

Thermal Decomposition of Microwave Pre-Treated Biomass Pellets

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Studies were carried out to evaluate the influence of microwave pre-treatment on the thermal decomposition of different lignocellulosic biomass pellets and on the yield of volatile compounds. Microwave pre-treatment of biomass pellets was performed using a 700 W heat capacity microwave oven by varying the mw irradiation time of biomass pellets along with estimation of the effect of mw pre-treatment on the mass density and elemental composition of pellets responsible for changes of the thermal decomposition and yield of volatiles during the gasification of pre-treated pellets. Experimental studies of the thermal decomposition of pre-treated biomass pellets and formation of volatile compounds (CO, H₂, C_xH_y) were conducted using a laboratory-scale setup with the heat capacity 5 kW which combines a biomass gasifier and a combustor. The results of the complex study allow to conclude that the microwave pre-treatment of biomass pellets promotes an increase of the weight loss rate by decreasing the mass density, but increasing the surface area and reactivity of the pre-treated pellets thus activating the thermal decomposition during the gasification of the pre-treated pellets with a faster and enhanced yield of combustible volatiles. The results of the experimental study suggest that mw pre-treatment of lignocellulosic pellets can be used as a tool to control the thermal decomposition of lignocellulosic pellets and the yield of combustible volatiles.

1. Introduction

The EU long-term strategy in the field of energy and environmental protection sets a target to develop climate-neutral economy with net-zero greenhouse gas emissions increasing the use of the renewable energy sources and energy efficiency at least by 20-27 % to 2050 while reducing domestic GHG by 40 % in 2030 and by 60 % in 2040 with reference to 1990 levels. Until recently, the main renewable resources for energy production, such as wind energy, solar energy, hydropower, geothermal and bioenergy contributed up to 20 % of the humans' global energy consumption, and there is a large potential to increase their applicability. However, the use of solar, wind and hydro energy is significantly limited by several unpredictable external factors, e.g., rainy periods which limit solar energy production, windless periods limiting wind energy production, and drought periods limiting hydropower production. Considering the impact of these factors on the production of renewable energy, the use of bioenergy from different lignocellulosic biomass feedstocks (wood waste, agriculture residues or peat) which can be converted to gaseous, liquid or solid biofuels (Bong et al., 2020) providing their thermo-chemical conversion by combustion, pyrolysis, gasification or liquefaction is becoming increasingly important (McKendry, 2002). The efficiency of renewable energy production is determined by the dissimilarity in structure, in elemental (Vassilev et al., 2010) and chemical composition of different biomass feedstocks (Gani et al., 2007) which influence their thermo-chemical conversion. Therefore, when different biomass feedstocks are used for energy production by combustion, biomass waste is briquetted or granulated to stabilize the energy production process and combustion characteristics. Previous research suggests (Barmina et al., 2013) that microwave (mw) pre-treatment of biomass can be used to additionally stabilize and improve the energy production process, which activates the thermal decomposition of hemicellulose, cellulose and lignin (Lanigan, 2010) during thermo-chemical conversion of pre-treated biomass and is influenced by variations of the pre-treatment regimes.

Therefore, to provide efficient mw pre-treatment of lignocellulosic biomass and to control energy production, studies have been carried out to assess the optimal microwave pre-treatment conditions which determine the thermal decomposition of activated biomass pellets and the formation of combustible volatiles. Such complex research aimed at assessing the main risk factors which limit the applicability of mw pre-processing to achieve efficient control and to improve the thermo-chemical conversion of the main Latvian regional biomass feedstocks (pelletized wood waste, agriculture residues and peat) is the main task of this work, which makes it possible to provide a wider use of these regional bioenergy resources for more efficient energy production. Besides, biochar from biomass produced at microwave pretreatment of pellets has a number of unique properties (Bonga et al., 2020), including the high surface area, porous structure, reactivity and functionality for different applications.

2. Experimental setup and research methodology

To study experimentally the influence of mw-pretreatment on the development of the main gasification/combustion characteristics, wood, straw and peat pellets with different elemental (Table 1) and chemical composition were used. The elemental composition of the pellets was measured using the methodology described in (Barmina et al., 2013) and the data from (Olsson, 2011, Barmina et al., 2016) to estimate the average values of the content of hemicelluloses, cellulose and lignin in biomass pellets.

Table 1: Elemental and chemical composition of biomass pellets

Composition	Wheat straw	Wood	Peat
C, %	46.43	50.59	52.81
H, %	5.79	5.45	5.2
N, %	0.59	0.17	1.17
O, %	43.5	43.4	37.43
HHV, MJ/kg	18.41	19.94	20.86
Ash, %	3.7	0.3	1.4
Moisture, %	10.2	7.34	8.9
Hemicelluloses, %	21-28	23-25	10-25
Cellulose, %	24-35	41-43	0-20
Lignin, %	16-20	28-29	6-40

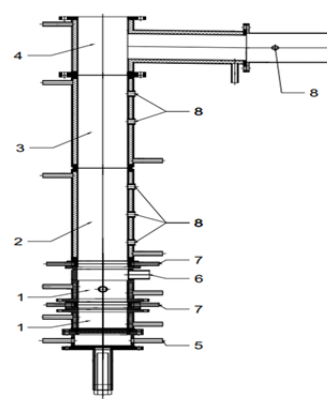


Figure 1: Schematic presentation of the batch-size experimental device: 1 – gasifier; 2, 3, 4 – water-cooled sections of the combustor; 5 - primary air supply nozzle; 6 – propane flame supply nozzle; 7 – secondary air supply nozzle; 8 - orifices for the diagnostic tools

The experimental work was carried out using a device, which consists of a batch-size biomass gasification reactor and a combustor with the heat capacity 5 kW (Figure 1).

The gasification reactor was filled with activated biomass pellets with an average mass load of pellets of 400-500 g. The thermal decomposition of pellets was initiated by additional heat supply into the upper part of the pellets' layer using a propane flame flow with the average heat input 1 kW during 400 s. The pellets were mw-pre-processed using a 700 W mw-power microwave oven by varying the duration of mw-pre-processing in the 0-300 s range along with measuring the weight loss and temperature at mw pre-treatment of the pellets by the Infrared-Thermometer ScanTemp 5020-0420. The thermal decomposition of the activated pellets was studied experimentally at the average air excess ratio in the reactor $\alpha = 0.4-0.5$. The primary air was supplied at the rate 40 l/min and the secondary - tangentially at 60 l/min. The experimental study of the mw pre-processing effect on the thermal decomposition of activated pellets involved complex measurements of the mixture weight loss rate (dm/dt) and yield of volatiles (CO, H₂, CO₂) by varying the pre-processing regimes and measuring the weight loss rate of the pellets and the yield of combustible volatiles during the thermal decomposition of the activated pellets. The pellets weight loss rate was estimated from the continuous measurements of the height of the biomass layer in the gasifier using a moving rod with a pointer, which allows to measure the change of the biomass height during the thermal decomposition of pellets with an accuracy of $\pm 1.5\%$ and to estimate the biomass weight loss rate (dm/dt, g/s) with an accuracy of $\pm 2\%$. Pt/Pt/Rh thermocouples were used for the local online measurements of the flame temperature. The yield of the volatiles (CO, H₂, C_xH_y) during the thermal decomposition of pre-treated pellets was controlled using a gas sampling probe along with FTIR spectrum analysis of the volatile composition using a Testo 350 XL gas analyzer with an accuracy of measurements of $\pm 0.5\%$.

3. Results and discussion

3.1 Effect of mw pre-treatment on main characteristics of pre-treated pellets

To estimate possibilities of the use of mw pre-treatment of biomass pellets (wood, straw and peat) to control their thermo-chemical conversion, studies on the weight loss of pretreated pellets and on the formation of volatile compounds have been carried out with pellets mw pretreated in a microwave oven by varying the duration of mw irradiation. With the constant power of the microwave oven (700 W), the mw pretreatment of pellets starts with a preliminary release of moisture and low-calorific volatiles, which is followed by the thermal decomposition of the main components of lignocellulosic biomass, i.e. hemicelluloses, cellulose and lignin. Analysis of the thermal decomposition of lignocellulosic biomass has shown that the exothermic thermal decomposition of hemicellulose with the highest yield of CO₂ and apparent changes of its structure occurs at T ≈ 500-590 K. The endothermic thermal decomposition of cellulose with the highest yield of CO, with the breakdown of the glycosidic structure and loss of crystallinity starts to develop at a temperature above 590 K, whereas the exothermic decomposition of lignin with the highest yield of H₂ and CH₄ occurs at a temperature above 430 K (Yang et al., 2007). Hemicelluloses decompose easily, whereas lignin is the most difficult to decompose, which determines the formation of solid carbonized residue. This suggests that by increasing the irradiation time of the pellets and their temperature above 430-500 K, the pellets' mw pretreatment can result in primary exothermic decomposition of hemicelluloses with a less pronounced thermal decomposition of cellulose and lignin. The experimental measurements of the temperature and weight loss of wood, straw and peat pellets during their microwave preprocessing (Figure 2a,b) showed that with equal times of mw pre-treatment (220 s) the highest temperature (up to 530 K) and the highest weight loss were achieved for wheat straw pellets (up to 26 %) which have a comparatively higher content of hemicellulose than wood or peat biomass (Table 1).

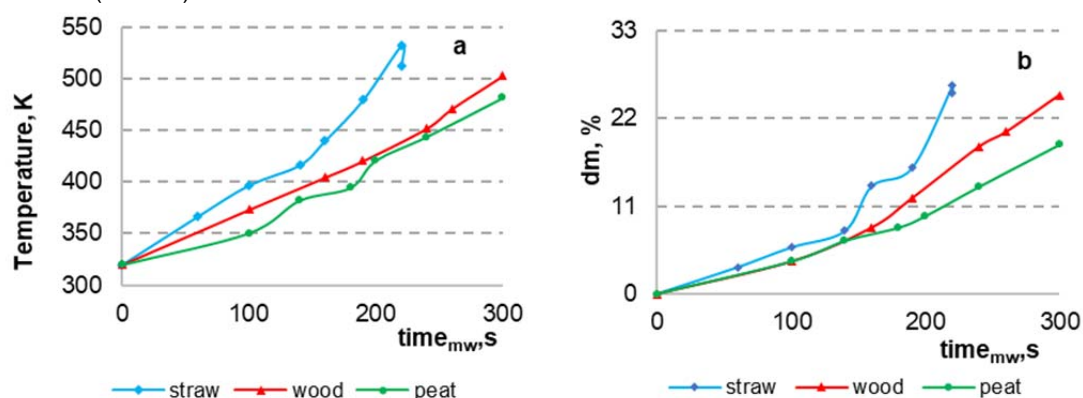


Figure 2: Duration of mw pre-treatment ($time_{mw}$) versus temperature (a) and weight loss (b) for wood, wheat straw and peat pellets

Moreover, the weight loss of wheat straw pellets strongly exceeds the moisture content in the pellets (9.09 %). This confirms that the microwave pre-treatment of straw contributes not only to the emission of moisture and light volatiles, but also can cause primary exothermic decomposition of the main components of lignocellulosic straw, which determines the intensive release of combustible volatiles (H₂, CO, C_xH_y). Such result is fully consistent with the data (Mierzwa-Herstek et al., 2019) confirming that the most intense yield of volatiles (up to 50 %) during mw pre-processing can be observed for wheat straws with the highest content of hemicellulose in the pellets. Therefore, there is a potential risk that increasing the duration of mw pre-treatment of pellets accompanied by the enhanced release of combustible volatiles during pellets' mw pre-treatment can reduce the amount of the energy produced during the burnout of combustible volatiles.

Not less important is the fact that the weight loss at mw pre-treatment decreases the mass density of the pellets thus initiating structural changes in the pellets and increasing their porosity, surface area and reactivity (Figure 3a), which provides wider functionality of the pre-treated pellets in different technical applications (Bonga et al., 2020). In accordance with approximation suggested by (di Blasi, 2006) reactivity of pellets was calculated from mass loss during their pre-treatment. For a nearly equal irradiation time of pellets ($t = 220$ s), the mass density of wood pellets during mw pre-treatment decreased by 13.4 %, the mass density of straw by 20.8 % and that of peat by 2.25 %, with the increased reactivity of pre-treated straw pellets to 1.6 ms⁻¹, that of wood pellets to 0.9 ms⁻¹, but with a less pronounced increase of the reactivity of peat pellets to 0.6 ms⁻¹.

Besides, the changes of the elemental composition during mw pre-treatment have caused changes in heating values of the produced biochar (Figure 3b). From the mw pre-treatment data of wheat straw pellets a faster rise of the calorific values during mw pre-treatment was observed if compared with wood or peat pellets. Moreover, at $T > 550$ K pre-treatment temperature, the heating value of the pre-treated straw pellets exceeds the HHV of the pre-treated wood pellets and reaches the HHV of the pre-treated peat pellets.

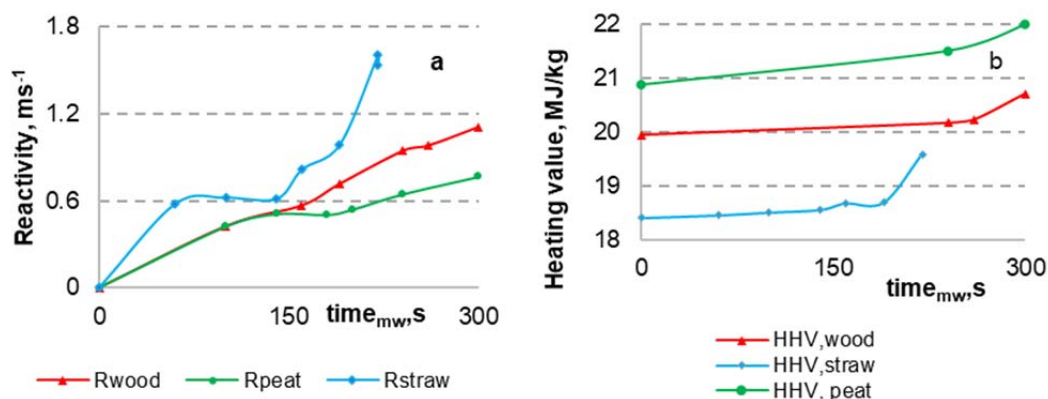


Figure 3: Increased mw irradiation of pellets versus reactivity (a) and heating values of mw pre-treated pellets (b)

3.2. Effect of mw pre-processing on thermal decomposition of pre-treated pellets

The kinetic study and analysis of the weight loss during thermal decomposition of pre-treated pellets in the gasification reactor confirm that changes in the reactivity and HHV of biomass pellets (wheat straw, wood and peat) after their mw pretreatment reduce the duration of their thermal decomposition along with the increase of the weight loss rate of the pre-treated pellets (Figure 4a,b).

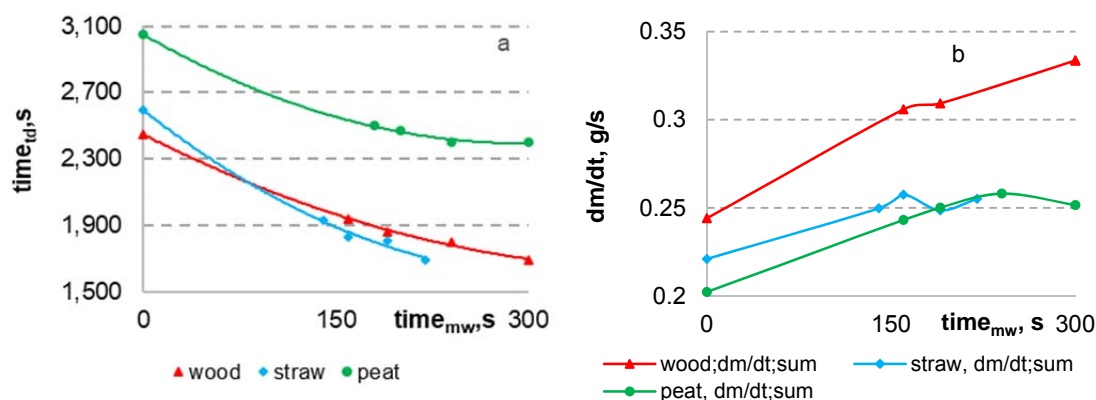


Figure 4: Duration of thermal decomposition of pellets (a) and variations of relative weight loss rate during thermal decomposition of pre-treated pellets versus irradiation time of mw pre-treatment (b).

As follows from Figure 4a, the time needed to ensure the complete thermal decomposition of the pre-treated pellets (t_{td}) depends on the duration of mw pre-treatment of the pellets ($time_{mw}$) and, with a high accuracy ($R^2 \approx 1$), can be expressed using a second-order polynomial approximation ($t_{td} \approx at_{mw}^2 - bt_{mw}$, where $a \approx 0.004$ - 0.009 , $b = 3.6$ - 5.9). The highest decrease in time to complete the thermal decomposition of the pre-treated pellets was observed for wheat straw ($\Delta t \approx 34\%$), which refers to a higher weight loss of the pellets after their mw pretreatment (Figure 2b) along with the highest increase of the reactivity after the pellets' mw pre-treatment (Figure 3a). The time needed to complete the thermal decomposition of pre-treated wood pellets decreased by 26% if compared with raw wood pellets, which refers to the pellets' weight loss by 18% after their mw pretreatment at the temperature of mw pre-processing $T \approx 440$ - 450 K (Figure 2a,b). The lowest impact of mw pre-treatment on the duration of thermal decomposition was found for peat with the lowest content of hemicelluloses and lignin in biomass (Table 1) when the time required for complete thermal decomposition of pretreated pellets decreased by about 21% with the correlating decrease of the pellets' weight loss by 13.4% during mw pretreatment (Figure 2b).

Thus, the performed kinetic study and analysis of the thermal decomposition of the mw pre-treated pellets suggest that, in accordance with the Arrhenius reaction rate equation (di Blasi, 2007), changes in the reactivity of the pellets after their mw pre-treatment are responsible for the faster thermal decomposition and yield of volatiles during the gasification of the pre-treated pellets (Figure 4a), whereas changes in the calorific value of the pre-treated pellets can cause variations of average values of the thermal decomposition rate (Figure 4b) and yield of volatile compounds. As follows from Figure 4b, the most pronounced changes of the weight loss rate during the thermal decomposition of pre-treated pellets were observed with increasing irradiation time for wood pellets, which up to the irradiation time about 220 s have a higher calorific value than the activated wheat straw (Figure 3b), whereas lower calorific value and lower activation energy than the mw pre-processed peat pellets (Larina et al., 2016), resulting in higher weight loss rate during the gasification of pre-treated wood pellets. It should be noted that the highest weight loss after mw pre-treatment of wheat straw pellets is followed by a decrease of the weight loss of the activated wheat straw pellets during their gasification (Figure 4b)

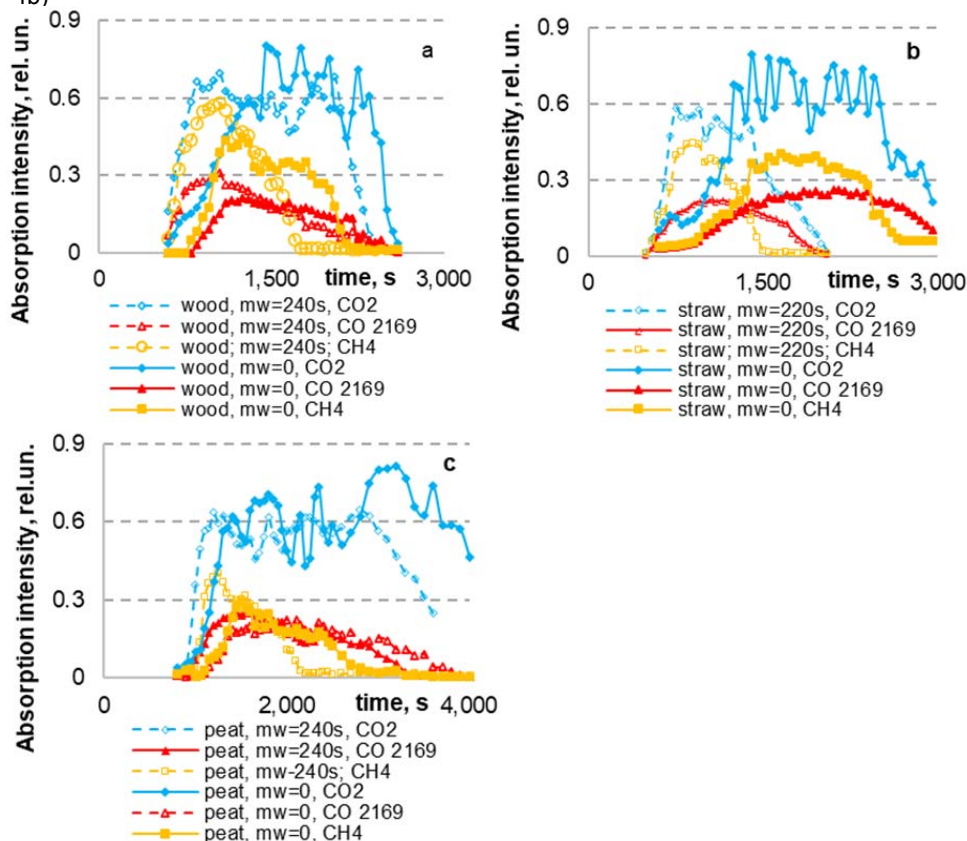


Figure 5: The yield of volatiles during thermal decomposition of MW pre-treated versus raw wood (a), wheat straw (b) and peat (c) pellets, where 2169 refers to wavenumber of CO absorption intensity, cm^{-1} .

This suggests that the higher weight loss of pellets with the higher yield of combustible volatiles caused by mw pre-treatment should limit the weight loss rate of pellets during thermal decomposition of pre-treated pellets, whereas the limited thermal decomposition of pellets at mw pre-treatment enhances the thermal decomposition of hemicellulose, cellulose and lignin during the gasification of pre-treated pellets responsible for the higher yield of combustible volatiles (CO₂, CO and CH₄), as it follows from Figure 5a-c.

Moreover, for all pre-treated pellets increasing the reactivity of the pellets during their mw pre-treatment correlates with the faster thermal decomposition of the pre-treated pellets (Figure 4b) determining the faster yield of volatiles (Figure 5a-c).

4. Conclusions

In the experimental study it has been found that mw pre-processing of different lignocellulosic pellets (wheat straw, wood, peat) results in complex variations of their weight loss and elemental composition responsible for variations of the reactivity and calorific values of mw pre-treated pellets which depend on the irradiation time and temperature during mw pre-treatment of pellets.

The weight loss of pellets during their mw pre-processing tends to increase with increasing irradiation time of pellets determining an increase of the reactivity of pellets. For the equal mw pre-treatment duration (220 s), the highest weight loss was observed for wheat straw pellets, reaching 25 %, for wood pellets - 16 %, and for peat pellets - 12 %. The increase in weight loss and reactivity of the pellets during their mw pre-treatment process activates the thermal decomposition of the pellets during their gasification, determining faster thermal decomposition of the pellets and decreasing the time required for complete thermal decomposition of pretreated wheat straw pellets by 35 %, wood pellets by 26.5 % and peat pellets by 21 %.

Increasing the duration of mw pre-treatment above 220s and the temperature of mw pre-treatment above 480-500 K can cause the partial thermal decomposition of hemicellulose, cellulose and lignin by enhancing the yield of volatile compounds with carbonization of pellets during their mw pre-treatment. This suggests that the increased weight loss with the enhanced yield of volatiles of pellets during mw pre-treatment can cause the limited yield of volatiles during thermal decomposition of pretreated pellets. The following conclusion is confirmed by the mw pre-processing of wheat straw pellets indicating that the highest weight loss of pellets during their mw pre-treatment results in reduced weight loss rate of pellets and the yield of volatiles during the thermal decomposition of pretreated pellets.

The results of the experimental study show that mw pre-processing of lignocellulosic pellets can be used as a tool for effective control of the thermal decomposition of pretreated pellets with the beneficial use of pre-treated lignocellulosic pellets as a fuel for energy production.

Acknowledgments

The authors would like to acknowledge financial support from the European Regional funding of project No. 1.1.1.1/19/A/010.

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