

INVESTIGATION OF EMISSION OF ALKALI RADICALS DURING THE COMBUSTION OF SINGLE WOOD AND STRAW BIOMASS PELLET UNDER HIGH TEMPERATURE USING FES METHOD

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Abstract

This study focuses on the measurement of Na*, Ca*, and K* emission intensities during the combustion of single wood and straw pellets doped with known concentrations of selected minerals. Flame emission spectrometry (FES) was used for optical detection of chemiluminescence spectra. Alkali metals emission was measured using optical bandpass filters mounted on an intensified charge-coupled device camera. The impregnated biomass pellets were suspended in a natural gas flat flame at 1200 °C. A biomass washing, and soaking procedure was used to demineralize and to dope the biomass samples with different concentrations (0.5%, 2%, 5%) of Na, Ca, and K. During the experiments, the temperature at the centre of the pellets and surrounding gas flame temperature were measured with a thermocouple and the combustion stages were identified. The results reveal that, at the 1200 °C gas temperature, the emission release rates of the selected alkalis are certainly higher in agreement with previous studies.

Keywords: biomass, pellet, alkali metals, FES, optical detection

1 Introduction

The biomass, together with other biological energy sources, has been long focused on due to its sustainable features such like clean, carbon-friendly and low cost, and thus more and more utilized in different industry sectors. The biomass, however, is not flawless [1] one of the problem it may cause is a set of ash-related problems from emissions of alkali metals such like slagging, fouling of heat transfer surfaces and bed agglomeration [2]. These problems are typical and really serious in the case of low quality biomass, especially those from herbaceous origins [3] and have already raised concern by many researchers. The wood and straw biomass is inescapable source of alkali metal emissions and some previous research found that under high temperature the emission could be magnified [4]. Many large scale power plants use pulverized fuel furnaces with combustion temperatures above 1600 K [5]. Therefore, investigation of the combustion under high temperature is needed. Previous works all focused on potassium (K), besides other important alkali metals such like Na and Ca are omitted and we need to perform further investigation. The main goal of this work is to investigate the emissions of three important alkali radicals K*, Na* and Ca* of wood and straw biomass under high temperature (1200°C) using flame emission spectroscopy method (FES).

In this study the spectroscopy method was applied to analyse the emissions of selected alkali metals of wood and biomass samples under high temperature. It was discovered that the temperature is still among the most important factors determining the release behaviour of alkali metals while certain element, Ca keeps similar mode as it has in lower temperature [6].

2 Materials and methods

2.1 Experimental setup and biomass sample preparation

The softwood and straw biomass samples were washed, underwent demineralization process and doped with K*, Na* and Ca* by 0.5, 2, and 5 concentration weight percent (wt. %). Combinations of kinds of alkali metals and concentrations were rendered. The doped samples were dried and then prepared into pelletized using a hand press. Properties of wood and straw biomass and detailed biomass treatment procedure was described in previous article [6]. The main method used is chemiluminescence analysis. Chemiluminescence method is a kind of emission spectroscopy

method. In a chemiluminescent reaction, a part of the released energy is used to excite an electronic state which is short-lived and relaxes through a number of mechanisms, including spontaneous photon emission. In the case of photon emission, species emit at a characteristic wavelength, signalling the presence of the species [7]. Other scientists [8, 9] has demonstrated successful application of chemiluminescence method for detection of alkali-metal emissions during combustion, also determined successful application of the same method of measuring organic group through combustion proving that it as a highly reliable method. The method extended its success in latest research [10] by measuring spontaneous emission of alkali metal under temperature up to 1000°C. The experiment setup is shown in Figure 1, the same as the previous one [10] with adjustments for measuring in 1200-1300 °C. Figure 1. Experimental setup. The ICCD camera was mounted with optical band filters with wavelengths of K, Na and Ca. A thermocouple (T_p) was inserted in the centre of the pellet to measure the central inside temperature.

The combustion fuel, natural gas, was mixed in mixing chamber with primary air supply while there was a secondary air supply controlling the flame temperature to ensure it was around 1200 - 1300 °C. Although secondary air supply was used, there was still a chance of fluctuations in the flame temperature of the natural gas. Based on the trial tests, excessive optical emissions by the metal holder under high temperature was observed and a stainless bar was installed in front of the metal holder to shade the excessive emission. The tip of thermocouple protruding into the pellet was vulnerable to damage under high temperature by melting parts from wood and straw, so the thermocouple was replaced upon damage.

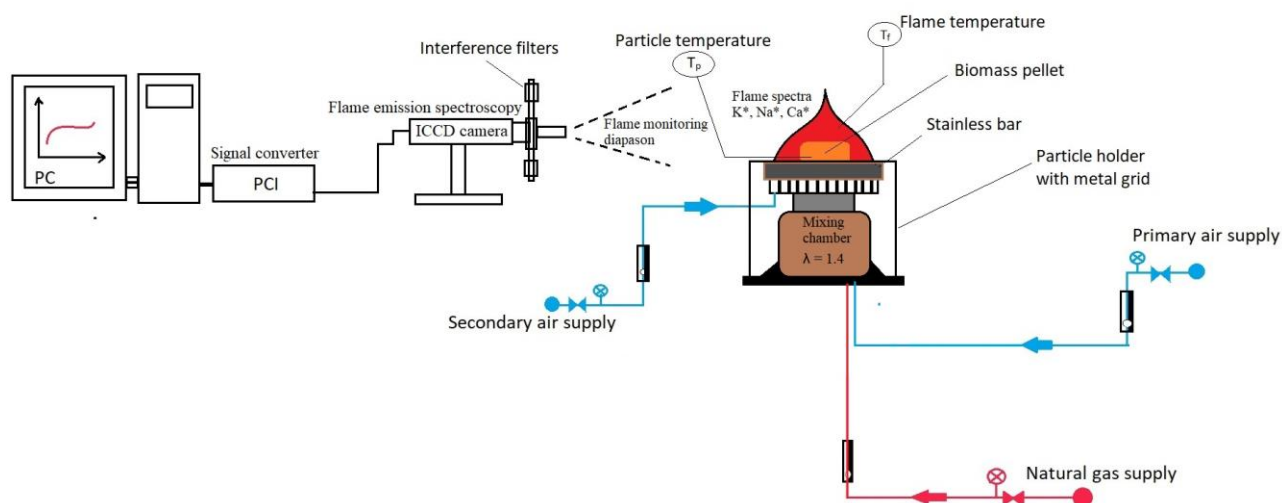


Figure 1. Experimental setup for FES measurement

The experiment of each sample with different parameters (e.g. raw/washed, different type and concentration of doping of alkali metals) was repeated 5 times. The temperature plots were recorded directly into a table in txt file and were processed by computer program. The processing of emission intensity was done firstly by the built-in software of ICCD camera Andor Istar and then the results were exported into Microsoft Excel and arranged into charts. The final results of temperature plots and emission intensities were taken from the average of all valid results.

3 Results and discussion

3.1 Centre temperature during the combustion of wood and straw pellets produced from raw and washed biomass for temperature of the supporting natural gas flame of 1200 °C

The combustion process can be summarized into mainly four major stages which are mostly relevant to focused issues of biomass [11, 12], that is volatilization, volatile combustion and, char combustion and “ash cooking” [4]. Volatilization stage goes with loss of volatile compounds and the formation of semi-coke; organic matters are oxidized releasing a lot of heat over volatile combustion [13]. Volatile combustion is described as a sharp peak in the emission profile. The interval of the ending point of the volatilization and the beginning of volatile combustion was set 460°C. The start char combustion can be found when a broad peak occurs. In the end, "ash cooking" curve is a very broad peak over an extended period, long after the end of combustion [4].

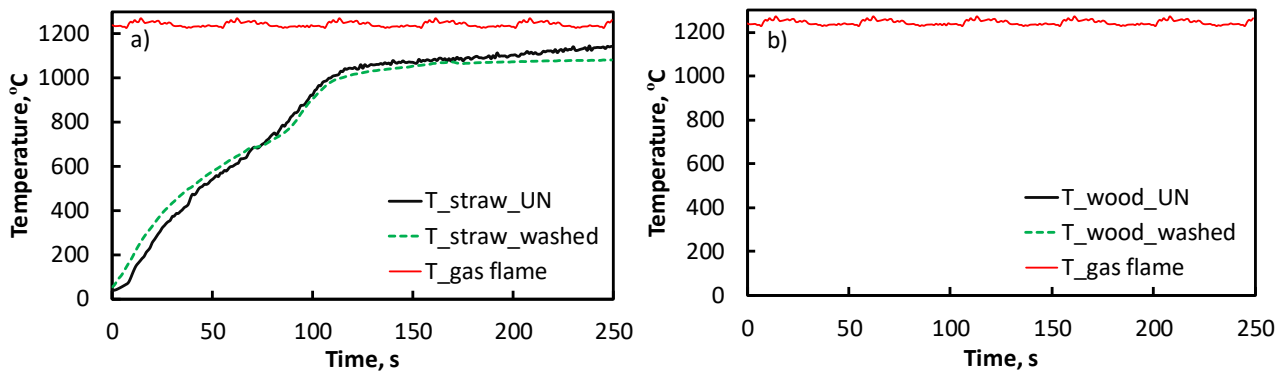


Figure 2. Raw and washed wood (b) and straw (a) pellet inlet temperature plots

Figure 2. (b) shows temperature plots of raw and washed wood pellet samples. The temperature of washed samples is higher than raw ones throughout the combustion process with distinct difference during volatilization stage and some volatile combustion stage, which can be identified in time range between 20 ~ 50 sec and slight difference in later stages. This can be explained as the destruction of rigid wood structures by acid during washing process which facilitated the volatilization. Clearly see then the combustion process is approaching the carbon burning stage 75 ~ 110 sec the temperature slightly increases until ash forming constant mode reached.

In straw case figure 2. (a), the washed samples have higher temperature than raw ones during volatilization 20 ~ 50 sec and half of volatile combustion stages 80 ~ 115 sec but the situation becomes reverse in later stages when ends char combustion period and ash remains. This is because the straw contains higher amount of alkali radicals especially potassium than wood and they have significant catalytic effect [14,13] which was quenched after washing.

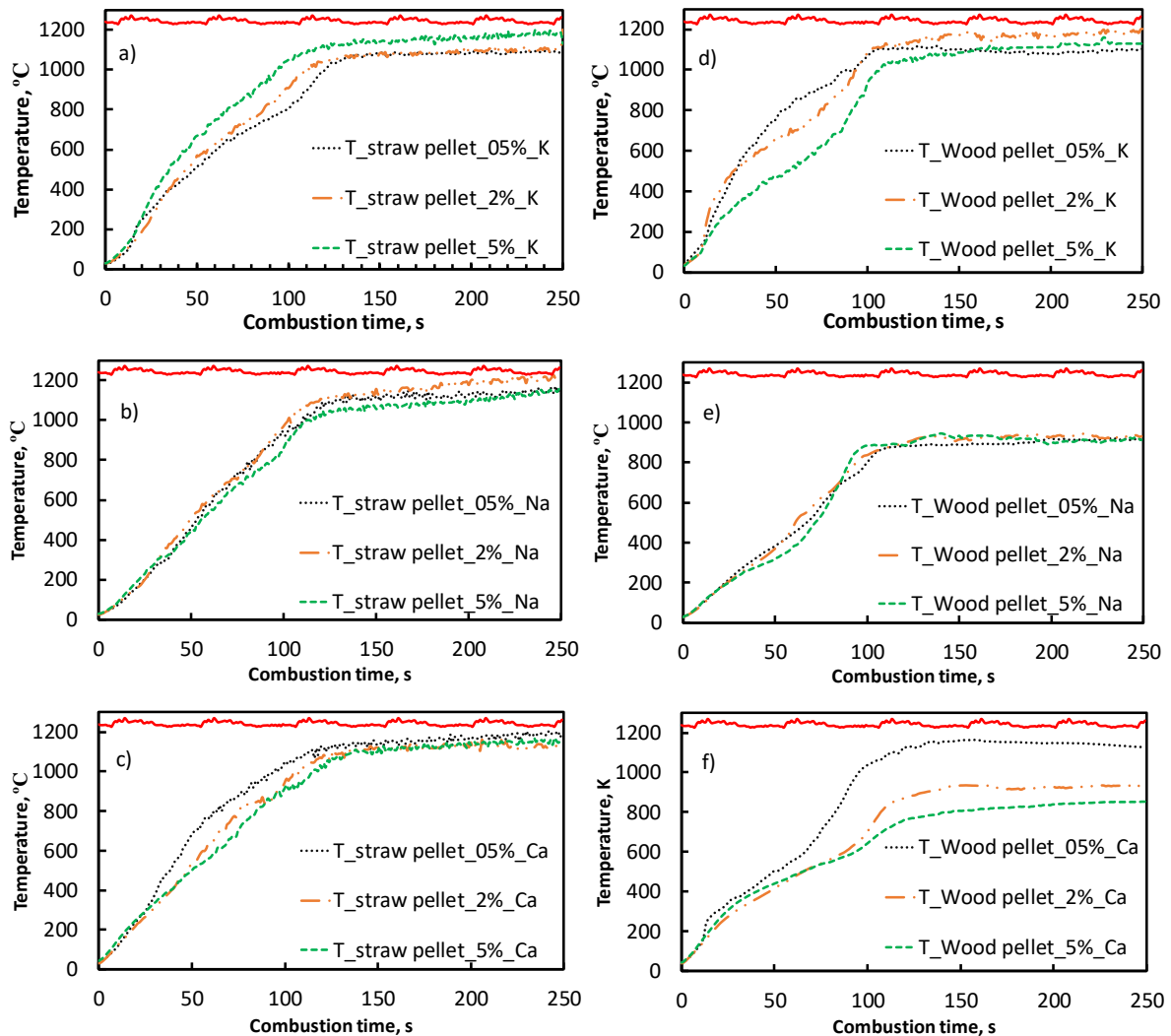
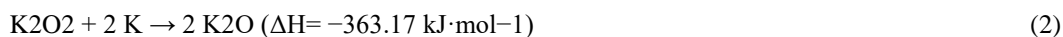


Figure 3. Measured internal temperature plots of straw and wood pellets doped with different concentrations of K*, Ca*, Na* minerals

Figure 3 (d, e, f) show the temperature curves of wood pellets with 0.5, 2, and 5 K, Ca, Na different concentrations. Concerning volatilization stages, it is obvious that all samples have shown retarding effect. The retarding keeps pronounced for K and Ca samples during volatile combustion stages.

K and Ca samples both end with noticeable difference in temperature in char combustion and ash-cooking stages. For K, the temperature during final stages are positively correlated with percentage of K, which indicates the release of energy from the combustion of K. The main reactions happened are [15]:



While for Ca it is negatively correlated with concentration (<1000 °C for two samples with higher concentration), which means that the dominant processes are endothermic and the exothermic oxidation reactions cannot compensate the heat loss. It can be inferred that Ca, under 1200 °C, still does not evaporate and it transfers into CaO [16].

The Na chart shows another situation that the higher amount of alkali metal results in only slight retarding and all samples have similar temperature in later stages. It is worth being noticed that Na samples end with temperatures lower than 1000 °C, which suggests that instead of any dominant endothermic process, all samples regard less of concentration reach an endothermic equilibrium. On the other hand, after 400 °C especially after 700 °C, the positive correlation of the increase speed (slop) and the concentration during volatile combustion stage, together with ending temperature of this stage – 900 °C, suggests that during volatile combustion stage, the most vibrant stage, the retarding effect is weak due to some noticeable yet moderate exothermic force and temperature - lowering equilibrium has formed.

Temperature plots mentioned in figure 3 (a, b, c) are straw pellet samples with different concentration of impregnation. All curves reached no less than 1000 °C in the latter stages (char combustion and ash cooking period), which demonstrates a different pattern than wood samples. Significant higher temperature plots than wood results suggest sufficient and unhampered combustion happened.

Given all temperature curves, K curves are positively correlated with concentration, unlike the counter part of wood samples in Figure 3 (d, e, f) and there is no retarding effect. Calcium plots are also negatively correlated with concentration as in wood results, which indicate the same endothermic process yet the gaps resulted from difference of concentration are much less. The situation of Na plots is mixed; it is worth being noticed that the plot of 2% samples reached and surmounted the surrounding gas flame temperature during later stages, which is the highest temperature ever reached.

All curves of K and Ca, irrespective of concentration, entered volatile combustion stage by 50 s. As for Na plots, only the plot of 2% concentration narrowly reached this stage and the sequence of temperature 2% > 0.5% > 5% has formed and continued till the end, which is the same in wood samples.

To summarize the findings of temperature plots of wood and straw samples, the overall temperature of wood is lower than surrounding flame and straw; the straw samples showed less difference among plots of different concentration. These suggests that some differences between properties of wood and straw samples influenced the combustion process in a greater extent which was not noticed in previous research that were under lower temperature.

3.2 Emissions of Na*, Ca* and K* during combustion at 1200 °C

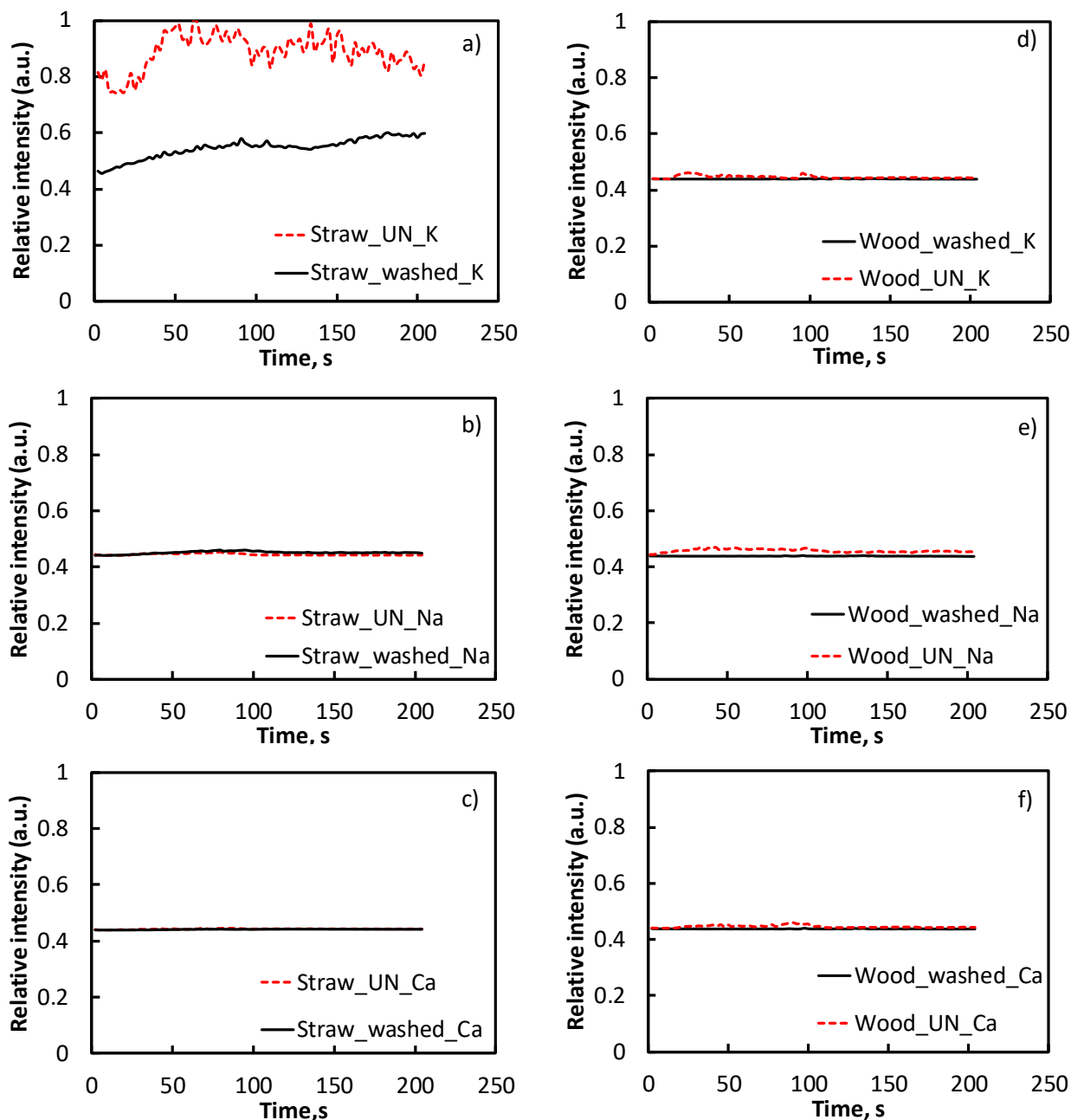


Figure 6. Relative intensities of K*, Ca*, and Na* emissions during the combustion of straw (a, b, c) and wood (d, e, f) pellets produced from raw and washed biomass before and after the washing procedure for a temperature of the supporting natural gas flame of 1200 °C.

From Figure 6 (-) it is seen that the emission of alkali radicals of raw and washed wood under high temperature have marginal difference as previous results under lower temperature [10]. This phenomenon, which is against the expectation that the alkali radicals in the raw wood pellet samples should become motile, will be used for further analysis to understand the whole picture. Emission curves of raw and washed straw pellet samples are shown in Figure 6 (-). It is seen that K emission curves show obvious difference while Ca and Na emissions of the raw and washed samples are highly similar.

In Figure 7 (d), potassium, as the most active alkali metal, shows the largest fluctuations during combustion of wood pellets. The emissions reach the first peak no later than 50 sec, which corresponds to the end of volatilization and the beginning of volatile combustion Figure 3. (d). In around 100s there is a plunge for all three ones which corresponds to char combustion and ash cooking stages. Scientists [17] proved that a temperature of 1150°C, between 50 and 90% total potassium was released to the gas phase. The low level of 0.5% sample in later stages indicates that the majority of K has emitted, while the occurrence of another peak in 2% and 5% samples indicates the remaining high amount of potassium that are to be released during char combustion and ash cooking stages. Comparing wood and straw K

emission profiles, in wood case noticeable high K emission was recorded. This was due to the used acid leaching procedure which led to inner structure abnormality [6].

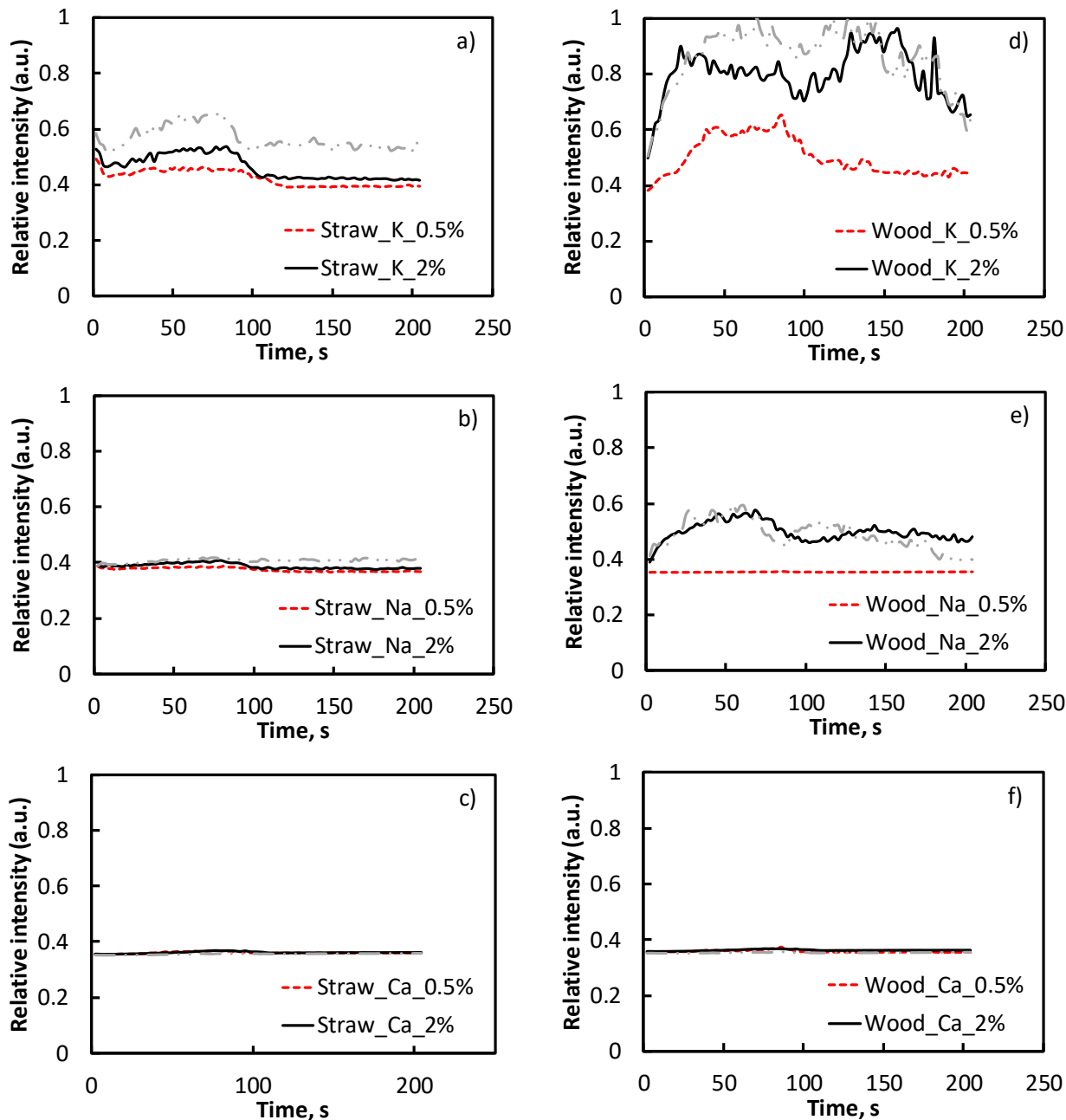


Figure 7. Relative intensities of K^* , Ca^* , and Na^* emissions during the combustion of wood (d, e, f) and straw (a, b, c) pellets doped with 0.5, 2, and 5 wt. % Ca, K, and Na for a temperature of the supporting natural gas flame of 1200 °C.

In Figure 7 (c and f) it is seen that Ca has a very stable yet high level emission all the time. The difference results in only a slight peak in around 100s which is the beginning of char combustion stage. This “flat profile” can be explained by same reason that calcium cannot vaporize and the Ca, organically bound in oxalate is converted to CaO during oxidation [16, 6]. Emission levels are positively correlated with concentrations of alkali metals for K, Na but negatively correlated with concentration of Ca. Because Ca, the only earth alkali metal among three radicals under investigation, does not undergo evaporation into gaseous phase and the melting make it endothermic and thus lower the temperature, which in turn lower the emission level by hindering the combustion process.

4 Conclusions and summary of results

The emissions of alkali metal K^* , Ca^* and Na^* from wood and straw biomass pellets doped with 0.5, 2, and 5 wt % Ca, K, and Na for a temperature of the supporting natural gas flame of 1200 °C. The experiments were carried out using bandpass filters mounted on an ICCD camera. The results contain temperature plots and emission curves.

Under high temperature 1200 °C, some phenomenon remains intact as in lower temperature, they include: (1) inactivity of Calcium, trapping effect on Potassium by aluminium and silicate and positive correlation of emission level with concentration of alkali metal upon having emitted.

Other phenomena were not seen or not well observed under lower temperature: (2) the difference of temperature plot including ignition time, peaks between the raw and washed wood and straw samples became negligible in contrast to those under 750 °C. Sodium reaction cycle is found and analysed through unconventional temperature and emission results; this is a self-hindering effect typical for wood samples. The differences of volatilization and ignition mode between wood and straw samples are pronounced which should undergo further investigation in order to have better knowledge in utilization of biomass fuels. These alkalis emission profiles and regularities can be used creating and developing new biomass combustion process optimization technologies.

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