Spontaneous atomic radiant emission of K and Na during combustion of wood and straw pellets

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Abstract

This work focuses on the measurement of spontaneous alkali release from biomass pellets during combustion by comparing two different techniques: a flame emission spectrometry (FES) and an inductively coupled plasma mass spectrometer (ICP-MS). The first trial was used for optical detection of chemiliuminescence spectra of selected metals using optical bandpass filters mounted on an iCCD (Intensified Charge Coupled Device) camera. For better understanding how alkali-metal releases, test runs with a single particle reactor (SPR) connected with ICP-MS have been performed. Time-resolved release profiles of relevant aerosol forming elements (K, Na) were determined and compared.

Introduction

These days the usage of solid biomass fuel extensively grows. With increase of biomass demand, the quality of biomass fuel becomes worse and worse. The biomass is often locally available renewable fuel. However, waste biomass combustion is related with certain technical challenges, which mostly are related to its inorganic constituents. The inorganics cause several problems during combustion and most important is the formation of aerosols, which might cause slagging, fouling or agglomeration formation on boilers walls. The formation of slags cause a very costly shutdowns of power plants for unexpected maintenance [1]. In general, it has been observed that ash deposition and corrosion problems are more common during combustion of biomass fuels with high alkali contents, such as hog fuel, straws or grasses. Correspondingly, clean wood biomass typically contain lower levels of chlorine, sodium and potassium than most other waste biomass fuels, but the corrosion also occur in wood-fired systems [2]. To prevent mentioned problems, fuel quality monitoring or early control of alkali release is necessary. Online detection of mentioned elements might help, but generally requires sophisticated measurement equipment [3-6]. The aim of the present work is to compare a recently developed online measurement technique with another method using a single particle reactor (SPR) to determine the release Na and K from a single pellet during combustion. Previous results [7] revealed that at the lower combustion temperature (750 °C) the spontaneous luminescence emissions of the Na* and K* was marginal. Therefore, to fully excite the alkali metals ions and get higher intensity a higher temperature is needed. This study examines the combustion of selected biomass pellets at 1000°C. The selected alkali emissions were investigated and release profiles from the results were obtained.

Experimental procedure

Two types of biomass, mainly hard wood and wheat straw, were used in experimental investigations. For combustion investigation, untreated and washed biomass particles were used. In order to remove alkalis from the samples a washing procedure with nitric acid was applied. Initially, raw wood and straw pellets are milled and sieved using a 500 μm mesh. Then 50 g of milled biomass was demineralized in nitric acid and water solution (pH=2) and stirred

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automatically for 1 h at 70 ºC. Afterwards, the biomass was filtered and washed with deionized water. Later, the biomass was dried at 105 ºC. Table 1 shows the alkali content found in the raw and washed samples. Finally, the biomass pellets with diameter of 8 mm were prepared.

Table 1. Alkali content in biomass before and after washing procedure

	Wood	Straw
Untreated, mg/kg		
K	339	16481
Na	4.46	45.06
After washing, mg/kg		
K	<0.1	1054
Na	<0.1	<0.1

Two different setups within the investigations were used. FES system mounted at Lithuanian Energy Institute in Kaunas (Lithuania), while SPR ICP-MS system at BIOENERGY 2020+ GmbH in Graz (Austria).

The first set of experiments capturing the flame emission spectra of selected radicals occurring during biomass pellets combustion was performed in the FES experimental setup. The experimental rig consists of a burner with a natural gas-air premixing chamber. The flame is created above the porous plate, while secondary air is used ensure a flame temperature of 1000 ºC, which is measured with a K-type (NiCr-Ni) thermocouple. Above the porous plate, a small grid is mounted in order to position the biomass particle in surrounding flame. The center temperature of the biomass pellet is measured with a K-type thermocouple.

The light emitted by the exciting of K* and Na* radicals was captured using an ICCD camera Andor Istar DH734-18U-E3. A detailed description of the camera system and parameters can be found in the previous works [7, 8].

The second part of experimental investigation was performed in the SPR ICP-MS experimental setup. The detailed description of setup and characteristics of the system is provided in literature [9, 10]. The experimental test rig consists of electrically heated reactor. The reactor has 4 horizontal side tubes, of which one port (two axial tubes on opposite sides) provides an optical access. The other ports are used for sample introduction and sample cooling. Inside the furnace, the biomass particle is placed on a sample holder, which is connected to a balance for the determination of mass loss during the thermal decomposition. During combustion of the biomass particle, the flue gases are released. A part of the flue gas is injected to an inductively coupled plasma mass spectrometer (ICPMS).

Results and discussion

The spontaneous radiant emission of measured alkalis radical by means of FES has a typical peak at the beginning of the biomass pellet combustion. Supposed, that this is related with a release of volatiles from biomass. During fuel devolatilization stage takes out some part of organic or inorganic compounds containing analyzed metals. By comparing, the two types of biomass can be seen that higher intensity of metal radical radiance occurs during straw pellet combustion. The raw straw pellets has the highest concentration of K (Table 1). Therefore, the detected intensity of luminescence was highest if comparing with wood pellet combustion. The emission peak of potassium was recorded at the end of the volatile combustion stage and the beginning of the char combustion stage. Analyzing the results obtained during combustion of washed biomass particles, the highest concentration of potassium was obtained in the straw sample. The behavior during combustion shows, that the intensity of K* radical was lower than that of untreated wood pellet, which has lower concentration of potassium (Table 1). Considering not full leaching of potassium from the straw sample, it can be assumed that the remaining K is

immobilized or chemically bond in certain not easily released compounds. Therefore, during combustion the remainder, K is releasing steadily without obvious peak.
The FES method for determination of alkali species occurring in biomass flames is quite simple and relatively cheap. Therefore, it might be attractive for industry. However, before starting to implement a specially designed sensor in real combustion units for further experimental investigations, it is necessary to compare the results obtained with an independent measurement technique like SPR-ICPMS setup.
An ICP-MS technique was used for online detection of relevant inorganic elements (K, Na). The time resolved trends were obtained for selected alkalis release by detecting the concentration of these elements in the flue gas during the combustion of wood and straw pellets. Similarly, as in the FES experiments, the highest intensity of alkali MS spectra were detected in the time range of fuel devolatilization.
The release of potassium displays specific profiles depending on the biomass type. In the case of the wood, it is possible to distinguish a peak occurring at ~100s from the particle inserting, while for straw a larger peak occurs earlier at ~70s. The obtained relative intensities of ICP-MS have a very similar behavior to those found in the FES experiments. The peaks of emissions correlate with the center temperature of pellets, which shows that at the certain time the volatiles release from the biomass. The results are consistent with time dependent inorganic elements releases found by other researchers [9].
The behavior of Na emissions during combustion of both fuel types is very similar to those found for potassium. The only difference is the concentration or radiant emission intensities for FES experiments.

Conclusions

This study focuses on the measurement of spontaneous alkali release from single biomass pellets during combustion in order to compare two different monitoring techniques: FES and ICPMS. The ICP-MS results prove the behaviour of K and Na emission in biomass combustion flames, which were established in a previous study [7]. Therefore, it can be concluded, that flame emission sensors might be suitable for monitoring the release of alkali species (potassium in particular) from biomass fuels during combustion processes and thereby support to prevent the biomass combustion appliances from unexpected faults.

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