Paper Science* 22 (1996), 17-23.
8. Okuno, T., Sonoyama, N., Hayashi, J., Li, C.-H., Sathe, C., Chiba, T., Primary Release of Alkali and Alkaline Earth Metallic Species during the Pyrolysis of Pulverized Biomass, *Energy & Fuels* 2005, 19, 2164-2171.