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2007

Link to publication

FINE PARTICLE EMISSIONS FROM SOLID BIOFUEL COMBUSTION STUDIED WITH SINGLE PARTICLE MASS SPECTROMETRY – IDENTIFICATION OF MARKERS FOR ORGANICS, SOOT AND ASH COMPONENTS

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Keywords: Biofuels, Single Particle Analysis, ATOFMS, Combustion

INTRODUCTION

An increased use of biofuels in residential heating is desired to decrease net emissions of green house gases, such as CO_2 to the atmosphere. This includes conventional woody biofuels, as well as novel crop fuels such as corn. It is well established that the particle emissions during less optimised combustion in small scale wood combustion are most often dominated by products of incomplete combustion, i.e. organic and elemental carbon (OC/EC), McDonald et al. (2006). In contrast during optimised combustion in modern domestic pellet combustion systems, the aerosol can be dominated by ash compounds, especially KCl and K_2SO_4 formed via heterogeneous reactions in the gas-phase. However, little research has focused on the variations in physical and chemical particle properties over the combustion cycle. This is partly due to the lack of experimental methods with sufficient time resolution to follow the inherently transient nature of batch wise wood log combustion. Further, little information is available on emissions from novel fuels such as corn. For example, corn has higher ash content than conventional wood fuels. In this work we used single particle mass spectrometry to investigate chemical signatures from three wood log fuels (oak, pine and birch) and corn.

METHODS

The wood fuels were combusted in a conventional wood stove, while the corn was combusted in a commercially available corn stove, which operates similarly to modern wood pellet stoves. Each wood-combustion experiment involved start-up from a cold stove with a full load of fuel. Fuel was then added once and experiments were conducted until only glowing embers remained. Particles were sampled and diluted with particle free air using a three stage dilution system which allowed dilution ratios between 1:10 and 1:10000. An Aerosol Time-of-Flight Mass Spectrometer (ATOFMS; TSI Inc., Shoreview, MN, USA) was used to study chemical signatures from single particles in the range 100-500 nm. In a few experiments a Differential Mobility Analyzer was applied upstream of the ATOFMS to determine the particle effective density. A Scanning Mobility Particle Sizer was used to determine the particle size distribution (20-800 nm). A Tapered Element Oscillating Microbalance was used to determine the total mass concentration (PM2.5) and a gas analyzer (TSI CA-6215) was used to determine the flue gas composition (O_2, NO_x, CO).

RESULTS AND CONCLUSION

The emission factors of $PM_{2.5}$, CO and NO_x varied strongly between corn and wood combustion. For corn the average $PM_{2.5}$, CO and NO_x emission factors were 28, 120 and 297 mg/MJ, respectively, while for wood combustion it was 102, 3100 and 97 mg/MJ. The emission factors were similar for the three wood fuels studied.

During the start-up phase and during throttling of the supply air in wood combustion, strong organic markers were present. Several of these, for example m/z =-45 ($C_3H_3O_2^-$), -59 ($C_3H_3O_2^-$) and -71 ($C_3H_3O_2^-$) have previously been detected from pure levoglucosan (Silva et al. 1999), a dominant organic component from low temperature wood combustion. Signatures of Poly Aromatic Hydrocarbons (PAHs) were also strongly enhanced during the start-up phase (Figure 1).

In the efficient combustion phase, many markers for organic compounds diminished, while $^{113}K_2Cl^+$ - $^{24}(C_2)^-$, $^{36}(C_3)^-$, $^{48}(C_4)^-$ were strongly enhanced (Figure 1). We interpreted this to mean that emissions during the start up phase were rich in organics while emissions during the efficient combustion phase were dominated by ash compounds such as KCl and soot. Signatures of particles from Oak, Birch and Pine showed strong similarities.
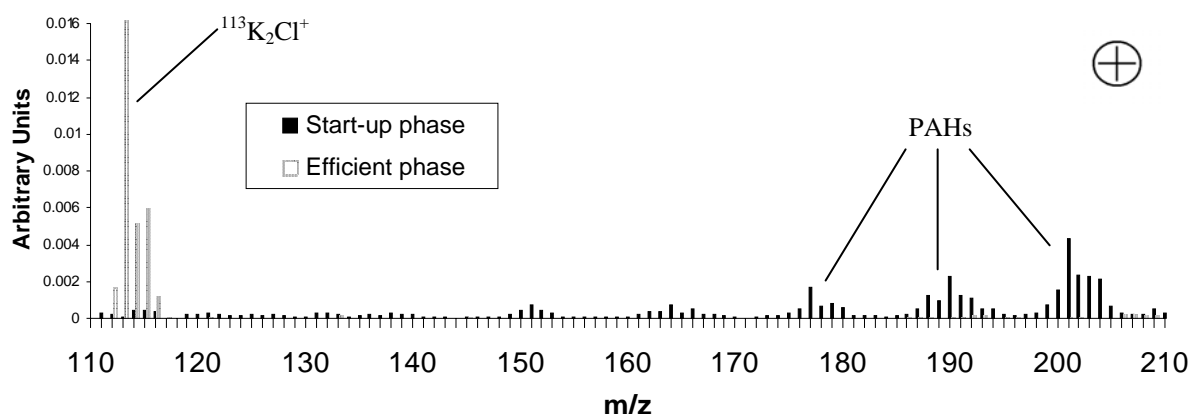

Figure 1. Average positive mass spectrum from ATOFMS measurements during the start-up phase and efficient phase in birch combustion.

When the corn stove was operating optimally, markers for inorganic ash components were dominant. These included $^{39}K^+$, $^{113}K_2Cl^+$, $^{97}HSO_4^-$ and $^{79}PO_3^-$. The largest difference between the composition of corn compared to wood emissions was the strong signature for phosphates and the generally weaker signatures for organics and soot. Note that the corn combustion process is semi-continuous as opposed to batch-wise log combustion, where distinct combustion phases can be identified.

Overall the laser-desorption ionization approach used in the ATOFMS instrument enabled us to detect signatures from organic compounds, soot and low volatility alkali salts, such as KCl. It is a promising tool to investigate the variations in particle chemical composition during the inherently transient nature of batch-wise wood log combustion. The combination of these three classes of signatures is promising for source receptor studies.

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