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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.

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 (SO_2) 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 SO_2 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 SO_2 as the main rapidly formed sulphur species in combustion with the radical pool present at combustion processes. Close to stoichiometric conditions, SO_2 promotes carbon monoxide (CO) oxidation and thus contributes to reducing CO concentration levels through the following reactions [22]:

$$SO_2 + H \leftrightarrow SO + OH \text{ and } SO + O_2 \leftrightarrow SO_2 + O$$

Subsequently the formed OH and O radicals oxidize – alongside other species – CO. However, SO_2 is not totally depleted by these reactions, there is another reaction pathway leading to its reformation via the HOSO radical:

$$SO_2 + H \leftrightarrow HOSO \text{ followed by } HOSO + H \leftrightarrow SO_2 + H_2 \text{ and } HOSO + OH \leftrightarrow SO_2 + H_2O$$

However, under leaner and fluidized bed combustion conditions it was also found that SO_2 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 SO_2 in reduction of soot formation has been explained by enhancing oxidation of already formed

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particles rather than inhibiting PAH formation as precursors to particle inception [19,20].

In this work, the effect of sulphur addition to PAH formation and concentration levels in the flue gas of a grate furnace combusting bark in Sweden is investigated. PAH concentrations are directly monitored in real time by REMPI-TOF-MS over several hours to study the long term effects of adding sulphur to the feedstock.

2. Experimental

The furnace for this study was a grate fired bark boiler, which has been previously chosen for sulphur and carbon monoxide measurements [32]. Bark from conifers as feedstock is fed to the grate by three chutes. Primary air is supplied in six zones, and the flue gases are recirculated. The main purpose of the facility is steam production at 6.5 MPa and 485 °C. Flue gas cleaning consists of an electrostatic precipitator (ESP) and a flue gas condensing unit. There is no unit for nitric oxides (NO_x) reduction. NO_x levels are however relatively low (40 mg/MJ on year average), but CO emissions are high (2000 ppm). From this, one can assess that this boiler is not representative of modern bark or biomass furnaces. However, for the purpose of this study, its high CO and consequential PAH levels combined with the low sulphur content of the bark fuel makes it ideal to investigate the fundamental influence and interaction of sulphur with respect to PAH concentrations.

Figure 1 depicts a scheme of the furnace showing the feedstock inlet, the combustion chamber, boiler section and flue gas pipe leading to the ESP. Sulphur addition was realized in two different ways. First, an ammonium sulphate solution (40%) was injected through the side walls of the combustion chamber. Temperature at the injection point was 850 °C. Alternatively elemental sulphur granulates were fed to the chute together with the bark feedstock. In each case, three rates of injection were chosen in a way that the sulphur dosage was corresponding to 23 mg S/MJ, 46 mg S/MJ, and 92 mg S/MJ, respectively, independent of the manner of sulphur addition. The actual applied flow- and feed-rates are summarized in Table 1. Since the fuel feeding rate was set to 8000 kg/h, the added sulphur content amounts to 0.035%, 0.075%, and 0.15%, respectively.

The sampling point for the on-line REMPI-TOFMS measurement was in the flue gas downstream of the economizer, but before the ESP unit. Temperature of the flue gas was between 125 °C and 150 °C. In the same location an isokinetic sampling point for conventional off-line chromatographic gas phase analysis of PAH according to EN-1948-2:2006 was set up. These GC/MS measurements with a sampling time of six hours were carried out for reference purposes.

The requirement on the sampling and inlet system for REMPI-TOFMS is a rapid transfer of polyaromatic substances to the mass spectrometer without losses. Therefore, sampling was conducted by means of a quartz tube and a sampling pump to maintain a gas flow of 5 l/min. Entrained

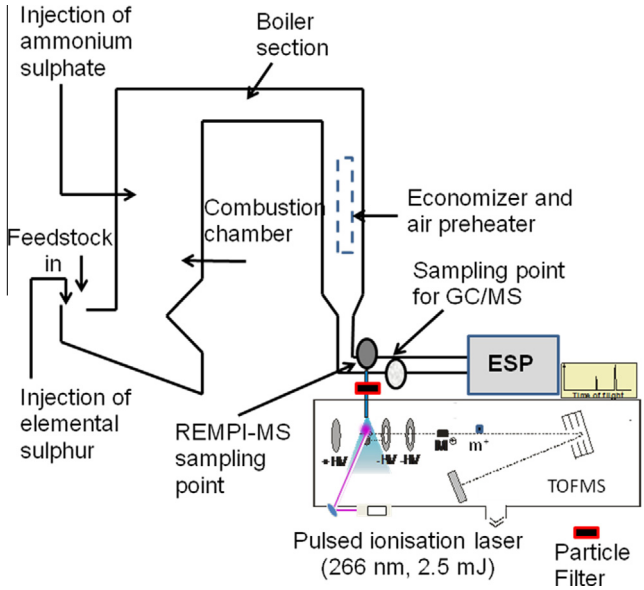

Fig. 1. Scheme of the furnace, boiler and flue gas duct of the bark combustion facility. The sampling points for REMPI-TOFMS online monitoring and conventional gas phase sampling are depicted.

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Table 1
Sulphur dosage to the combustion chamber of the bark boiler and naphthalene concentrations (six hour average measured by REMPI-TOFMS) in the flue gas of the bark boiler.

Sulphur dosage	Averaged naphthalene concentration [μg/m^3]
No sulphur addition	42.0
Flow-rate of $(NH_4)_2SO_4$ [l/h]	
25	10.0
50	5.0
95	3.5
Feed-rate of elemental sulphur [kg/h]	
2.9	5.0
5.8	4.0
11.6	1.0

particles were removed using a surface filter (pressed glass fibres). A small portion of the de-dusted gas, ca 10 ml/min, was drawn through a deactivated fused-silica transfer capillary (200 μm i.d.) to the ion source of the mass spectrometer. All parts of the sampling train outside the flue gas duct were heated to a temperature of 220 °C to avoid condensation. The transfer capillary ran in a heated flexible line. At the end of the transfer line, the capillary was embedded in a heated stainless steel needle, the tip of which was located between the electrodes of the ion source. The effusive beam formed was directly hit underneath the needle tip by laser pulses.

The utilized laser was a compact frequency quadrupled Nd:YAG laser (Quantel Laser, Les Ulis, France) providing intense pulses ($\lambda = 266$ nm, 2.5 mJ pulse energy, 10 Hz repetition rate) to the REMPI process. Ions formed in the ionization source of the reflection time-of-flight mass spectrometer (Stefan Kaesdorf, Munich, Germany) with a mass resolution of 650 at 106 m/z were detected by a two-stage multi-channel plate detector (MCP, 40 mm diameter). The ion source and the flight tube are differentially pumped by two 210 l/s turbo-molecular pumps (TMU 261, Pfeiffer Vacuum, Aslar, Germany). TOFMS mass spectra were recorded by two transient recorder cards (250 MHz, 1 GS, signal resolution 8 bits for 256 points) from Acqiris in Switzerland. One card monitored continuously the low-voltage region of the spectrum (typically below 50 mV) with a resolution of 8 bit and the other card monitored the whole region up to 5 V. This combination of cards yields a greater dynamic range. TOFMS spectra from 100 consecutive laser shots have been averaged, yielding a time resolution of 10 s. Data processing was carried out using LabView (National Instruments, USA) and purpose-written software.

Production of quantified data is difficult with the described setup and in this study was limited to naphthalene. Since the conventional GC/MS measurements had been at hand, a new approach was applied for quantification. A standard gas (nitrogen containing 100 ppb each of benzene, toluene and p-xylene) was used to calibrate the mass spectrometer with respect to these compounds before and after each measurement cycle. Naphthalene was indirectly calibrated by determining its REMPI cross-section at 266 nm relative to that of toluene.

These relative REMPI cross-sections were measured by dissolving a known amount of naphthalene in methanol, injecting the solution with a constant flow-rate into a stream of nitrogen, drawing off a small portion of this gas stream into the ion source of the mass spectrometer and comparing the resulting TOFMS signal with that for 100 ppb toluene. A response factor for naphthalene ionization is then calculated. Comparison of the two daily REMPI-MS calibrations (before and after each measurement period) showed relatively low deviations: the parameters of the set-up of the instrument such as laser power, which was monitored continuously throughout the experiments, and TOFMS performance etc. were robust and seemed to be reliable for the whole day. The subsequent calculated six hour average concentrations of naphthalene from four different monitoring experiments could then be compared to the values obtained by GC/MS after six hour sampling. The mean deviation of the REMPI-TOFMS derived value amounted to $6.9 \pm 1.2\%$, which was deemed feasible for this approach to quantify on-line naphthalene concentrations. A more detailed discussion of the procedure will be the subject of a forthcoming publication.

3. Results and discussion

Figure 2 gives an example of the average PAH pattern from the measurement without sulphur addition to demonstrate which PAH could be detected in general. Compounds that could be identified unambiguously comprise benzene, toluene and phenol as monocyclic aromatic compounds. Furthermore, naphthalene, phenanthrene and its alkylated homologues as well as pyrene are observed. The isomers of phenanthrene and pyrene, respectively, i.e. anthracene and fluoranthene could be excluded, since their relative cross sections at the ionization wavelength of 266 nm are two orders of magnitude lower. Finally, retene at 234 *m/z* could be assigned as typical marker compound of combustion of coniferous biomass. Signals at other *m/z* values had to be assigned to more than one contributing compound. At 118 *m/z*, both indane and benzofuran are possible. The two isomers of methylnaphthalene could not be distinguished and the signal at 142 *m/z* represents the sum value of both. The signals at 154 *m/z* and 168 *m/z*, respectively, could either

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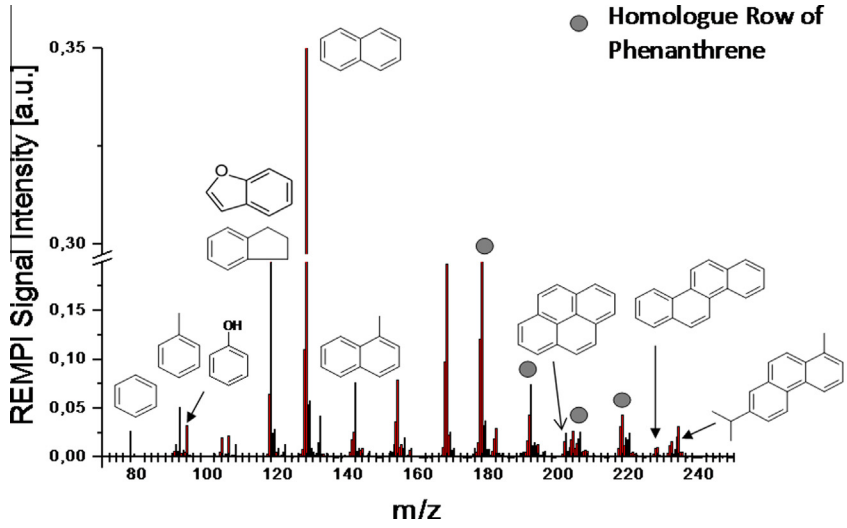

Fig. 2. REMPI-TOFMS spectrum averaged over two hours sampled in the flue gas duct of the bark boiler when operating without sulphur addition.

originate from lignin decomposition products such as syringol and vanillic acid or hydrocarbons such as biphenyl. Finally, chrysene has to be regarded as the most likely species assigned to the signal at 228 *m/z*, but contributions from its isomers cannot be precluded.

When moving over to time-resolved results, it could be observed that without sulphur addition PAH emissions occurred in several distinct peaks at certain times, during which the emissions showed exceptional high values. In the intervals between the peaks, PAH signals dropped to low levels near to the limit of detection, which was around 1 ppb for naphthalene. All detected PAH depicted very similar trends with time, i.e. they peaked and dropped simultaneously. Moreover, carbon monoxide concentrations, which were measured routinely at the facility, showed the same behaviour, corroborating the correlation between CO and PAH emission. Since naphthalene accounted for 75% of all detectable aromatic compounds, and all PAH showed the same course with time the following figures are restricted to naphthalene concentration. Figure 3 depicts the time-resolved naphthalene concentration of the monitoring experiment without sulphur addition. The large emission peaks are clearly visible, elevating naphthalene concentration up to 250 ppb. After some peak events, concentrations did not drop to ground level before the next peak emission occurred. However, there was an intermediate phase of approximately 20 min duration (between 17:50 and 18:10), where the concentration was almost negligible. This implies that phases of good and bad combustion alternated in unforeseeable manner and PAH emissions were caused by such peak events of bad combustion, which occurred however not permanently during the monitored time span. CO concentration was continuously monitored as well and exhibited a very good correlation to the PAH signals, thus confirming the phases of good and bad combustion.

The effects of sulphur addition on naphthalene concentration – other detected aromatic compounds behaved in the same manner – are on the one hand listed in Table 1, which depicts the respective six hour average concentration values. Even the lowest sulphur dosage led to a significant reduction of naphthalene level in the flue gas. The reduction was 75% when ammonium sulphate was used as source of sulphur, and 88% when elemen-

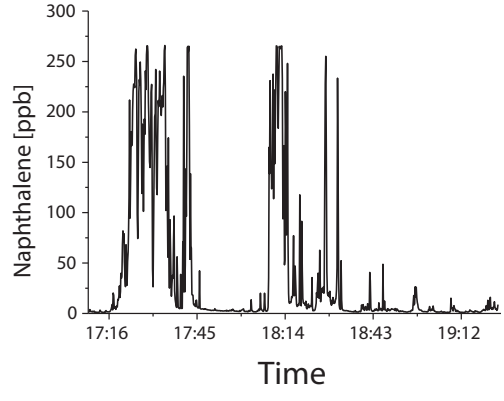

Fig. 3. Time-resolved naphthalene concentration measured by REMPI-TOFMS in the flue gas duct of the bark boiler when operating without sulphur addition (same experiment as in Fig. 2).

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tal sulphur was added. Increase of the sulphur dosage enhanced the reduction further, forcing naphthalene concentration down to the limit of detection for the highest dosage of elemental sulphur. Thereby, the decrease in naphthalene level was in all cases slightly larger with elemental sulphur, albeit the differences were not overly pronounced between the two variants of sulphur injection.

Figure 4 reveals the actual changes in the temporal course of naphthalene concentration when sulphur is added to the bark combustion. In Fig. 4A the monitoring experiment is shown with the lowest dosage of elemental sulphur (2.9 kg/h). When compared to Fig. 3, the number of emission peaks was considerably reduced despite the measurement was drawn out to more than six hours. Peak concentration values could still reach 200 ppb, but on the average such a peak emission happened only once in an hour. With the highest sulphur dosage (11.6 kg/h, Fig. 4B) over the course of six hours only one single peak emission could be registered with an almost insignificant peak height of 3 ppb. Apart from this, naphthalene levels ranged in the order of the limit of detection. The same trends were observed when ammonium sulphate was injected as sulphur source (see Fig. S1).

Hence the decrease in average naphthalene concentration was primarily due to the suppression of the peak emission events or in other words the diminishing of bad combustion phases when sulphur was added. This was further supported by the behaviour of carbon monoxide concentration, which during the sulphur injection experiments was observed to follow the course of naphthalene and the other PAH. Increased averaged sulphur dioxide concentrations had only resulted with the highest level of sulphur dosage. With the lowest and middle dosage SO_2 levels remained within the fluctuations that occurred during combustion without sulphur addition and which were due to the sulphur content of the fuel in combination with the highly varying combustion conditions.

The question remains open how the introduced sulphur – most likely in the form of sulphur dioxide, in which the injected sulphur should be transformed in combustion – interacts with intermediates and radicals present in the combustion region. From the model prediction the main reaction of SO_2 in the connection to carbon monoxide decrease is with the H radical promoting oxidation of CO [22]. However, this is difficult to transfer to PAH forming reaction pathways, where H radicals are formed beside the aromatic compounds [26]. The main effect of sulphur addition at the investigated facility seems to consist in an improvement of the combustion quality, which would affect all products of incomplete combustion such as CO, volatile organic compounds

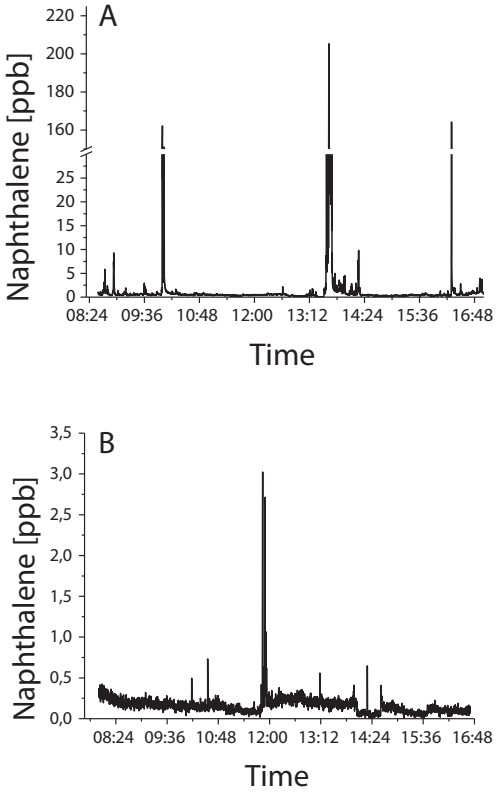

Fig. 4. Time-resolved naphthalene concentration measured by REMPI-TOFMS in the flue gas duct of the bark boiler when operating with sulphur addition (elemental sulphur pellets). (A) Lowest dosage (2.9 kg/h). (B) Highest dosage (11.6 kg/h).

and PAH in the same way, resulting in an overall decrease of concentration levels. This may hint at sulphur dioxide acting along the pathway of oxidation, being transformed to SO_3, which is another potential reaction of SO_2 in combustion models [24]. Consequently, the detailed unravelling of the mechanism will have to be investigated in future experiments designed especially for that purpose, where various ancillary conditions could be varied.

4. Conclusions

REMPI-TOFMS proved to be a reliable measurement tool for online and real time detection of PAH under field conditions. Consecutive monitoring for more than six hours of two to four-ring PAH in the flue gas of a bark boiler facility has been realized. The addition of sulphur either as ammonium sulphate solution or as elemental sulphur directly added to the feedstock has resulted in a significant reduction of PAH concentration levels. The effect was more pronounced the more

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sulphur was added, however, there is an economic component to be considered. Moreover, the portability of these results to other combustion facilities would have to be investigated; at first the findings reported here are only valid for the utilized installation. Since the main effect has been revealed as improvement of the combustion quality, at first glance there is no difference between sulphur injection and optimization of combustion, which should yield the same reduction of CO and PAH levels. The mechanism of the SO_2 impact on PAH concentration is still unknown and should be investigated more thoroughly under laboratory conditions looking at the basic reactions.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.proci.2014.07.046.

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