



**DEPARTMENT OF CHEMISTRY AND MOLECULAR  
BIOLOGY**

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN NATURAL SCIENCE,  
SPECIALIZATION IN CHEMISTRY

**Alkali Metals and Tar in Biomass  
Thermochemical Conversion:  
Development and Application of Online  
Measurement Techniques**

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The thesis will be defended in English on Friday, 2<sup>nd</sup> of March 2018,  
at 10:00 in the room KC, at Kemigården 4,  
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ISBN: 978-91-629-0460-9

## Abstract

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Biomass is a renewable resource that can substitute the fossil-based products we depend on today. However, the conversion techniques require further improvement in order to be competitive with the traditional industry. One of the limitations is associated with the absence of measurement methods with sufficient time resolution that can be used to characterize the complex systems and optimize process conditions.

This thesis presents the development and application of novel measurement methods, capable of time-resolved characterization of tar and alkali metals, which are key components in biomass gasification. The measurement methods are mainly adapted from aerosol science and based on thermal analysis and surface ionization of aerosol particles. Long-term measurements are achieved by dilution and conditioning of hot product gas, which allow condensable components to form aerosol particles that are subsequently analyzed.

The developed methods are used to determine alkali, tar and particle concentrations in industrial scale facilities for biomass gasification. The aerosol characterization methods are also applied in flame chemistry and radiation research. Studies performed in dual-fluidized bed (DFB) gasification systems indicate that the alkali metal content of biomass to a large extent is emitted during the gasification process, and observed concentrations are close to the levels predicted by equilibrium calculations. The high alkali concentrations have implications for catalytic processes in the fluidized beds and for downstream processes including corrosion, fouling, and upgrading to commercial products.

The developed methods are employed to characterize the transient conditions when changes in operational parameters and additives are used to optimize the gasification process. A significant increase of the alkali metal concentration was observed when alkali salts were inserted directly to a gasifier, which suggests a fast volatilization in the reducing environment. Additives to the combustion side of the DFB imposed notable effects in the product gas, and the results provide information regarding the transfer mechanisms of inorganic compounds in the system. Additions of olivine and ilmenite reduced the gas-phase alkali metal concentration, indicating a fast reaction between alkali metal compounds and the minerals. The applied changes also affected the production of condensable tar, and the tar concentration was found to anti-correlate with the alkali metal concentration when a sand bed was used, while no clear trend was observed with an olivine bed.

The studies confirm that several options are available to improve the alkali metal and tar behavior in biomass gasification, and suggest that online monitoring is needed to study and optimize the underlying processes.

**Keywords:** Tar, Alkali Metals, Biomass, Thermochemical conversion, Online Measurements.

ISBN: 978-91-629-0460-9