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Influence of sulphur addition on emissions of polycyclic aromatic hydrocarbons during biomass combustion

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Abstract

Emissions of polycyclic aromatic hydrocarbons (PAH) in the flue gas of a bark fuelled combustion facility were monitored in real time by time-of-flight mass spectrometry combined with resonance-enhanced multiphoton ionization. Sampling and on-line analysis could be maintained up to more than six hours consecutively, providing an insight in the aromatic profile of gaseous emissions as a function of varying combustion conditions. Naphthalene concentrations were quantified by determining a response factor of the ionization signal relative to toluene, which served as an external standard. Limits of detection of 1 ppb could be achieved with a time resolution of ten seconds. The emission of PAH occurred in peaks displaying exceeding levels of concentration. Between such emission peaks PAH concentration could drop to ground level near the limit of detection. Addition of sulphur to the combustion chamber – either as ammonium sulphate solution or elemental sulphur pellets – caused a significant decrease in the number of emission peaks, yielding an overall diminishment of average PAH concentration up to 88%. This was accompanied by a simultaneous decrease in concentration of carbon monoxide and volatile organic compounds, indicating an improvement in combustion quality after sulphur injection.

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Keywords: Biomass combustion; Online mass spectrometry; Photo ionization; Sulphur; Polycyclic aromatic hydrocarbons

1. Introduction

Combustion of biomass has gained increasing interest in recent years as an alternative to fossil fuels with respect to energy and heat generation. Despite being a regenerative and carbon dioxide neutral energy source, biomass combustion shares a number of similarities with its fossil fuel ana-

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logue. Thereby, the generation of products of incomplete combustion, e.g. carbon monoxide, polycyclic aromatic hydrocarbons (PAH) as well as other organic compounds is of importance with respect to environmental and health issues. The actual formation of such hazardous compounds is dependent on the utilized fuel, the design and operating conditions of the combustion appliance as well as the installed remediation and flue gas cleaning techniques.

Monitoring PAH emissions from larger scale combustion facilities in real time is often a challenging task due to the complexity of the combustion off-gases and their high dynamic behaviour. Optical diagnostic methods, especially jet-cooled laser induced fluorescence (LIF) have recently received increased relevance for the investigation of PAH in flames [1,2]. Mass spectrometry as a versatile and fast yet sensitive analytical method also appears as a feasible approach for this scope of work. However, the most common ionization method in mass spectrometry, electron ionization, bears the drawback of ionizing every component of the flue gases and executing a hard ionization, i.e. heavily fragmenting the transient organic combustion products. Although PAH are relatively stable species that are showing little fragmentation and ample signals of their molecular ions, the appearance of fragments from aliphatic species and the high abundance of ions from the bulk gases could considerably affect the interpretation of EI mass spectra.

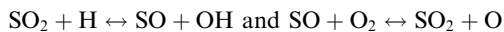
Resonance enhanced multi-photon ionization (REMPI) [3–5] with intense pulsed laser light constitutes an alternative selective and sensitive ionization technique for PAH detection in real time. For ensuring a fast monitoring REMPI is usually combined with time-of-flight mass spectrometry (TOFMS) enabling temporal resolutions in the range of one second or even a few hundred milliseconds.

An interesting deliberation with respect of monitoring and controlling emissions is the correlation of the various products of incomplete combustion among each other. A better understanding of such interrelations might be helpful, if for example one compound is susceptible to be influenced by elevated concentrations of other components. However, the determination of such correlations often proves a difficult task in itself due to the large number of potential interactions between the numerous species present. Moreover, it is difficult to transfer correlations verified under laboratory conditions to large scale plants, and results from one combustion facility may not be valid for others.

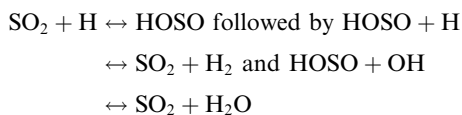
In this connection the role of sulphur merits attention. This element is already known to influence corrosion phenomena in wood combustion plants by reducing corroding alkali chlorides and transferring them to less corrosive alkali sulphates

[6]. Furthermore, addition of sulphur to incineration processes could effectively reduce the formation of polychlorinated dioxins and furans by converting chlorine to hydrogen chloride and inhibiting the catalytic activity of copper based metals [7–13]. Beyond that, the presence of sulphur dioxide (SO₂) may affect either thermal nitric oxide (NO)-formation by catalyzing radical recombination, leading to a reduction of thermal-NO exit emissions [14,15] or fuel-nitrogen conversion to NO [15–17]. However, the subject of sulphur/nitrogen interaction is still a field of uncertainties. Inhibition of soot formation by adding SO₂ or hydrogen sulphide has been reported as well [18–20]. There are also hints at a reduction of carbon monoxide in flue gases of biomass combusting plants [21]. Although carbon monoxide is usually strongly correlated to PAH concentrations, the effect of sulphur addition on the behaviour of PAH has been ambiguous in the same experiments.

Apart from these experimental observations there are several publications engaging in unravelling the mechanisms of pollutant formation in combustion and especially how sulphur compounds are working on a molecular level to achieve these effects [22–28]. These studies reveal very complex interactions of SO₂ as the main rapidly formed sulphur species in combustion with the radical pool present at combustion processes. Close to stoichiometric conditions, SO₂ promotes carbon monoxide (CO) oxidation and thus contributes to reducing CO concentration levels through the following reactions [22]:



Subsequently the formed OH and O radicals oxidize – alongside other species – CO. However, SO₂ is not totally depleted by these reactions, there is another reaction pathway leading to its reformation via the HOSO radical:



However, under leaner and fluidized bed combustion conditions it was also found that SO₂ may inhibit CO oxidation by catalyzing oxygen-radical recombination [29,30], or that there is no effect at all [31], adding further to the complexity of the mechanistic interactions. As a consequence, the observed reduction of CO in [21] by addition of relatively low amounts of sulphur does not agree with model predictions. To what extent these findings could be transferred to the formation of PAH remains unclear. Incidentally the role of SO₂ in reduction of soot formation has been explained by enhancing oxidation of already formed

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