Monitoring of alkali particles from thermal processing of biomass

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Alkalis in biomass and waste feedstocks are causing severe corrosion and fouling problems in gasification and combustion processes. Furthermore, the alkali containing producer gases pose a risk for delicate downstream facilities which are needed for efficient power generation and/or fuel production. The understanding of the physico-chemical behavior and fate of alkalis in thermal processes is therefore a key factor in developing new biomass-based renewable energy systems. It has been shown that a significant fraction of alkali species in thermal processing of biomass is released in form of particles less than 100nm in size (Jimenez, 2006). One of the most exigent challenges is to measure the alkalis at large scale facilities in which the required concentrations are often very low (ppb to ppm range), the content changes due to the heterogeneous feedstock and process parameters. Moreover, producer gases can contain high particle and tar loads.

The most common alkali measurement techniques are gas washing methods, where the sampled gas is led through a series of impingers or scrubbers to capture the alkali species in a liquid solvent (Mojtahedi et al, 1990). The solution is subsequently analyzed by a standard analytical method like atomic emission spectrometry or liquid chromatography. These techniques are only applicable as a batch method and lead to average values over a period of minutes to hours. Therefore, these methods cannot offer any information on short-term changes in the alkali concentration.

Our research is focusing on a method for measuring alkalis based on the principle of positive surface ionization. In the Surface Ionization Detector (SID) a platinum filament is heated to 1200°C, which serves as the ionization source. Alkalis that impinge on the surface of the platinum filament get ionized because the energy gained by the platinum when absorbing an electron (the negative energy of the work function) is greater than the energy needed to remove an electron from the alkali compound. Subsequently, the ionized alkalis are forced to fly to a collector by means of an electric field. The measured neutralization current between filament and collector has been shown to accurately represent the actual alkali content in the gas.

A first prototype SID was developed in our group by Kowalski (Kowalski, 2007; Kowalski et al, 2007) inspired from a publication of a similar device developed in Sweden (Davidsson et al, 2002). During the last two years a new detector has been designed and constructed where the focus of the development was kept on the providing long-term stability and reproducibility the measurements.
In a set of experiments the detector has been calibrated by the use of an ultrasonic nebulizer (USN), which generates alkali aerosols in different concentrations. The calibration measurements demonstrated a linear correlation of the alkali content to the measured current over a range of almost three orders of magnitude (Figure 1).

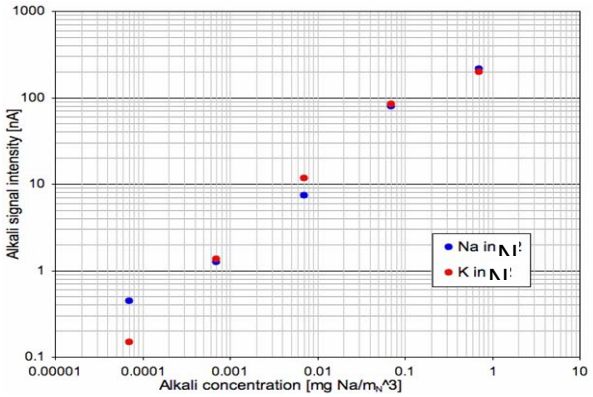

Figure 1: Calibration of the alkali detector with aerosols generated from a ultrasonic nebulizer

In a measurement campaign at the Paul Scherrer Institute the *SID* was used to quantify the slip stream of alkalis from a gas washing setup. The gas washing setup was fed with raw gas from a bubbling fluidized bed reactor. The gasifier has a size of approximately 5 kilowatts and was fed gras pellets.
The concentration is given as micrograms per norm cubic meter. Data points were recorded in intervals of 1 second, which allows to represent the short term fluctuations in removal efficiency of the gas washing system.

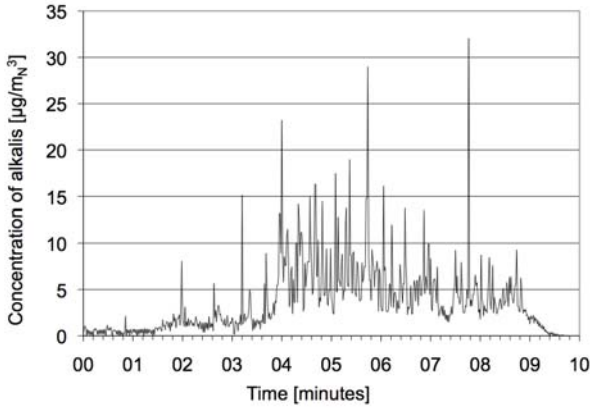

Figure 2: Slip stream of alkalis measured downstream of a gas washing system

To increase the accuracy of the measurements in the sub-ppb range, that render dilution of the sample gas feed impossible, a calibration of the detector under varying gas compositions is planned. Additional steps to optimize the detector include improved electromagnetic shielding to reduce background noise as well as a dedusting system to allow for an extended duration (>12h) of maximum measurement sensitivity.

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- Kowalski, T., Evaluating a Surface Ionization Detector for Measuring Alkalis in Biomass Gasification, PhD-Thesis, Diss. ETH Nr. 17067, ETH Zürich, 2007.
- Kowalski, T., C. Ludwig, and A. Wokaun, Qualitative evaluation of alkali release during the pyrolysis of biomass, Energy and Fuels, 2007, 21, p 3017-3022.

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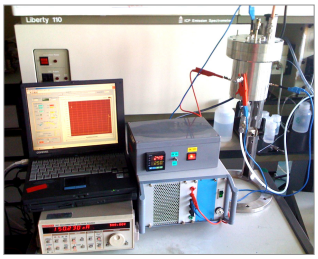
Introduction

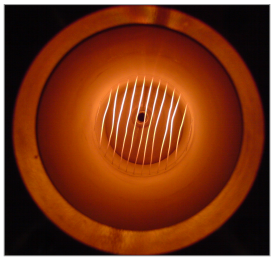
When using biomass feed stocks to efficiently produce power and heat one has to cope with its contents of different heteroatoms. Besides posing a potential threat to the environment these heteroatoms can also damage machinery parts or negatively influence downstream processes. Among the trace elements that are typically present in the process gas are alkalis, heavy metals, sulfur and halogens. The contents are reported to vary widely even within one type of biomass and the resulting level of emissions depend strongly on process parameters such as temperature, redox conditions, and pressure. Therefore, analytical methods are needed that enable online measurements of elemental compositions in process gas.

Measuring alkalis with a surface ionization detector (SID II)

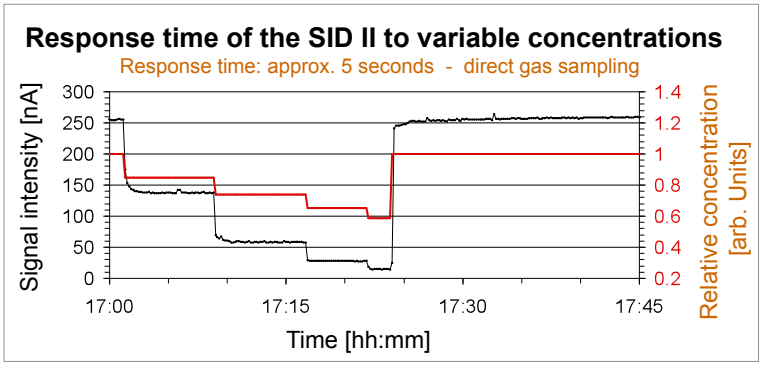
A platinum filament that is heated to 1200°C serves as the ionization source. Alkalis that impinge on the surface of the platinum filament get ionized and are subsequently forced to fly to a collector by means of an electric field. Then the neutralization current between filament and collector is measured. The measured current is proportional to the alkali content in the gas. As apparent from the chart below, the signal of the alkali detector reacts within seconds to changes in concentrations. This allows to monitor short-term fluctuations in alkali levels as demonstrated in this laboratory based experiment.



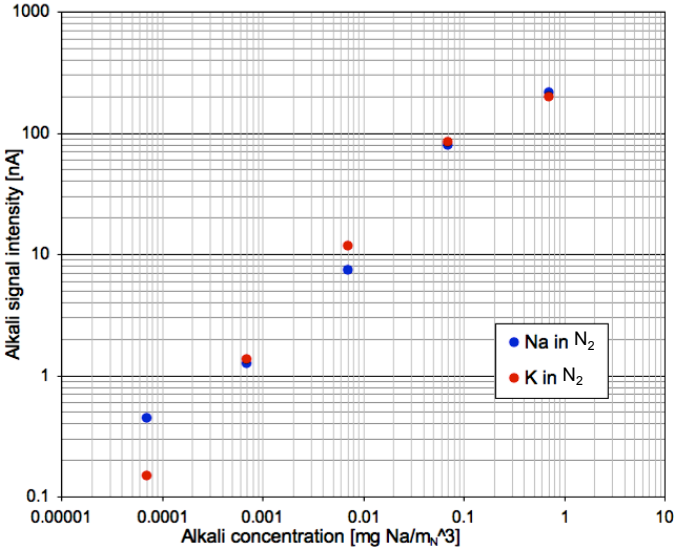
Measurement setup of the SID II



Heated platinum filament inside the detector

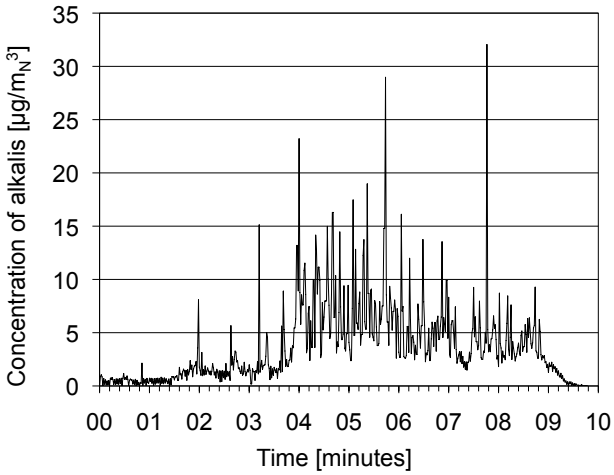


Calibration of the alkali detector with aerosols generated from a ultrasonic nebulizer



Alkali slip stream of a gas washing system

fed with raw gas from a bubbling fluidized bed reactor using grass



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Kowalski, T., "Evaluating a Surface Ionization Detector for Measuring Alkalis in Biomass Gasification", PhD-Thesis, Diss. ETH Nr. 17067, ETH Zürich, 2007.