

Laser measurement of KCl vapor in 4 MW CFB boiler during straw combustion and ferric sulfate injection

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ABSTRACT

Combustion of the renewable solid fuels and the mixed fuels causes serious corrosion and slagging problems in combustion boilers. One cause of the problems is alkali chloride vapors, e.g. KCl, that is formed during combustion due to the high content of alkali and chlorine in the biomass. In order to prevent these problems with proper fuel content and/or additive injection, a sensitive and reliable monitoring technique for the alkali chlorides is required.

A laser measurement technique was applied to monitor the KCl concentration through the flue gas channel of a 4 MW circulating fluidized bed boiler during combustion of straw and wood. The straw composition in the fuel was changed from 0% to 100 %, and ferric sulfate injection was used to control the KCl concentration in the furnace. Chlorine is known to occur mainly in forms of KCl and HCl in the flue gas due to the high content of potassium in straw. The vaporous KCl can be converted to less harmful potassium sulfate and HCl with ferric sulfate injection. Single measurement curves are discussed and the operation of the laser measurement in two longer-term experiments is demonstrated. The laser measurement resulted stable concentration values in steady combustion conditions and followed transients due to the furnace operational changes with time resolution less than a minute. The online laser measurement enables a stable and controlled KCl concentration due to actively adjusted ferric sulfate injection rate.

1 INTRODUCTION

Environmental aspects and increasing price of the fossil fuels have increased the interest of the renewable fuels in power production. One good alternative as a largely CO₂ neutral fuel, is biomass that can be harvested, for example, as agricultural residues. However, the combustion of the renewable solid fuels and the mixed fuels causes serious corrosion and slagging problems in combustion boilers /1/. One cause of the problems is the alkali chloride vapors that are formed due to the high content of alkali and chlorine in the biomass. In order to prevent these problems with proper fuel content or a control substance a sensitive and reliable monitoring technique for the alkali chlorides is required.

Recently, an optical method called collinear photofragmentation and atomic absorption spectroscopy (CPFAAS) for detection of KCl vapor at parts per billion (ppb) level was introduced /2/. CPFAAS is a derivative of Beer-Lambert law and its calibration in gas sensing is directly based on the physical constants /3/. The method combines the benefits of the previously presented KCl detection techniques, excimer laser induced fragmentation fluorescence (ELIF) /4/ and differential optical absorption spectroscopy (DOAS) /5/, in sensitivity and in diagnostics of large sample volumes.

In this study, a KCl detector based on CPFAAS was integrated to the flue gas channel of 4 MW_{th} circulating fluidized bed boiler. The performance of the KCl detector was studied during the start-up of the boiler and during KCl mitigating ferric sulfate additive injections. The measured KCl values were compared to HCl readings from FTIR in order to verify their reliability.

2 EXPERIMENTAL METHODS

2.1 Measurement environment

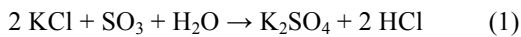
The 4 MW_{th} combustion test facility used for the tests has a height of 13 m and a furnace cross-section area of 1.21 m². The boiler is water cooled, and the output heat is used in the local district-heating network. The CFB furnace is provided with optional cooling surfaces to facilitate the heat transfer for various test configurations. The furnace was combusted with straw during the ferric sulfate injection experiments. The composition of the used straw is presented in Table 1. Due to the high content of the potassium in the fuel, the chlorine occurs mainly in forms of KCl and HCl in the flue gases.

Table 1. Composition and heating value of straw used as fuel.

Total moisture	9.7 %	Gross calorific value, dry basis	18 MJ/kg
Bulk density	570 kg/m ³	Net calorific value, dry basis	17 MJ/kg
Analysis moisture	5.9 %	Net calorific value, as received	15 MJ/kg
Ash 550 °C, dry basis	8.1 %	Aluminium (Al)	280 mg/kg
Ash 815 °C, dry basis	7.5 %	Phosphorous (P)	300 mg/kg
Volatile matter, dry	74 %	Potassium (K)	7600 mg/kg
Carbon, C dry	46 %	Calcium (Ca)	3700 mg/kg
Hydrogen, H dry	5.9 %	Magnesium (Mg)	590 mg/kg
Nitrogen, N dry	0.61 %	Manganese (Mn)	21 mg/kg
Oxygen, O dry, calculated	40 %	Silicon (Si)	23000 mg/kg
Fluoride, F dry	0.01 %	Iron (Fe)	160 mg/kg
Chloride, Cl dry	0.29 %		
Sulfur, S dry	0.13 %		

2.2 Ferric sulfate reaction with KCl

The superheater corrosion risk of high- potassium and high- chlorine fuels is reduced through changing of the flue gas atmosphere with fuel fractions containing sulfur or additives containing elemental sulfur or sulfate /6,7/. In this study the ferric sulfate was used to eliminate alkali chlorides in the flue gases. Ferric sulphate is thermally dissociated in high temperature followed by the formation of SO₃. Sulfur trioxide reacts with KCl through reaction



to less corrosive potassium sulfate and hydrogen chloride. Equation 1 indicates that the absolute changes in HCl concentration can be used to estimate the absolute changes in KCl concentration.

2.3 Online laser measurement

The physical steps in collinear photofragmentation and atomic absorption spectroscopy (CPFAAS) are presented in Fig. 1. The method is based on the continuous monitoring of the potassium atoms in the sample with an infrared laser having wavelength of 766.5 nm that corresponds to the absorption line of the potassium atoms. Fig. 1 a) shows how the IR laser beam is aligned to go through the sample containing KCl molecules. IR transmission may fluctuate significantly, when the sample itself is unstable. The actual measurement event starts when a UV pulse is triggered to pass the sample along the same optical path with the IR laser beam (Fig 1. b)). The wavelength of the UV pulse is selected to correspond to the dissociative UV absorption band of KCl molecules and, therefore, the amount of K atoms is temporarily increased. The increased amount of K atoms decreases the transmission of the IR laser due to the atomic absorption. Fig 1. c) shows how the K atoms recombine with Cl atoms or react with ambient gas compounds, when the IR transmission recovers to same level where it was just before the triggering of the UV pulse. A single measurement event lasts typically less than 5 μs. Transmission fluctuations, due to e.g. fly ash movement on measurement path, are negligible within short measurement time window and can be ignored.

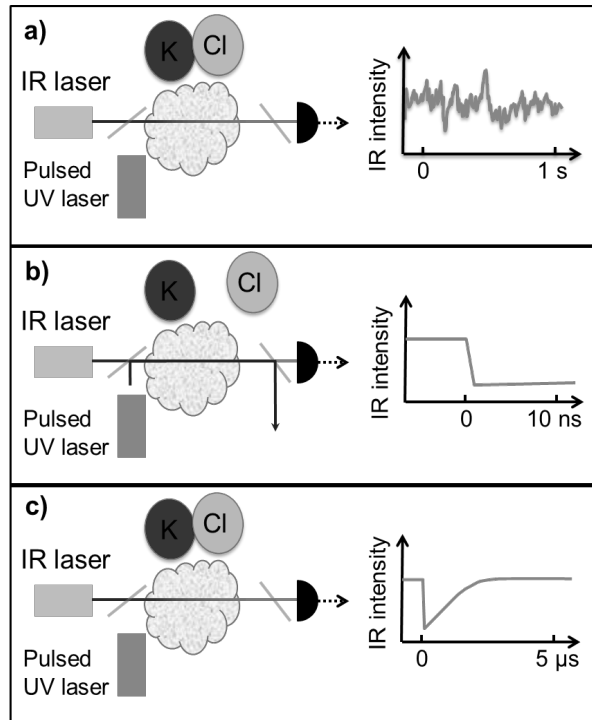


Figure 1. The principles of KCl detection using CPFAAS. a) IR laser measures the temporal transmission through the sample. b) UV pulse fragments KCl molecules inducing a fast decrease in IR transmission. c) The released K atoms react with ambient gases and IR transmission recovers its original level. The recovery is fast compared with sample fluctuations.

CPFAAS is shown to be capable of measuring accurate KCl concentrations from pure samples in laboratory conditions [3]. The power plant environment sets new challenges to CPFAAS technique due to other gas species absorbing the same 266 nm UV wavelength than KCl. The absorption by the other gases decreases the intensity of fragmenting UV pulse faster than it would be decreased in pure KCl sample and, therefore, a smaller amount of KCl molecules is fragmented.

In this study the distortion due to the other gases was minimized by measuring the UV intensities before and after the sample. The UV attenuation was approximated to be even through the sample, when a profile for the UV intensity through the furnace could be solved. By adding the approximated UV intensity profile to the previously introduced equation [3] the relation between the maximum absorbance αL_{max} , achieved right after the UV pulse has passed the sample, and a true KCl concentration x_{KCl} could be solved.

The highest measurement repetition rate in CPFAAS technique is limited by the recovery time of the K atoms and the maximum pulse repetition rate of the UV laser. In this study KCl detector was set to collect data with 7 HZ repetition rate and in 200 signal sequences corresponding to ~30 s measurement windows.

3 RESULTS AND DISCUSSION

Three single transmission curves resulting KCl concentrations of 5 ppm, 50 ppm and 230 ppm are presented in Fig. 2. The fragmentation of KCl molecules was induced with average UV input energy of 23 μJ and UV beam cross sectional area of 3.6 cm^2 . The presented single transmission curves demonstrate the potential of the technique. In all example signals signal to noise ratio was found to be 25 or better. The fast drop at $t=0$ becomes deeper as sample concentration is increased. The recovery times were found to vary, which indicates the fluctuations in gas atmosphere of the flue gas. The fluctuation in the base levels of the signals at $t < 0$ indicates the changing visibility through the sample.

The evolution of the KCl concentrations during the start-up of the furnace is presented in Fig. 3 a). The fuel was composed of 15 % of straw and 85 % of wood. The KCl readings are presented as distributions of KCl concentrations measured within 30 measurement time windows. The distributions are normalized with their maxima in order to enhance the contrast of the figure. The startup is done in three steps, which are seen as three

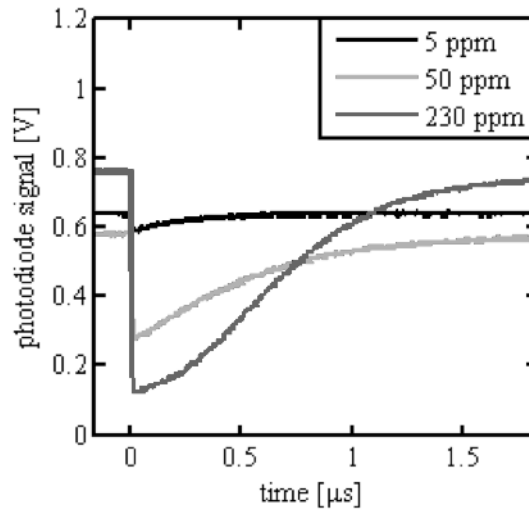


Figure 2. Three single CPFAAS transmission curves recorded in the vicinity of the UV fragmentation. The concentrations are calculated from the depths of dips at $t=0$.

different KCl levels. Within stable combustion conditions KCl detector resulted readings with small $\sim 5\%$ variation. The lowest reliably detected KCl concentration was 0.5 ppm. Fig. 3 b) presents an experiment, in which the load and the fuel of the furnace remained constant, but the flue gas atmosphere was modified with ferric sulfate injections. Ferric sulfate was injected with four different injection rates. The injection times are highlighted in Fig. 3 b) with double arrays and numbers 1, 2, 3 and 4.

At the beginning of the measurement the furnace was fired with 100 % of straw. The KCl and HCl concentrations were 235 ppm and 71 ppm, respectively. When the injection was turned on KCl concentration decreased within one minute to 85 ppm and simultaneously HCl increased up to 179 ppm. Similar KCl decrease and HCl increase behavior was observed when injection rate was increased in phases 2, 3 and 4. At the end of the experiment the injection was turned off, when KCl increased to 249 ppm and HCl decreased to 72 ppm. The temperature of the flue gas decreased 20°C when injection was started and increased 20°C when injection was turned off. The difference between the flue gas temperature at start point and the end point was $\sim 10^\circ\text{C}$.

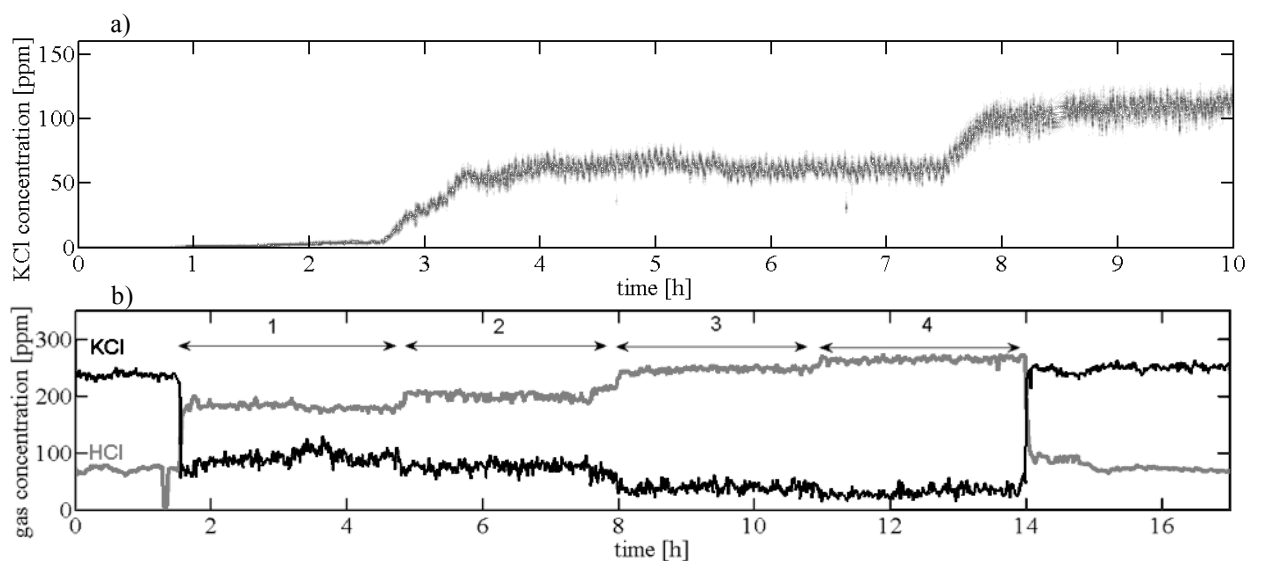


Figure 3. a) Evaluation of KCl concentration during start-up of furnace, and b) average KCl (black) and HCl (gray) concentrations during ferric sulfate injections.

Table 2. Measured gas concentrations at different injection phases.

Phase	HCl [ppm]	KCl [ppm]
beginning	71	235
1	179	85
2	199	69
3	249	39
4	268	25
end	71	249

The measured gas concentrations at the different ferric sulfate injection phases are listed in Table 2. The most dramatic changes are seen when injection is started and ended, but these reference points are invalid for comparison of ΔKCl and ΔHCl due to changed temperature of flue gas. Otherwise, the temperatures remained nearly constant between the additive injection rates changes and comparisons between ΔKCl and ΔHCl was reasonable.

The comparison of the absolute changes showed approximately relation of $\Delta\text{KCl} \approx 0.75 \cdot \Delta\text{HCl}$. The observed relation justifies the order of the measured KCl values. The 25 % difference between ΔKCl and ΔHCl is reasonable when the gas sampling is taken into account. FTIR collected gas sample from the single point in the middle of the flue gas channel while the KCl detector measured the average gas concentration through the whole channel. Therefore, already small differences in spatial spreading of the injected additive caused different kind of measurement conditions for the two detectors. The 25 % difference can also be partly explained with estimated 1 m sample length. The accuracy of the sample length was 10 % that scales directly to the calculated KCl concentrations.

4 CONCLUSIONS

CPFAAS method was applied to monitor KCl vapor concentration in the flue gas channel of 4 MW_{th} circulating fluidized bed boiler. Single measurement curves were discussed and the operation of the detector in two longer term experiments was demonstrated. The detector measured stable concentration values in steady combustion conditions and followed the changing concentrations due to the furnace operational changes with time resolution less than a minute. The measured KCl concentration changes during the additive injections were also compared to HCl concentrations measured with FTIR detector. The relation between the detected KCl and HCl concentration changes was found to be $\Delta\text{KCl} \approx 0.75 \cdot \Delta\text{HCl}$, which verifies the correct order of magnitude for the measured KCl readings. The presented online laser measurement of KCl is suitable for continuous online monitoring as the calibration of the device can be maintained by following the UV laser pulse energies at the laser output and after the transmission through the process volume. Thus, the technique enables a stable and controlled KCl concentration in biomass combustion due to actively adjusted ferric sulfate injection rate.

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