

A Comparison of Two Methods for Determination of K and Na Release Behavior from a Single Biomass Pellet during Combustion

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Abstract: This study focuses on the measurement of spontaneous alkali release from biomass pellet during combustion in order to compare two different techniques. Flame emission spectrometry (FES) was used for optical detection of chemiluminescence spectra of selected metals using optical bandpass filters mounted on ICCD (Intensified Charge Coupled Device) camera Andor iStar DH734. To gain better understanding about alkali-metal release processes and to compare obtained results, test runs with a single particle reactor (SPR) connected with an inductively coupled plasma mass spectrometer (ICP-MS) have been performed. By coupling the reactor to an ICP-MS, time-resolved release profiles of relevant aerosol forming elements (K, Na) were determined and compared with those obtained by FES experiments.

Key-Words: biomass, pellet, straw, wood, combustion, alkali metals, FES, ICP-MS

1 Introduction

Nowadays the demand of biomass extensively grows year by year. Biomass products are beneficial because they often are waste products from forestry and wood industries. Therefore, biomass is often locally available and easy and relatively cheap. Nevertheless, the inorganic constituents of biomass cause several problems during combustion. The most important problem is the formation of aerosols during biomass combustion, which might cause slagging, fouling or agglomeration formation on boilers walls. These problems emerge 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 straws and grasses. Similarly, woody biomass fuels generally contain lower levels of chlorine, sodium and potassium than most other biomass fuels, corrosion effect also occurs in wood-fired systems [2]. To prevent mentioned problems, early control of alkali release is necessary and online detection techniques might help. The aim of the present work is to compare the low-cost effective technique with other method using single particle reactor (SPR) to determine the

release Na and K from single pellet during combustion. From previous results [3] revealed that at the lower combustion temperature the spontaneous chemiluminescence emissions of the Na* and K* was marginal. Therefore, to fully excite the alkali metals ions and get higher resolution the higher temperature needed. This study examines the combustion of prepared biomass pellets at 1000°C. The selected alkali emission (K and Na) was investigated and release profiles were obtained from the results. The pellet center temperature during combustion was measured to prove the stages of fuel decomposition where the most of selected elements releases.

2 Material and methods

2.1 Biomass sample and preparation

Two types of biomass, wood and straw, were used in experimental investigation. The proximate and ultimate analysis of selected biomass are presented in Table 1. To remove alkali metals from the samples a procedure of washing with HNO₃ acid solution were applied. At first, raw wood and straw

pellets were milled and sieved using a 500 μm grid. Then 50 g of milled biomass was demineralized by leaching in nitric acid – water solution (pH=2) in a flask of 500 ml and stirred automatically for 1 h at 70 °C. Afterward, the biomass was filtered and washed thoroughly with 250 ml of de-ionized water. The filtering-washing procedure was repeated twice. Finally, the biomass was dried at 105 °C. Table 2 shows the alkali content found in the raw and washed samples.

Table 1. The properties of biomass used in experimental investigations

	Wood	Straw
<i>Ultimate analysis, wt.% dry basis</i>		
C	51.38	49.06
H	5.58	5.41
O (diff.)	39.48	40.72
N	<0.01	0.42
S	<0.01	<0.01
Cl	0.042	0.226
<i>Proximate analysis, wt.%</i>		
Ash	3.50	4.15
Moisture	2.90	4.04
VM	78.10	73.11
FC	15.50	18.70
HHV, MJ/kg	19.12	17.53
LHV, MJ/kg	18.05	16.52

Table 2. Alkali content in biomass before and after washing procedure

	Wood	Straw
<i>Untreated, mg/kg</i>		
K	339	16481
Na	4.46	45.06
<i>After washing, mg/kg</i>		
K	n.d.	1054
Na	n.d.	n.d.

2.2 Experimental setup

2.1.1 Setup for K* and Na* measurement by FES

The first set of experiments capturing flame emission spectra of selected radicals occurring during biomass pellets combustion was performed in the experimental setup shown in Fig.1 [3]. The stand consist of a flat flame burner with natural gas-air premixing chamber. The flat flame is created above the porous matrix, while secondary air is used to control and ensure flame temperature of 1000 °C. The flow of fuel and air is controlled by mass

flowmeters. Above the porous plate, a small grid is mounted to position the biomass pellet in the flame. The center temperature of biomass pellet is measured with a K-type thermocouple.

The light emitted by the exciting of K* and Na* radicals was captured by an ICCD camera Andor Istar DH734-18U-E3. A detailed description of the camera system and parameters can be found in the previous works [3, 4]. The optical interference bandpass filters with specified wavelengths of 590 ± 2 nm for Na* and 770 ± 2 nm for K* were used in this work. The intensity of spectra recorded from particle ignition to the combustion of volatile matter, which typically takes about 200 seconds.

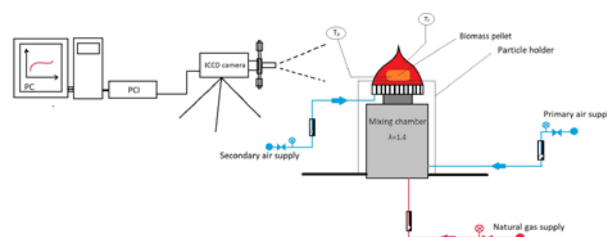


Fig.1. Simplified scheme of experimental setup for chemiluminescence measurement

2.1.2 Setup for K and Na measurement by ICP-MS

In order to compare results obtained by spectra capturing with ICCD camera and ICP-MS technique, a set of experiments in a single particle reactor was performed (see Fig.2). The detail description of setup and characteristics of the system is provided in works [5, 6]. The experimental rig consist of an electrically heated (250 - 1050°C) with height of 755 mm and diameter of 50 mm. The reactor also has a 4 horizontal side tubes (length 177 mm, inner diameter 28 mm), 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. In side the furnace, the biomass particle is placed on a sample holder which is connected to a scale for the determination of mass loss during the thermal decomposition. During combustion of biomass particle, the flue gases are released. A part of the flue gas is ejected to an inductively coupled plasma mass spectrometer (ICP-MS). The carrier gas N₂/air mixture, 11 l/min and 4 l/min respectively. The flow is controlled with mass flow controllers (Sierra Smart Trak 2, Series 100) and flows through the reactor from below and is heated up to a defined set-temperature until it reaches the position of the sample holder. The weight of sample is ~1.3 g. At the sample, two thermocouples Type N (NiCrSi-

NiSiMg) are placed to measure the temperatures in the center and at the surface of the particle.

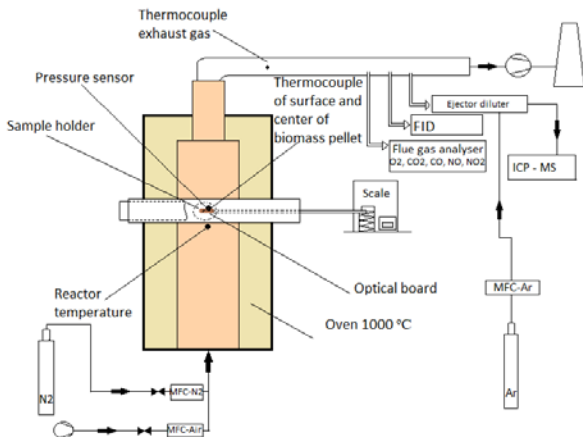


Fig.2. Simplified scheme of the single particle reactor (SPR)

3 Results and discussion

3.1 Spontaneous emission of K* and Na* during combustion of single biomass pellet using FES setup

Fig.3 shows the relative intensities of K* and Na* emissions during the combustion of the wood and straw pellets produced from untreated and washed biomass for a temperature of the supporting natural gas flame of 1000 °C. As can be seen from the figure, the spontaneous radiant emission of

specific alkalis has a typical peak at the beginning of biomass pellet combustion. This is mostly related with release of volatiles from biomass, which takes out some part of organic or inorganic constituents containing selected metals. By comparing a two types of biomass, it can be seen that more intensive excited radical radiance occurs in the case of straw pellet combustion. The untreated straw has highest concentration of K (Table 2); therefore, detected intensity of luminescence was higher than in the case of wood pellet combustion. Raw straw shows a typical release profile, which is not surprising given that it is the sample with the largest amount of potassium. The emission of potassium was recorded until ~125 s in the case of the straw, which is consistent with the end of the volatile combustion stage and the beginning of the char combustion stage.

Analyzing the case of washed biomass, the highest concentration of remaining potassium in the straw sample was obtained. However, the behavior during combustion shows, that intensity of excited K* radical was lower than that in the case of untreated wood pellet, which has lower concentration of potassium.

Considering not full leaching of potassium from the straw sample, it can be assumed that remaining K is immobilized or chemically bond in certain not easily treating compounds. Therefore, during combustion the remainder K is releasing gradually without evident peak.

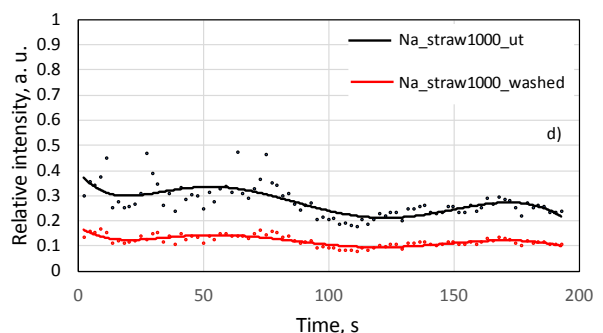
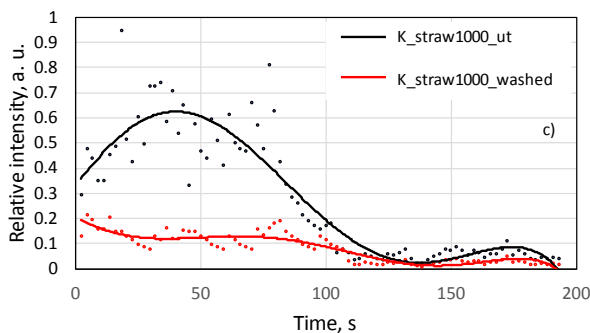
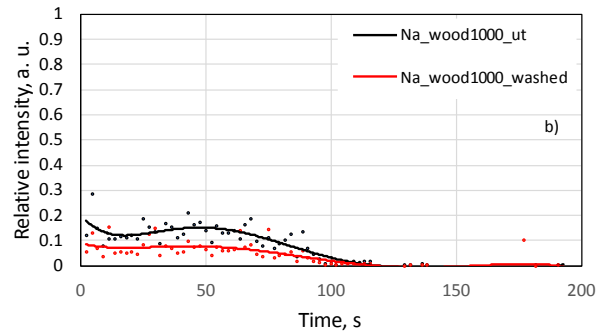
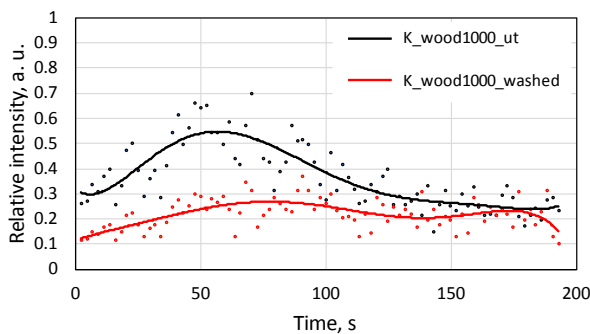


Fig.3. Relative intensities of K^* and Na^* spontaneous emissions during combustion of untreated and washed wood (a, b) and straw pellets (c, d)

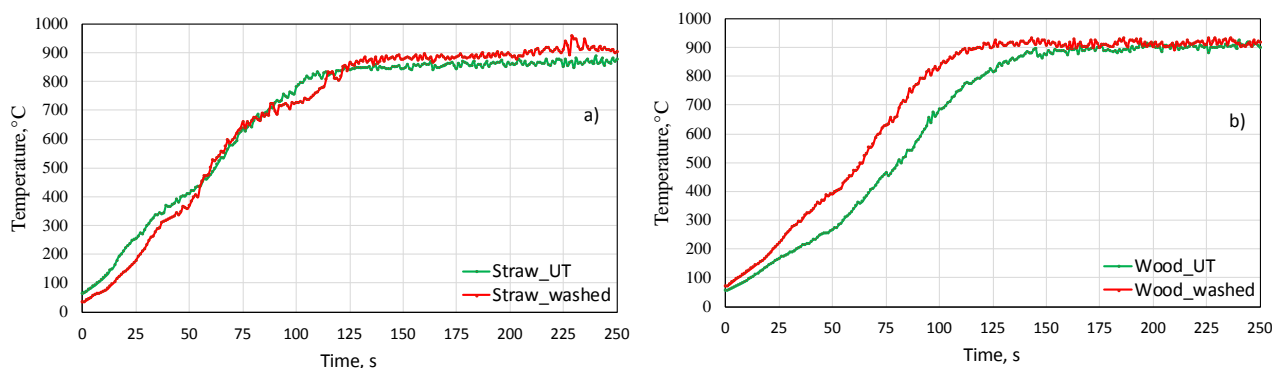


Fig.4. Behavior of center temperature of untreated and washed wood (a) and straw (b) pellets during combustion

The emission profiles sodium shows that there was no significant release of these species. Only 30 – 75 s interval can be distinguished where clearly see marginal peak of sodium for both wood and straw pellets.

Figure 4 shows the evolution of the center temperature of the particles produced from untreated and washed biomass during combustion. In the case of the raw biomass particle, it was found, that the center temperature of the straw particle reaches 900°C after 130 s from placing it in the flame. For the case of the woody pellet, the situation slightly differs: the sharp increase of the temperature stops after 140 s when 900°C is reached. Further, the temperature rises slower until 150 s when the temperature reaches 1000°C. Here, the nature of biomass plays the major role too: it is known that during the pyrolysis stage of raw biomass, a certain reactions are exothermic and foster the rise of the center temperature. After the washing procedure for both types of biomass, the profile of the temperature rise is the same way, except for the faster devolatilization stage. The first visible rise is at 40 s and the second one with a higher peak is at 65 s. Comparing these temperature profiles, can be seen that during combustion of the straw particle, devolatilization stage is shorter than for the wood particle. This is in good correlation with the release of spontaneous emission of potassium.

3.2 Spontaneous emission of K and Na during combustion of single biomass pellet using ICP-MS setup

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, prior start the wider experimental investigation adapting special designed sensors to real combustors, it is necessary to compare the results obtained by more reliable measurement, namely by meant of ICP-MS.

An ICP-MS from Agilent Technologies series 7700x was used for the online detection of relevant inorganic elements (K, Na). Data gained from the fuel gaseous residues analysis are used to calculate the overall release of inorganic elements to the gas phase during an experiment. The Fig.5 shows the time resolved emission intensity trends of K and Na, which were measured in gaseous phase during combustion of untreated and washed wood and straw pellets. Similarly, as in the FES experiments, the highest amount of alkalis emitted to the gaseous phase in the time range of 50 and 150s were detected. The results confirm that at the combustion stage of fuel volatiles occurs decomposition of certain compounds containing alkali metals, which leads to notable emission peak.

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, while for straw larger peak occurs at ~70s (Fig. 5, a, c). The obtained counts of mass spectra and the peaks of K release obtained during the measurement, has a very similar behavior to those found in the FES experiment. The peaks of emission correlates with the center temperature of pellets, which shows that at mentioned time moment the volatiles releases from the biomass. The results are consistent with other researcher works [5] where inorganic elements releases processes described in more detailed way.

The behavior of Na emission 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.

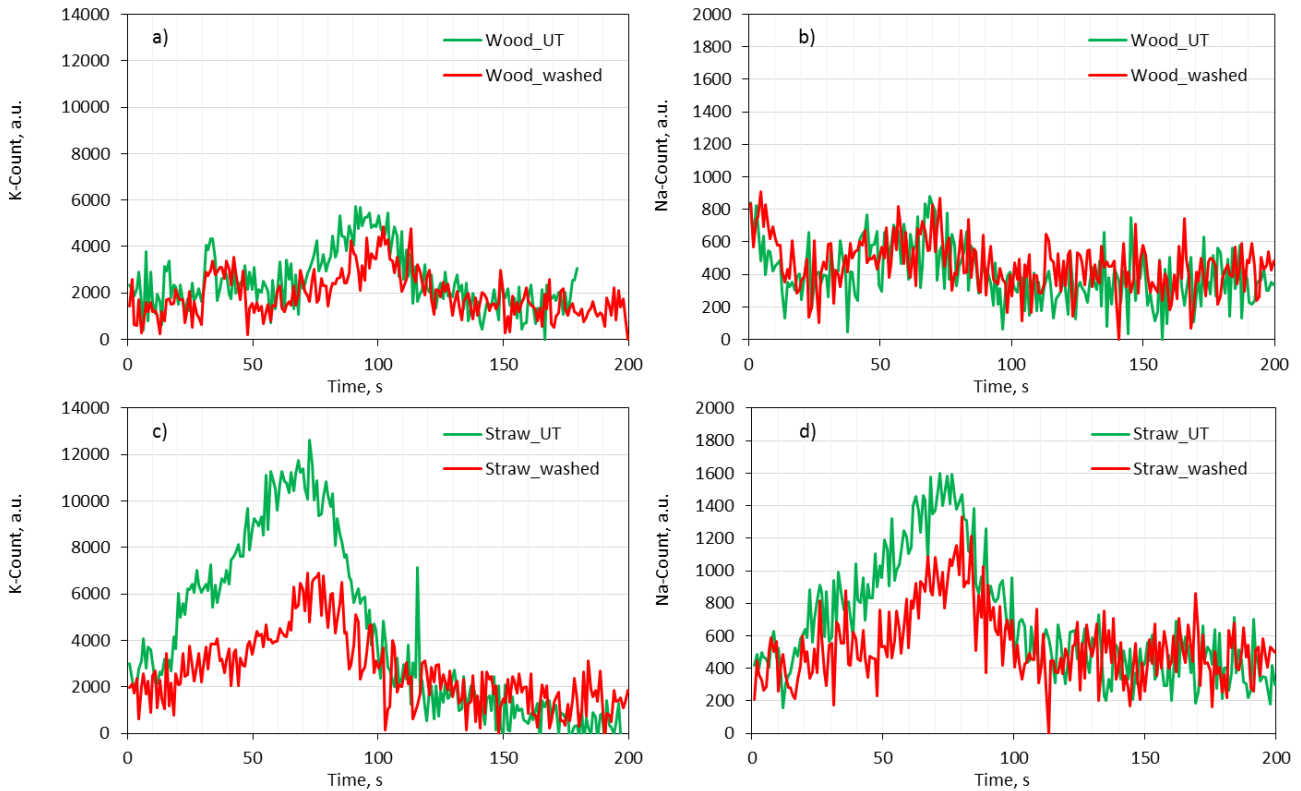


Fig.5. Emission intensities of K and Na spontaneous emissions during combustion of untreated and washed wood (a, b) and straw pellets (c, d) for ICP-MS measurements

Fig.6 shows the center temperature profiles of biomass pellets for the ICP-MS experiments. Comparing the temperature profiles with the case of FES runs (Fig.4), it can be seen several differences in shape of rise, which are mostly related to the heating rate of pellets. In case of FES, the center temperature increases gradually. While for ICP-MS, a steep rise of temperature in time interval between 80 and 100 s take place (wood pellets). Shorter rise of temperature between 20 and 75s occurs during combustion of straw pellet. The difference between

wood and straw center temperature rise is mostly caused of different biochemical structure [9]. Despite the differences in the SPR reactor and a flat flame burner setups the prevailing laws of combustion stages can be identified and therefore were established, that spontaneous release of alkalis, mainly K and Na, mostly takes place during the stage of fuel devolatilization.

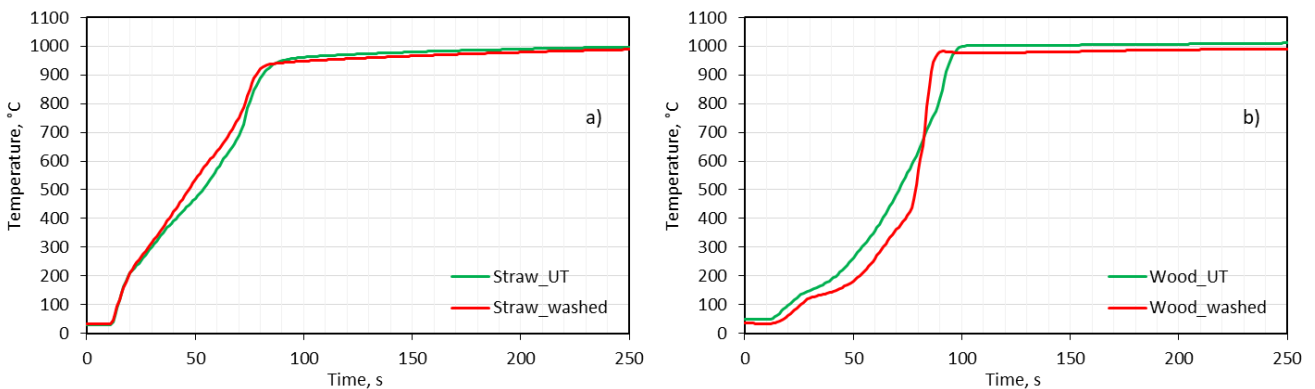


Fig. 6. Behavior of center temperature of untreated and washed wood (a) and straw (b) pellets during combustion for ICP-MS measurements

4 Conclusion

This study focuses on the measurement of spontaneous alkali release from biomass pellet during combustion in order to compare two different techniques: FES and ICP-MS. Despite the differences in the SPR reactor and a flat flame burner setups the prevailing laws of combustion stages were identified and therefore were established, that spontaneous release of alkalis, mainly K and Na, mostly takes place during the stage of fuel devolatilization. The ICP-MS results proves the behaviour of K^* and Na^* chemiluminescence spectra in biomass combustion flames, which were established in previous study [3]. Therefore, it can be concluded, that flame emission sensors might be sensitive for detection of alkalis presence in the fuel, especially of potassium, and prevent the biomass combustion appliances from unexpected faults.

References:

- [1] Leffler, T.; Brackmann, C.; Berg, M.; Li, Z. S.; Aldén, M. ON-Line Alkali Measurement for Fuel Quality Control in Biomass-Operated Boilers. *Ind. Combust.* 2016, 2016 (1).
- [2] Niu, Y.; Tan, H.; Hui, S. Ash-Related Issues during Biomass Combustion: Alkali-Induced Slagging, Silicate Melt-Induced Slagging (Ash Fusion), Agglomeration, Corrosion, Ash Utilization, and Related Countermeasures. *Progress in Energy and Combustion Science.* 2016, pp 1–61.
- [3] Sadeckas, M.; Striugas, N.; Andriūnas, P.; Praspaliauskas, M.; Rabaçal, M.; Costa, M. Spontaneous emission measurements of selected alkali radicals during the combustion of a single biomass pellet. 2018. *Energy & Fuels Article*
- [4] Navakas, R.; Saliamonas, A.; Striugas, N.; Džiugys, A.; Paulauskas, R.; Zakaruskas, K. Effect of Producer Gas Addition and Air Excess Ratio on Natural Gas Flame Luminescence. *Fuel* 2018, 217, 478–489.
- [5] Sommersacher, P.; Kienzl, N.; Brunner, T.; Obernberger, I. Simultaneous Online Determination of S, Cl, K, Na, Zn, and Pb Release from a Single Particle during Biomass Combustion. Part 2: Results from Test Runs with Spruce and Straw Pellets. *Energy and Fuels* 2016, 30 (4), 3428–3440.
- [6] Sommersacher, P.; Brunner, T.; Obernberger, I.; Kienzl, N.; Kanzian, W. Application of Novel and Advanced Fuel Characterization Tools for the Combustion Related Characterization of Different Wood / Kaolin and Straw / Kaolin Mixtures. 2013.
- [7] Johansen, J. M.; Jakobsen, J. G.; Frandsen, F. J.; Glarborg, P. Release of K, Cl, and S during Pyrolysis and Combustion of High-Chlorine Biomass. *Energy and Fuels* 2011, 25 (11), 4961–4971.
- [8] Knudsen, J. N.; Jensen, P. A.; Dam-Johansen, K. Transformation and Release to the Gas Phase of Cl, K, and S during Combustion of Annual Biomass. *Energy and Fuels* 2004, 18 (5), 1385–1399.
- [9] Paulauskas, R.; Džiugys, A.; Striugas, N. Experimental Investigation of Wood Pellet Swelling and Shrinking during Pyrolysis. *Fuel* 2015, 142, 145–151.