Thermo-Chemical Conversion of Microwave Activated Biomass Mixtures

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Abstract. Thermo-chemical conversion of microwave activated wheat straw mixtures with wood or peat pellets is studied experimentally with the aim to provide more effective application of wheat straw for heat energy production. Microwave pre-processing of straw pellets is used to provide a partial decomposition of the main constituents of straw and to activate the thermo-chemical conversion of wheat straw mixtures with wood or peat pellets. The experimental study includes complex measurements of the elemental composition of biomass pellets (wheat straw, wood, peat), DTG analysis of their thermal degradation, FTIR analysis of the composition of combustible volatiles entering the combustor, the flame temperature, the heat output of the device and composition of the products by comparing these characteristics for mixtures with unprocessed and mw pre-treated straw pellets. The results of experimental study confirm that mw pre-processing of straw activates the thermal decomposition of mixtures providing enhanced formation of combustible volatiles. This leads to improvement of the combustion conditions in the flame reaction zone, completing thus the combustion of volatiles, increasing the flame temperature, the heat output from the device, the produced heat energy per mass of burned mixture and decreasing at the same time the mass fraction of unburned volatiles in the products.

1. Introduction
The EU 2020 strategy targets on climate change and energy, which comply with the Kyoto Protocol, prescribe the increased use of cleaner renewable energy sources (by 20%), partially replacing the fossil fuels with the second-generation fuel – wood and agriculture residues [1] with growing demand for application of agriculture residues for energy production [2–5]. The main advantage of using straw (wheat straw, rape straw) as fuel in the energy sector - straw is carbon (CO₂) neutral fuel and does not contribute to an increase of greenhouse gas (GHG) emissions from energy producers. However, straw has been known as a more problematic fuel if compared with wood because of its lower heating values (LHV, HHV), higher nitrogen and ash contents in biomass [6, 7]. To ensure wider use of straw for energy production, co-combustion of straw with renewable or fossil fuels is used, reducing the greenhouse gas emissions during the heat energy production and improving the main combustion characteristics compared to straw [8–12]. Moreover, it has been demonstrated that an interesting and efficient alternative for biomass conversion to high quality biofuel is mw-pretreatment of biomass with direct influence on the main gasification/combustion characteristics and composition of the products [13–17]. The results of previous research confirm that mw pre-processing of biomass pellets reduces their moisture content and partially decomposes hemicelluloses, cellulose and lignin, decreasing the hydrogen-to-carbon (H/C) and oxygen-to-carbon (O/C) contents while increasing calorific value of pellets. This leads to faster and more complete thermo-chemical conversion of pre-processed pellets by
increasing the produced heat energy per mass of burned biomass pellets [18, 19]. Besides, this prognosis that an additional improvement of the main combustion characteristics at co-combustion of straw with wood or peat pellets can be obtained using the selective microwave (mw) pre-processing of straw pellets with activation of the thermo-chemical conversion of straw mixtures. Hence, the main aim of the current research is to provide the detailed experimental study of the main combustion characteristics at co-combustion of straw with wood or peat pellets providing the selective mw pre-processing of straw pellets to assess and analyze the effect of mw pre-processing on the development of the main gasification/combustion characteristics, heat output of the device and composition of the products at thermo-chemical conversion of activated mixtures.

2. Experimental
The effects of mw pre-processing of the mixture components (wheat straw mixtures with wood or with peat pellets) on the gasification/combustion characteristics were studied using a pilot device (60 mm in diameter and 600 mm in length) with a heat output up to 2 kW. The device combines a biomass gasifier (1) filled with biomass pellets and the water-cooled sections of the combustor (2) (figure 1).

![Figure 1](image)

The experiments were carried out using mixtures of straw with wood or peat pellets. The mass load of straw in the mixture was 30%. To provide activation of the straw thermal decomposition, the straw pellets were pre-processed in a microwave oven with power 700 W and the frequency \( v = 2.45 \) GHz with duration of microwave pre-processing 180 s. The gasification/combustion characteristics were studied experimentally using the primary air \( q_1 \) supply below the biomass layer (3) at the average rate \( q_1 = 20 \) l/min to sustain the formation of axial flow of combustible volatiles (CO, H\(_2\)), which produced during the thermal decomposition of the biomass mixtures. The secondary swirling air flow was supplied at the bottom of the combustor (4) at the average rate \( q_2 = 30 \) l/min to sustain the burnout of the volatiles downstream the combustor. A propane flame flow was supplied into the upper part of the biomass layer (5) to initiate the thermal decomposition of the biomass pellets. The supply was stopped after ignition \( (t = 360 \) s).

To assess the influence of straw mw pre-processing on the development of the main gasification/combustion characteristics at thermo-chemical conversion of activated mixtures, the experimental study involved joint measurements of the main characteristics (elemental composition, heating values) of parent samples (straw, wood and peat pellets) and pre-treated straw pellets, DTG and DTA analysis of their thermal decomposition [18] and complex time-dependent measurements of weight loss rates of the mixtures \( (dm/dt, g/s) \), the composition of released volatiles entering the combustor, the flame temperature, the heat output from the device and the composition of the products. FTIR spectrum analysis in the mid-IR range is used for measurements of volatiles composition entering the combustor.
The gas sampling probe was inserted through the gas sampling orifice (6). Pt-Pt/Rh thermocouples were used to measure the flame temperature with data online registration by Pico logger. To assess the influence of the straw pre-processing on the heat output of the device, calorimetric measurements of the cooling water flow were made using thermos-sensors AD590 with online data registration using Data Translation DT 98005 series data acquisition module. The composition of the products (CO, H₂, CO₂, NOₓ) and the combustion efficiency were measured using a Testo 350 gas analyzer. The biomass weight loss rate was estimated from time-dependent variations of the biomass layer height in the gasifier using a moving rod with a pointer. Online data registration of the main gasification/combustion characteristics was made once per second.

3. Results and discussion

The comparative analysis of the main characteristics of the parent and mw-pre-processed samples of wheat straw, wood and peat pellets has shown a considerable difference of their elemental composition and heating values (table 1). Wood and peat pellets have a higher carbon and hydrogen contents and higher heating values, whereas straw pellets have higher nitrogen and ash content. Therefore, measurements of the main characteristics of biomass pellets suggests that mixing of wheat straw with wood or peat pellets is preferable to create a fuel mixture with improved elemental composition and heating values (HHV) compared to straw (table 1). Therefore, it is believed that co-combustion of straw with wood or peat pellets will allow to improve the main combustion characteristics by increasing the heat output from the device and to improve the products composition so determining wider use of straw for energy production.

Table 1. The elemental composition and heating values (HHV) of unprocessed straw, mw pre-processed straw, wood and peat pellets, and mixtures of both unprocessed (30%) and mw pre-processed straw with wood or peat pellets.

| Parameter | wheat straw | wheat straw (mw) | wood | peat | wood + 30% of straw | straw | straw (mw) | peat + 30% of straw |
|-----------|-------------|------------------|------|------|---------------------|-------|------------|---------------------|
| C, %      | 46.62       | 49.70            | 49.79| 53.83| 48.84               | 49.76 | 51.66      | 52.59               |
| H, %      | 5.09        | 5.25             | 5.15 | 5.12 | 5.132               | 5.18  | 5.11       | 5.16                |
| O, %      | 42.72       | 38.15            | 44.24| 36.93| 43.78               | 42.41 | 38.66      | 37.30               |
| N, %      | 1.31        | 1.46             | 0.18 | 1.11 | 0.52                | 0.56  | 1.17       | 1.215               |
| Ash, %    | 4.26        | 5.44             | 0.64 | 3.02 | 1.73                | 2.08  | 3.39       | 3.75                |
| H₂O₆, %   | 9.09        | 1.07             | 6.32 | 11.44| 7.151               | 4.745 | 10.74      | 8.33                |
| HHV₅b     | 18.47       | 19.68            | 19.52| 21.24| 19.20               | 19.57 | 20.41      | 20.77               |

₅Moisture content.
₆High Heating Value, MJ/kg.

The results of previous research have shown that additional improvement of the elemental composition and main combustion characteristics of lignocellulosic biomass pellets can obtained at their microwave pre-processing [18, 19], which starts with the removal of the physically bounded water and is followed by the changes in their chemical composition with the breakdown of the glycosidic structure of polysaccharides into smaller fragments, reducing the crystallinity of cellulose and providing carbonization of the cell wall structure [13–16]. Similar structural transformation along with partial destruction of hemicelluloses and cellulose and variations of the elemental composition are observed at microwave pre-processing of wheat straw pellets indicating a decrease of the moisture, hydrogen and oxygen contents in pellets, whereas increases the carbon content and heating values (HHV) of pellets (table 1). The main negative effect of mw pre-processing of wheat straw pellets is an increase of nitrogen and ash contents in pellets by limiting their use as fuel for energy production. To minimize these negative effects, co-combustion of activated wheat straw with wood or peat pellets is still preferable (table 1) suggesting that co-combustion of these pellets will allow to control and improve the elemental
composition of fuel mixtures with direct influence on their thermal decomposition and combustion of volatiles.

To predict the thermal decomposition of biomass mixtures, detailed DTG analysis of the main components – wheat straw (parent and activated samples), wood and peat pellets in oxidative atmosphere was carried out indicating that difference in their elemental and chemical composition (table 2) influences their thermal decomposition and the formation of combustible volatiles.

| Biomass sample | Hemicelluloses, % | Cellulose, % | Lignin, % |
|----------------|-------------------|--------------|-----------|
| wheat straw    | 21 – 28           | 24 – 35      | 16 – 20   |
| wood           | 23 – 25           | 41 – 43      | 28 – 29   |
| peat           | 10 – 25           | 0 – 20       | 6 – 40    |

Table 2. Chemical composition of biomass pellets [5, 18].

In accordance with data reported in [20–23] the formation of the weight loss peaks at thermal decomposition of lignocellulosic biomass in oxidative environment can be related to the first step of the low-temperature formation of volatiles and char residue with the next step of lignin thermal decomposition and char conversion. DTG analysis of unprocessed wheat straw thermal decomposition in oxidative atmosphere indicates the formation of the weight loss peaks at T \( \approx \) 560 K, 650 K and at around 711 K (figure 2-a). The detailed analysis of wheat straw thermal degradation suggests [21] that below T \( \approx \) 630 K dominates the thermal decomposition of hemicelluloses and cellulose, whereas at T \( \approx \) 630–670 K dominates the thermal decomposition of lignin, which is highly responsible for char formation and conversion. The results of DTA analysis (figure 2-c) indicate that up to 540 K develop the endothermic processes of the thermal decomposition of hemicelluloses and cellulose, while the exothermic processes of volatile ignition and combustion start to develop at T \( > \) 540 K promoting a fast increase of the wheat straw weight loss rate and temperature of pellets up to their peak values, which are detected at T \( \approx \) 560 K. The formation of exothermic peaks at T \( \approx \) 640–650 K and T \( \approx \) 700–710 K can be related to combustion of volatiles and char conversion, which is produced at thermal decomposition of wheat straw lignin [21]. The enhanced thermal decomposition of hemicelluloses, cellulose and lignin is observed at microwave pre-processing of wheat straw pellets increasing the weight loss peaks at around 550–560 K and 640–650 K, whereas slightly reduces the weight loss peak at T \( \approx \) 710 K, which can be related to char conversion (figure 2-b).

The pronounced weight loss peaks at thermal decomposition and char conversion in oxidative environment are observed also for wood and peat pellets (figure 2-a). As follows from figure 2-a, the thermal decomposition of wood pellets occurs at higher temperature T \( \approx \) 607 K, because wood pellets have higher content of cellulose and lignin compared to straw (table–2), which decomposes at higher temperature than hemicelluloses producing higher content of volatiles and char than straw. The weight loss peak at T \( \approx \) 720 K for wood pellets can be related to char conversion, which is produced during the thermal decomposition of cellulose and lignin. DTA analysis of wood pellets (figure 2-c) suggests that the formation of weight loss peaks at T \( \approx \) 607 K and T \( \approx \) 716–720 K for wood pellets can be related to combustion of volatiles and char conversion.

The formation of the weight loss peaks at T \( \approx \) 560 K and T \( \approx \) 650 K is observed at the thermal decomposition of peat pellets with more pronounced weight loss peak at T \( \approx \) 650 K, which can be related to char formation and conversion (figure 2-a).

This suggests higher lignin content in peat pellets, which produces more char during their thermal decomposition. The results of DTA analysis in oxidative environment confirm the enhanced char formation and conversion for peat pellets with enhanced increase of the temperature during the char conversion stage. Hence, due to differences of elemental and chemical composition between straw, wood and peat pellets, the thermal decomposition of their mixtures is influenced by the main characteristics of the mixture components, and can be quite different varying the mixture composition, which is confirmed by the kinetic study of the thermal decomposition of straw pellets and their mixtures with wood or peat.
Figure 2. The weight loss rate (DTG) and temperature (DTA) of biomass pellets (a, c) and their variations at mw pre-processing of straw (b, d).

Comparative kinetic study of the of the weight loss rates for unprocessed and mw pre-processed wheat straw pellets at their thermal decomposition developing in the gasifier of the pilot device (figure 1) has shown that microwave pre-processing of wheat straw provides enhanced thermal decomposition of straw pellets. The average weight loss rate increases from 0.1 g/s for unprocessed wheat straw pellets up to 0.12 g/s (by about 20%) at microwave pre-processing of straw. In accordance with data of DTG analysis (figure 2) the formation of a primary sharp weight loss peak for mw activated wheat straw pellets refers to flaming combustion of volatiles (t = 400–900 s). The next weight loss peak, the formation of which is observed during the time interval t ≈ 1000–1400 s, can be related to the enhanced thermal degradation of straw lignin [21] followed by the enhanced formation and combustion of volatiles with char formation and combustion at t > 1400 s (figure 3–a).

The results of kinetic study show that mw pre-processing of straw pellets makes an influence on the weight loss rates of activated straw mixtures with wood or peat pellets (figure 3–b, c) increasing their average weight loss rates. The average weight loss of straw mixture with wood pellets increases from 0.11 g/s for unprocessed straw pellets up to 0.13 g/s (≈ 15-16%) at selective mw pre-processing of straw. By co-firing of straw with peat pellets the average weight loss rate of their mixture increases from 0.094 g/s for unprocessed straw pellets up to 0.116 g/s (≈ 23.4%) regarding the selective mw pre-processing of straw. It should be noted that for mixture of activated straw with peat pellets the weight loss of the mixture increases both during the flaming combustion of volatiles and after flame smoldering or char conversion stages. The enhanced thermal decomposition of mixtures at mw-pre-processing of straw pellets correlates with the enhanced thermal decomposition of wood and peat pellets providing faster burnout of activated mixtures (figure 3–b, c). This suggests the thermal interaction between the
components, when the enhanced volatilization of pre-processed straw pellets and combustion of volatiles promotes the enhanced heat release with activation of the thermal decomposition of wood or peat pellets and thermo-chemical conversion of their mixtures.

Because of the enhanced thermal decomposition of activated mixtures larger amounts of combustible volatiles are produced. This is confirmed by the results of FTIR analysis of the volatiles composition entering the combustor (figure 4). The FTIR analysis of volatiles composition confirms the enhanced release of combustible volatiles (H₂, CO, CₓHᵧ) (figure 4–a, b) at thermal decomposition of activated mixtures (figure 4).

![Graphs showing weight loss rates and release of combustible volatiles](image)

**Figure 3.** Effect of mw pre-processing of wheat straw pellets on the weight loss rates at thermo-chemical conversion of straw (a) and of mixtures of straw with wood (b) and with peat (c) pellets.

![Graphs showing release of combustible volatiles CO](image)

**Figure 4.** Effect of mw pre-processing of wheat straw pellets on the release of combustible volatiles (CO) at thermochemical conversion of activated straw mixtures with wood (a) and with peat (b) pellets.
When comparing the kinetics of the formation of volatiles for the activated mixtures of straw with wood or with peat pellets, one can see a difference in time-dependent variations of the formation of combustible volatiles. Co-combustion of wood pellets with activated straw resulted in an enhanced release of CO during the primary stage of thermal decomposition of activated mixture ($t < 800–1000$ s), when in accordance with data of DTG analysis dominates the enhanced thermal decomposition of hemicelluloses and cellulose. In contrary, the mixture of activated straw with peat pellets demonstrated the enhanced release of CO during the after-flame char conversion stage indicating that enhanced thermal decomposition of peat lignin promotes the enhanced char formation and conversion.

![Figure 5. Effect of wheat straw mw pre-processing on the heat output from the flame reaction zone at thermochemical conversion of activated straw mixtures with wood (a) and peat (b) pellets.](image)

Because of the enhanced thermal decomposition of activated mixtures, the mass flow of combustible volatiles entering the combustor increases. For the constant primary and secondary air supply rates into the device, the thermo-chemical conversion of the unprocessed straw mixtures with wood or with peat pellets is developing at the average air excess ratio in the flame reaction zone about $\alpha \approx 1.6–1.7$. Hence, increasing the mass flow of combustible volatiles into the combustor provides a decrease of the air to fuel supply ratio decreasing the average value of the air excess ratio in the flame reaction zone. By co-firing of straw with wood pellets the average air excess ratio at microwave pre-processing of straw decreases from $\alpha \approx 1.7$ to $\alpha \approx 1.4$ demonstrating improvement of the combustion conditions. Similar improvement of the combustion conditions is observed by co-firing of straw with peat pellets, when the average air excess ratio at microwave pre-processing of straw decreases from $\alpha \approx 1.65$ to $\alpha \approx 1.35$ providing faster and more complete combustion of volatiles with correlating increase of the peak and average values of the heat output from the device (figure 5–a, b) and produced heat energy per weight of the burned mixture. The average heat output from the reaction zone at thermo-chemical conversion of the activated straw-wood mixture can be increased by $\sim 25\%$ increasing the total heat output from the device by $\sim 12\%$. The heat output from the reaction zone for the activated straw-peat mixture grew up by $\sim 13\%$ with the correlating increase of the total heat output from the device by $\sim 20\%$. The produced heat energy per mass of activated mixtures of straw with wood or peat increases by $\sim 3–6\%$, which confirms that the mw activation of straw pellets results in more complete thermo-chemical conversion of the mixture. It should be noted however that produced heat energies per mass of activated straw and burned pellets of wood or peat are not additive. This is confirmed by the results of experimental study indicating that produced heat energy per mass of activated mixtures slightly (by about $5–7.3\%$) exceeds the total amount of heat energy produced at thermo-chemical conversion of activated straw and biomass pellets (wood or peat). This suggests that thermal decomposition of activated mixtures influences the composition of volatiles entering the combustion (figure 4) and reactions developing in the flame reaction zone.
Figure 6. Effect of wheat straw pellets mw pre-processing on greenhouse carbon (CO\textsubscript{2}) (a, c) and polluting NO\textsubscript{x} emission (b, d) at thermo-chemical conversion of activated straw mixtures with wood (a, b) and with peat (c, d) pellets.

Finally, the activation of the thermal decomposition of mixtures shows the influence on the products composition (figure 6–a, c). At thermo-chemical conversion of activated straw mixtures with wood pellets the average value of the CO\textsubscript{2} volume fraction in the products increases by ~2%. For the mixture of activated straw with peat pellets the average volume fraction of CO\textsubscript{2} in the products increases by ~2.2% with correlating decrease of the mass fraction of volatiles (CO, H\textsubscript{2}) in the products. The average mass fraction of CO decreases from 1190 ppm to 350 ppm, whereas the average mass fraction of H\textsubscript{2} in the products decreases from 340 ppm to 270 ppm indicating more complete combustion of volatiles. In addition, the co-combustion of straw with wood at average mass load of straw 30% results in a decrease of the average values of the polluting NO\textsubscript{x} emissions from 214 ppm to 190 ppm (by ~10%). A slight growth of the NO\textsubscript{x} emission in the products (by ~5%) was observed for the mixture of straw with peat, which predominately can be related to the higher nitrogen content in the peat pellets (1.14%) in comparison with straw (1.01%).

4. Conclusions
The co-combustion of straw with wood or with peat pellets, with the 30% straw mass load in the mixture, was studied experimentally to provide wider use of straw as a fuel with more complete thermo-chemical conversion of pellets, increased heat output from the device and reduced polluting NO\textsubscript{x} emission in the products in comparison to the thermo-chemical conversion of straw.

Additional improvement of the combustion conditions and composition of emissions is achieved by mw pre-processing of straw pellets. The activation of straw pellets by mw pre-processing provides enhanced thermal decomposition of the activated straw mixtures with wood and with peat pellets promoting enhanced release and more complete thermo-chemical conversion of the combustible...
volatiles (CO, H2) and thus increasing the total heat output from the device by about 12% at the co-combustion of straw with wood and by about 20% at the co-combustion of activated straw with peat.

The enhanced release and more complete thermo-chemical conversion of volatiles result in increase of the average value of the carbon-neutral CO2 fraction in the products by about 2–2.2%. The thermo-chemical conversion of the activated straw mixture with wood pellets leads to reduction of the mass fraction of polluting NOx emissions in the products by about 10%, and, in contrary, the emission of NOx at the thermo-chemical conversion of the activated straw mixture with peat slightly increases (by about 5%) of, which is the main negative result at co-combustion of straw with peat.

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