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Thermal Decomposition and Combustion of Microwave Pre-Treated Biomass Pellets

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Abstract: The objective of the study was to investigate a more effective use of commercially available biomass pellets (wheat straw, wood, peat) using microwave pretreatment to improve heat production. Pellets were pretreated using the originally designed microwave torrefaction device. The effects of microwave (mw) pretreatment were quantified, providing measurements of the weight loss and elemental composition of pellets and estimating the effect of mw pretreatment on their porosity, surface area and calorific values at pretreatment temperatures of $T = 448\text{--}553$ K. Obtained results show that the highest structural variations and elemental composition during mw pretreatment were obtained for wheat straw pellets, with an increase in reactivity, a decreasing in the duration of the thermal decomposition by about 40% and an increase in the yield of combustible volatiles. Increased reactivity of pretreated pellets enhanced the ignition and burnout of volatiles, decreasing the duration of the burnout of pretreated wheat straw, wood and peat pellets by 40%, 24% and 9%, respectively, and increasing the peak and average values of the flame temperature, heat output, and produced heat energy by 40–50%, with a correlating increase of combustion efficiency and the mass fraction of carbon-neutral CO₂ emission. Thus, the applicability of microwave pretreatment for the control and improvement of heat production was confirmed.

Keywords: microwave pretreatment; reactivity; heating value; wheat straw; wood; peat; pellets; thermal decomposition; combustion



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1. Introduction

The present experimental study is in line with the key targets of the European Commission climate and energy framework for 2030, specifying at least a 40% reduction in greenhouse gas emissions (from 1990 levels), at least a 32% share for renewable energy and at least a 32.5% improvement in energy efficiency, gradually replacing fossil fuels with renewable energy sources [1]. Among these sources are lignocellulosic biomass feedstocks (harvesting or agriculture residues, bog peat, etc.), which have great potential as alternatives to fossil fuels for green energy production. Nowadays, the applicability of these renewable feedstocks to energy production is limited due to the dissimilarity of their structure as well as their low energy density and reactivity when compared with solid, liquid, or gaseous fossil fuels. To widen the use of biomass feedstocks in energy production, they should be converted to biofuels with higher energy density and reactivity. This can be partially achieved by their granulation or briquetting. For an additional improvement of densified biofuels main characteristics, microwave (mw) pretreatment is recognized as a promising tool to produce biofuels with higher energy density, increased reactivity, and reduced emission of GHGs during energy production [2,3]. It has been shown that the effect of mw pretreatment of lignocellulosic biomass depends on the ability of lignocellulosic biomass components (hemicellulose, cellulose and lignin) to absorb and convert the energy

of high frequency ($f = 2.45$ GHz) electromagnetic field oscillations into heat; this is due to the dissipative effects ($Q = \epsilon''E^2$) dependence on the response of polar molecules and ions to high frequency oscillations [4–6]. Previous experimental studies evaluating the effect of mw pretreatment on the thermal decomposition of biomass samples of different origins and parameters characterizing the combustion process have shown that microwave-induced oscillations produce variations in the biomass structure, composition, and the heating value. This results in a decrease of the mass density of pretreated biomass, faster thermal decomposition, faster yield, ignition, and burnout of combustible volatiles, an increase in the energy output and average values of carbon-neutral CO₂ emissions in the products [7,8]. Furthermore, results of previous experimental studies have shown that the effect of mw pretreatment on combustion characteristics is highly influenced by the chemical composition of the lignocellulosic biomass content of hemicelluloses, cellulose and lignin, with a more pronounced effect of mw pretreatment on the combustion characteristics for straws with a higher content of hemicellulose in biomass [7,8].

It should be noticed that microwave-assisted processing of biomass for bioenergy production offers a wide range processing technologies, such as pretreatment, gasification, pyrolysis, extraction, liquefaction and drying, with low energy consumption, a high rate of reactions, and a high yield of production and high pretreatment efficiency [3,9,10]. Additionally, mw pretreatment technology allows for the combination of mw pretreatment of lignocellulosic biomass with other physical and chemical pretreatment methods to produce different types of biofuels and chemicals, increasing sugar yield and the efficiency of bioethanol production [11–14].

To provide efficient mw pretreatment of lignocellulosic biomass, many studies have assessed the optimal pretreatment conditions, pretreatment time and energy, which are the main factors that influence the pretreatment efficiency by enhancing hemicellulose removal and cellulose digestibility [9,15,16]. Previous studies confirm that these factors also significantly affect the thermochemical conversion of different origin lignocellulosic biomass pellets and their mixtures [7]. An increase of the mw pretreatment time correlates with an increase in weight loss of biomass samples, mainly due to the evaporation of physically bounded moisture, partial thermochemical degradation of biomass carbohydrates and the release of volatile compounds, which depends on the chemical composition of the raw biomass [7]. Thus, there are several factors determining the efficiency of biomass mw pretreatment; to achieve effective control of the combustion characteristics and composition of emissions, detailed studies must be conducted to determine the main effects responsible for the thermal decomposition of activated biomass pellets as well as the formation of combustible volatiles and their ignition, combustion, heat energy production and composition of emissions. Carrying out such complex research and assessing the main factors that might limit the applicability of mw preprocessing to achieve the optimal combustion conditions for the primary solid fuels of Latvia (wood, wheat straw, peat pellets) is the main task of this work. It is foreseen that a smart technology of improving thermochemical conversion of biomass and know-how will be created to provide a wider use of these bioenergy resources for a cleaner and more efficient energy production.

2. Experimental Setup and Research Methodology

Two types of pilot-scale experimental devices were used to study the thermal decomposition and combustion processes of microwave-activated biomass pellets [17,18]. A microwave reactor was used for the pretreatment of different origin commercial pellets: wheat straw pellets with an average diameter of 8 mm and moisture content of 10.2%, wood (softwood) pellets with an average diameter of 6 mm and moisture content of 7.14%, and peat pellets with an average diameter of 8 mm and moisture content of 8.9%. The length of all pellets varied from 5–25 mm. Pretreatment was carried out using a two-stage process of biomass heating, which combined convective and mw heating of pellets in the argon atmosphere [17]. The main components of the mw reactor were magnetrons with a power of up to 0.9 kW, a tubular resonator and the coaxial waveguide attached to

the bottom of the resonator. A total of 300 g of pellets were loaded into the reactor and then placed inside the resonator, providing preliminary convective heating of pellets up to a temperature of 350 K, followed by mw dynamic heating up to 450–570 K, and then isothermal mw heating for 20 min at the given temperature. The weight loss of pellets after mw pretreatment and the yields of solid and condensable fractions were determined by weighing. The weight of non-condensable fractions was calculated as the difference between total weight loss and weight of the collected condensable fraction. To estimate the effect of mw pretreatment on the main characteristics of biomass pellets, the content of C, H, N were measured according to national standard (LVS EN15104:2011), using a vario MACRO elemental analyzer (ELEMENTAR Analysensysteme, Germany). The ash content was measured as a residue after ignition at 823 ± 10 K in a Carbolite ELF 11/6B furnace (Turkey), according to the LVS EN 14775:2010 standard. The higher heating value (HHV) of pretreated samples was calculated using a regression equation and the data of elemental composition [17]. The porous structure of the pellets was evaluated from N_2 sorption/desorption isotherms, determined in a sorptometer Quntachrome NOVA 4200e (Boynton Beach, FL, USA). Degassing was performed at room temperature for 120 h. The specific surface area was assessed using Quantachrome software and was based on Brunauer-Emmet-Teller (BET) theory.

A pilot device with an average heat capacity up to 5 kW, which combined a gasifier of biomass pellets and a combustor [18], was used to study the thermal decomposition and combustion of mw pretreated pellets (Figure 1). The gasifier was filled with pretreated biomass pellets (340–500 g); the thermal decomposition was initiated using additional heat supply by a propane flame flow into the upper part of the biomass layer and was supported using the primary air supply below the layer of biomass pellets at an average air supply rate of 40 L/min. The thermal decomposition of pretreated lignocellulosic biomass pellets produced the axial flow of volatiles, which was injected into the combustor, attached to the upper part of the gasifier.

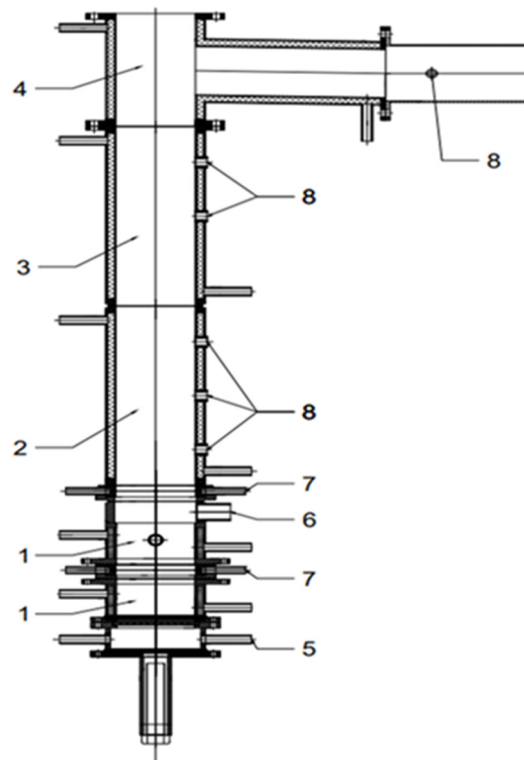


Figure 1. A sketch of the experimental device: 1—gasifier; 2, 3, 4—water-cooled sections of the combustor; 5—primary air supply nozzle; 6—propane flame supply nozzle; 7—secondary air supply nozzle; 8—orifices for the diagnostic tools.

The burnout of volatiles downstream of the combustor was enhanced using the secondary swirling air supply at an average air supply rate 60 L/min. The effect of mw pretreatment on the thermal decomposition of pretreated pellets and combustion of volatiles was estimated, providing the complex measurements of the kinetics of the weight loss rate of pretreated pellets and the yield of volatiles during their gasification (using the sampling procedure and a Testo 350 gas analyzer (Vietnam), kinetics of the flame temperature, heat output from the device and composition of emissions, using methodology described in [18].

3. Results

3.1. The Effect of MW Pre-Treatment on the Main Characteristics of Lignocellulosic Pellets

The preliminary experimental study of the time-dependent variations of the weight loss of wood, straw and peat pellets showed that, for equal times of mw pretreatment (240 s), when the temperature of pellets nears 480–500 K, the highest weight loss (dm/m_0 , %) during the microwave pretreatment was observed for wheat straw pellets (up to 24%), which strongly exceeded the initial moisture content in the raw pellets (10.2%). Relatively less weight loss during microwave pretreatment was observed for wood (12%) and peat (7%) pellets, with the initial moisture content in the pellets being 7.14% for wood and 8.9% for peat. The changes in weight loss of pellets dm/m_0 during their mw pretreatment in the microwave oven can be expressed in the following order: straw > wood > peat. During mw pretreatment of wood, wheat straw and peat pellets in the rotating reactor, the temperature of pellets was increased up to 570 K, determining the enhanced weight loss of pellets. The weight loss of wheat straw pellets was increased up to 53%, but nearly equal weight loss was observed for wood and peat pellets ca. 32%. Because the content of volatiles in straw is about 79.4% [19], more than half of the straw was converted into gas products. The process of drying was dominant for wood and wheat straw biomass for mw pretreatment at 448–498 K. Negligible transformation of the biomass structure occurred in this temperature range. At temperatures >498 K, the above-mentioned process of chemical structure transformation took place actively for both treated biomasses. For peat, the measurable weight loss due to biomass thermal destruction was observed at a lower temperature range of 448–473 K, which linearly increased with an increase of the processing temperature, in contrast to wheat straw and wood, for which exponential increase in weight loss was dependent on the treatment temperature (Figure 2).

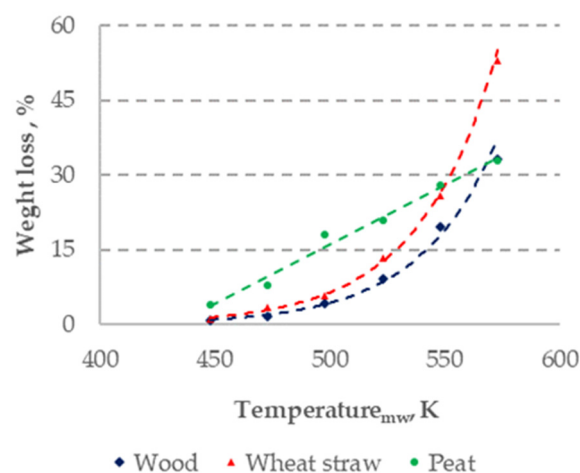


Figure 2. The weight loss of biomass pellets (on dry matter basis) as dependent on mw-assisted pretreatment temperature.

This suggests that the microwave pretreatment of pellets contributes not only to the release of moisture, but also to the primary decomposition of hemicelluloses, cellulose, and

lignin. Analysis of the thermal decomposition of lignocellulosic biomass has shown that the exothermic thermal decomposition of hemicelluloses, with apparent changes in its structure, occurs at $T \approx 490\text{--}590$ K; endothermic thermal decomposition of cellulose, with breakdown of glycosidic structure and loss of crystallinity, starts to develop at $T \approx 590\text{--}670$ K; the decomposition of lignin occurs at temperatures between 430–1100 K [6,20].

Hemicelluloses decompose easily, while the lignin is most difficult to decompose but is most available for development of inter-condensation processes, carrying out the highest increment into the formation of char residue [20,21]. Hence, by increasing the pretreatment temperature of pellets above 470 K, the mw irradiation of pellets starts with the primary endothermic decomposition of polymer-like hemicelluloses, responsible for higher CO₂ yield in results of decarboxylation reaction, and is followed by endothermic decomposition of celluloses, which is responsible for the high yield of chemically bonded H₂O, CO and CO₂. Along with such products as methanol and acetic and formic acid, anhydrosugars were formed as a result of the thermal degradation of the carbohydrate complex of biomass in the temperature range under study [22]. The decomposition of lignin produced higher yields of H₂ and CH₄. Simultaneously, the condensation of major biomass components took place also with the formation of novel C=C bonds [22]. The contribution of condensation processes of biomass components in charcoal formation was decreased in the range: lignin > cellulose > hemicellulose [21]. The enhanced yield of gas products promoted variations in the surface structure, increasing the porosity of pellets (Table 1).

Table 1. The effect of increasing the temperature of mw pretreatment on changes of the surface area and porosity of pretreated pellets.

Temperature of Torrefaction	Wood		Wheat Straw		Peat	
	Specific Surface Area (BET), m ² /g	Total Pores Volume, mm ³ /g	Specific Surface Area (BET), m ² /g	Total Pores Volume, mm ³ /g	Specific Surface Area (BET), m ² /g	Total Pores Volume, mm ³ /g
Non-treated	0.28	0.72	0.62	0.5	0.38	0.97
473 K	0.43	1.74	0.59	0.72	0.29	1.28
523 K	0.45	1.44	0.71	0.95	0.59	1.95
573 K	0.52	1.39	1.02	3.22	0.59	3.22

The variations of the surface structure and porosity of pellets promoted an increase in their reactivity, which is defined in terms of the conversion rate per remaining mass ($1/m_t \cdot dm/dt$) [23] and can be expressed as follows:

$$\alpha = \frac{m_t - m_f}{m_0 - m_f} \quad (1)$$

where m_0 , is the mass of the biomass substrate at the beginning of reaction or initial time, m_t is the mass of the biomass substrate at any time, t , and m_f is the mass of the biomass at the end of the reaction time.

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) (1 - \alpha)^n \quad (2)$$

where α is the degree of conversion of pellets at time, t ; A , E and R are the frequency factor, activation energy and gas constant, respectively; n is order of reaction according to the assumed reaction model.

The partial decomposition of the main constituents of lignocellulosic biomass with the enhanced yield of gas products during mw pretreatment of pellets promotes not only the structural changes of pellets, but also causes variation in their elemental composition and heating values, which are presented in Figure 3a–f, normalized to main characteristics of raw pellets for $T = 300$ K.

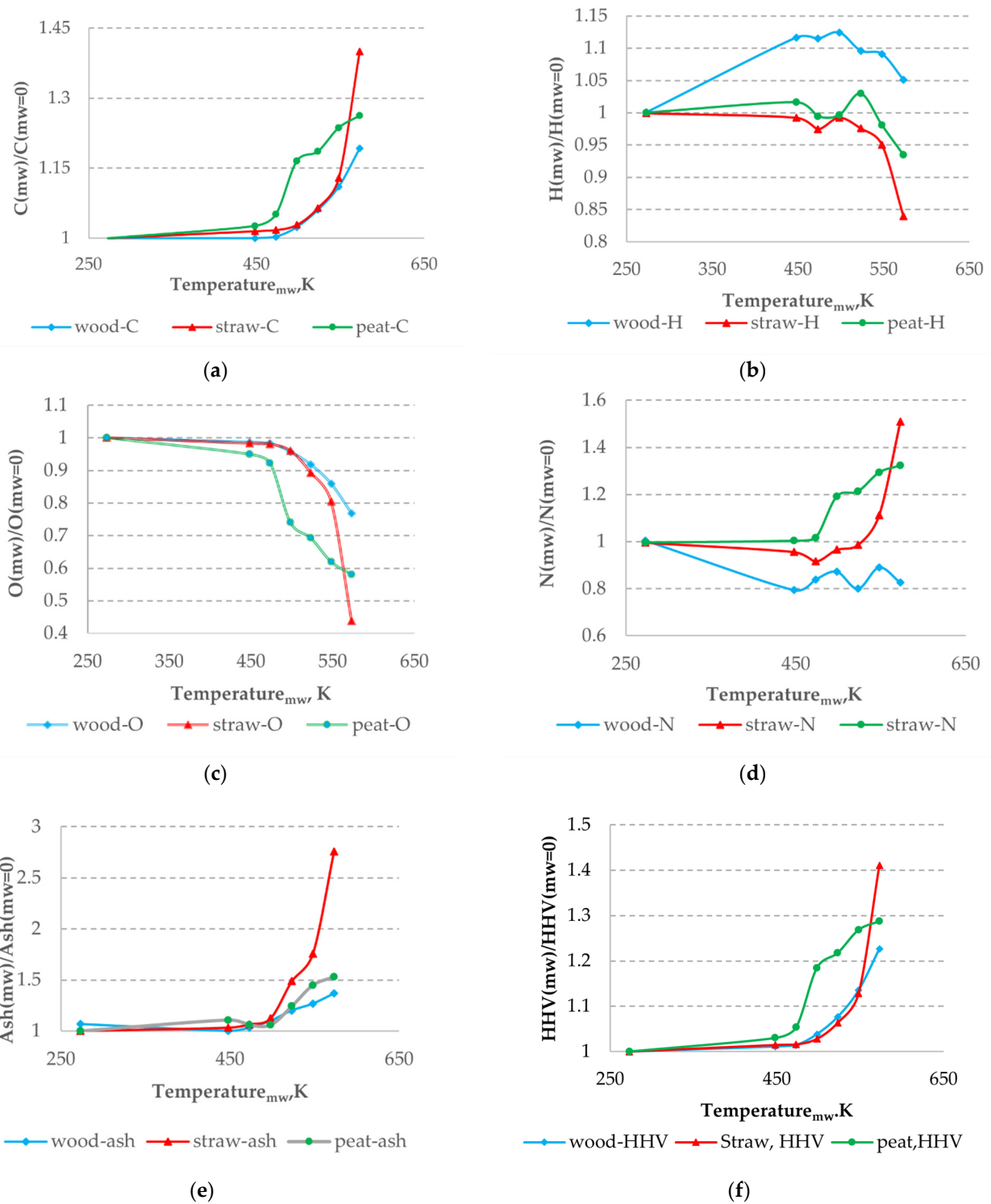


Figure 3. The effect of increasing the temperature of mw pretreatment of wood, wheat straw and peat pellets on the relative changes of carbon (a), hydrogen (b), oxygen (c), nitrogen (d), and ash (e) contents and higher heating value (f) of pre-treated pellets.

As follows from Figure 3, increasing the temperature of mw pretreatment above 470 K correlated with an increase of the carbon content in the pretreated pellets, while a decrease of the hydrogen and oxygen contents dominated. In addition, for straw and peat pellets, the nitrogen content in pellets tended to increase, while it tended to decrease with the mw pretreatment of wood pellets. This suggests that the different chemical composition of

pretreated biomass pellets is responsible for the different yield of gas products (H_2 , CO , CO_2 , CH_4 , NO_x) during the microwave pretreatment of pellets. Hence, a decrease of H_2 content in pellets after mw pretreatment can be related to the enhanced yield of H_2 and CH_4 due to cracking and deformation of lignin with a higher content of aromatic ring and $O-CH_3$ functional groups [20]. Thermal decomposition of cellulose due to a higher carbonyl content results in the highest CO yield during mw pretreatment of pellets, while the thermal decomposition of hemicellulose with higher carboxyl content results in the highest CO_2 yield [20].

It was shown that the yields of non-condensable fractions consisted predominantly of CO , CO_2 , CH_4 ; H_2 was increased with increasing mw pretreatment temperatures for all biomass under study (Figure 4a–d).

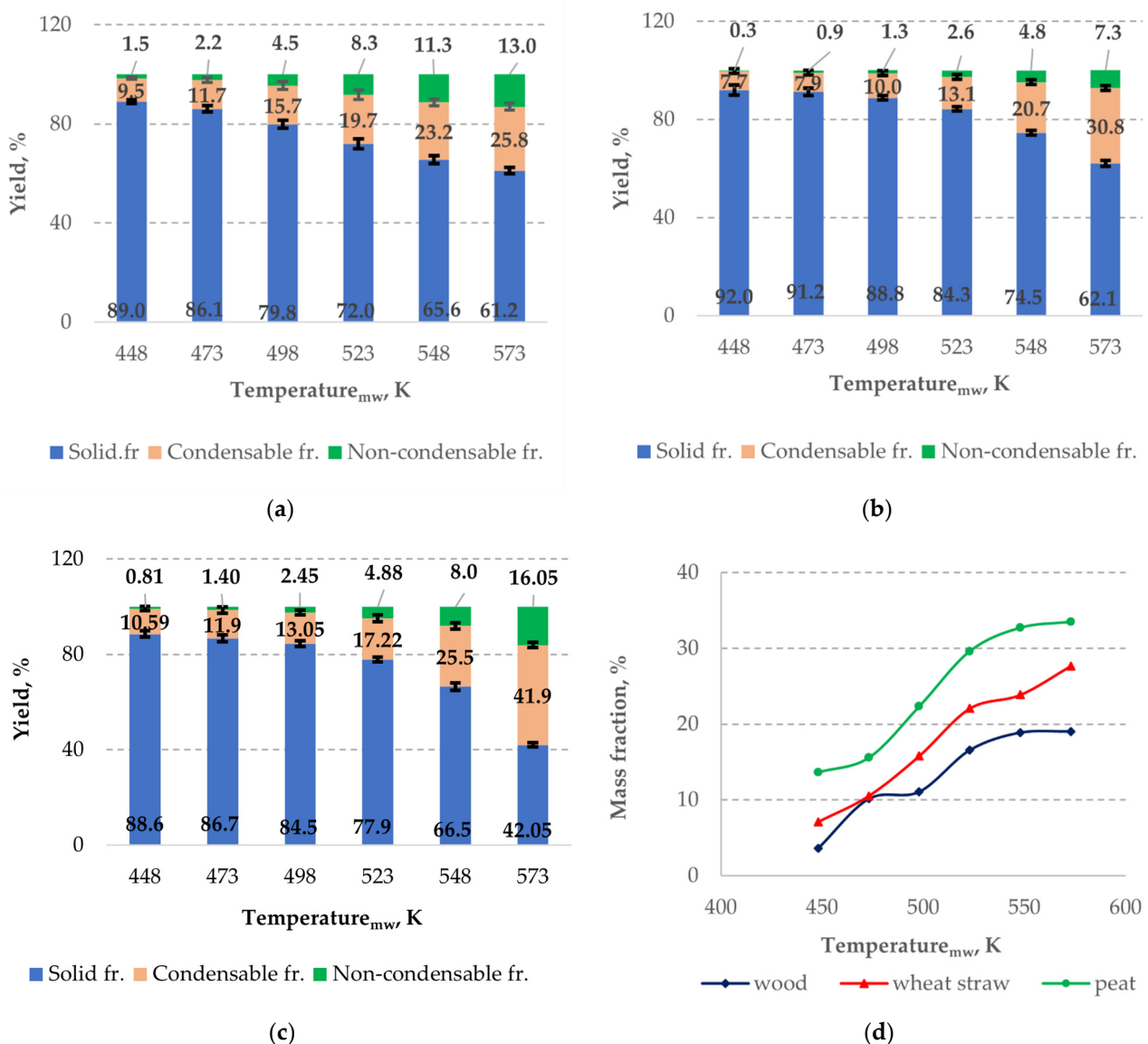


Figure 4. The yields of products (normalized to 100%) of mw-assisted pretreatment of different biomass depending on temperature: wood (a), peat (b), wheat straw (c) and the mass fraction of non-condensable gases in released volatiles (d).

The highest weight loss and the highest yield of non-condensable gases in degradation products were established in the case of wheat straw that was mw pretreated at 570 K, which can be explained by the highest portion of thermolabile hemicellulose in its composition as well as an amorphous structure of cellulose in comparison to that ordered in wood

biomass composition. In this case the portion of non-condensable gases in degradation products of peat was the highest over the entire range of pretreatment temperatures. This can be explained by the fact that, unlike wood and wheat straw, peat consists of degraded plant vegetation. As a result of the long-term microbiological and pyrolytic influences in anaerobic conditions, deep degradation/transformation of the plant cell wall components takes place, with the formation of humic compounds; these are high molecular heterogenic compounds with complicated structures whose properties and structure differ greatly from their precursors, including polyphenolics, carbohydrates, proteins, etc. [24].

For all samples under study, water was the dominant component of condensable fraction removed from biomass by mw pretreatment, resulting in not only physical water elimination but also dehydration reactions of carbohydrates and condensation reactions within lignin and cellulose substituents. This is the reason for a significant decrease of a relative portion of oxygen in pretreated biomass. With an increase in the torrefaction temperature from 470 K up to 570 K, the water content in the collected condensates decreased from about 99% (for all biomass samples under study) to 68%, 87% and 86% for wheat straw, wood, and peat, respectively. This indicates that, with an increase of the mw pretreatment temperature, comparatively high molecular fragments of biomass components become volatile, thus modifying the structural and elemental composition of pretreated biomass. The portion of these compounds is the biggest in the case of wheat straw, indicating its higher thermolability in relation to wood and peat.

The enhanced yield of H₂O, CO₂ and CH₄ during mw pretreatment is responsible for the enhanced decrease of oxygen and hydrogen content in pretreated pellets when compared with relative changes to the carbon content in pretreated pellets, which tends to increase, resulting in an elevated HHV of carbonized residue (Figure 3a,f). The HHV of untreated pellets was 19.94 MJ/kg for wood, 18.41 MJ/kg for straw and 20.86 MJ/kg for peat. The highest increase of the HHV after mw pretreatment of pellets was for wheat straw (41%), with the highest increase of the carbon content, while there was a decrease in the oxygen and hydrogen content in pretreated pellets (Figure 3b,c). A relatively smaller increase of HHV was seen for wood (22%) and peat (28%), with a smaller decrease of hydrogen and oxygen content after mw pretreatment of pellets and a smaller increase in the relative carbon content in pretreated pellets.

The mw pretreatment of pellets also promoted the variation in relative ash content in biomass, determining a relatively higher increase of the ash content in wheat straw pellets, while a relatively smaller increase was seen for wood and peat (Figure 3e), which is the main negative effect of mw pre-processing of pellets.

3.2. The Effect of MW Pre-Treatment on the Main Characteristics of Lignocellulosic Pellets

From the data summarized in Table 1, it can be concluded that increasing the temperature of mw pretreatment results in a partial thermal degradation of the main constituents of lignocellulosic biomass pellets (hemicelluloses, cellulose and lignin), enhancing the yield of volatiles, the total pore volume and the surface area of the pellets, which are key factors for increasing the reactivity of pretreated pellets, determining faster and more efficient thermal decomposition of pretreated pellets during their gasification. This is confirmed by the kinetic study of the weight loss of the pretreated pellets (Figure 5a–c) and the yield of gas products (CO₂, H₂, CO, C_xH_y) during their gasification (Figure 6a–d); increasing of the temperature of mw pretreatment correlated with a faster weight loss rate and the yield of gas products, decreasing the relative duration of the thermal decomposition normalized to those for raw, non-treated pellets (mw = 0 in plots) (Figure 5d).

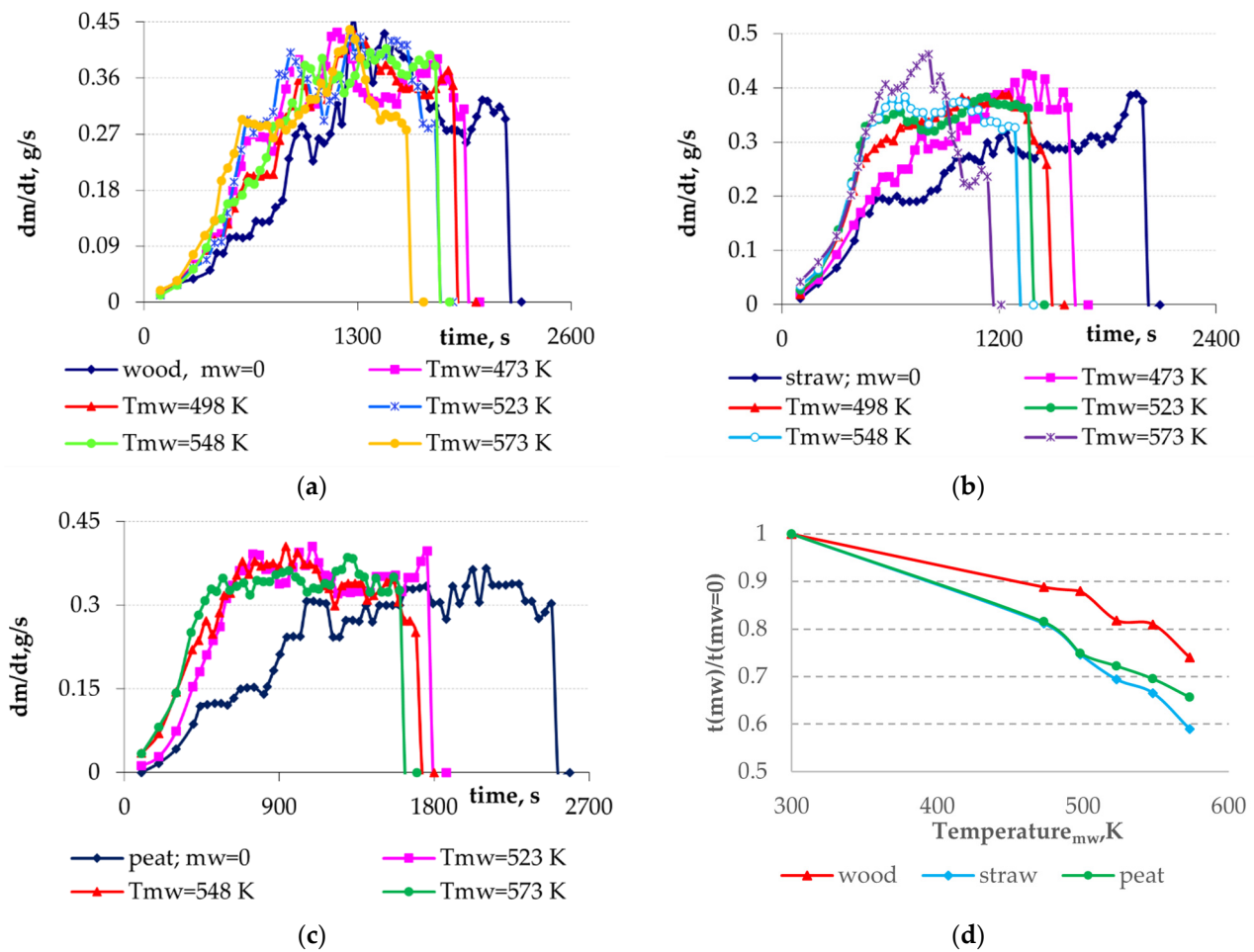


Figure 5. The effect of increasing the pretreatment temperature on the kinetics of the weight loss rate during the thermal decomposition of the pretreated pellets (a–c) and relative duration of the thermal decomposition (d).

Under equal temperatures of the m_w pretreatment (573 K) the total pore volume and the surface area of the pretreated wheat straw pellets was larger than that for pretreated wood or peat pellets (Table 1). As a result, the higher reactivity of the m_w pretreated wheat straw pellets caused more a pronounced decrease of the duration of the pretreated wheat straw thermal decomposition (by about 40%) when compared with the thermal decomposition of the pretreated wood or peat pellets (by about 27–30%). In addition, the higher reactivity of the wheat straw pellets correlated with the enhanced yield of volatiles (CO , H_2) during the gasification of the pretreated wheat straw pellets, increasing the peak value of the yield of CO from 31.8 g/cm^3 for the raw pellets up to 113 g/cm^3 for the pellets pretreated at 573 K. Correspondingly, the yield of H_2 increased from 0.4 g/cm^3 up to 3.8 g/cm^3 . As follows from Figure 6a–f, increasing the temperature of m_w pretreatment of pellets also enhanced the formation of secondary peaks of the yield of combustible volatiles (CO , H_2) during the end stage of the thermochemical conversion of pretreated pellets $t > 1000$ s, which correlated with a slight increase of the weight loss of pellets (Figure 5a–c).

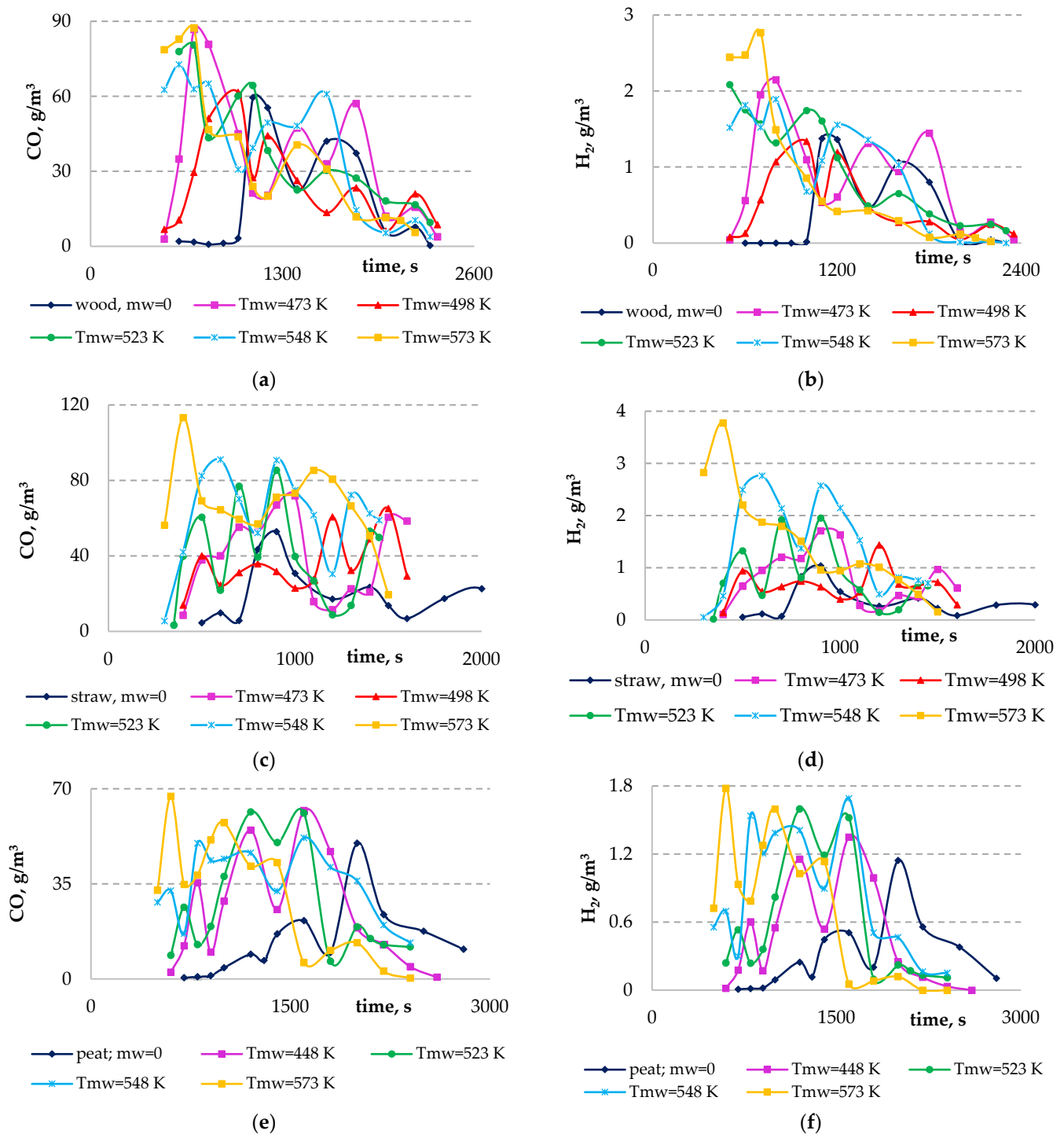


Figure 6. The effect of increasing the pre-treatment temperature on the kinetics of the yield of combustible volatiles (CO, H₂) during thermal decomposition of pre-treated pellets; (a,b) the yield of CO and H₂ at thermal decomposition of wood pellets; (c,d) the yield of CO and H₂ at thermal decomposition of wheat straw pellets; (e,f) the yield of CO and H₂ at thermal decomposition of peat pellets.

Increasing the temperature of mw pretreatment also influenced the average values of the yield of H₂, CO and CO₂ during their thermal decomposition, increasing average values of the yield of CO, H₂, CO₂ and the weight loss of pellets up to maximum values. The maximum value of the yield of CO₂ was fixed at the lower temperatures of mw pretreatment of lignocellulosic pellets ($T \approx 470\text{--}500$ K), while the yields of CO and H₂

tended to increase when increasing the pretreatment temperature up to $T \approx 548\text{--}573\text{ K}$ (Figure 7a–c).

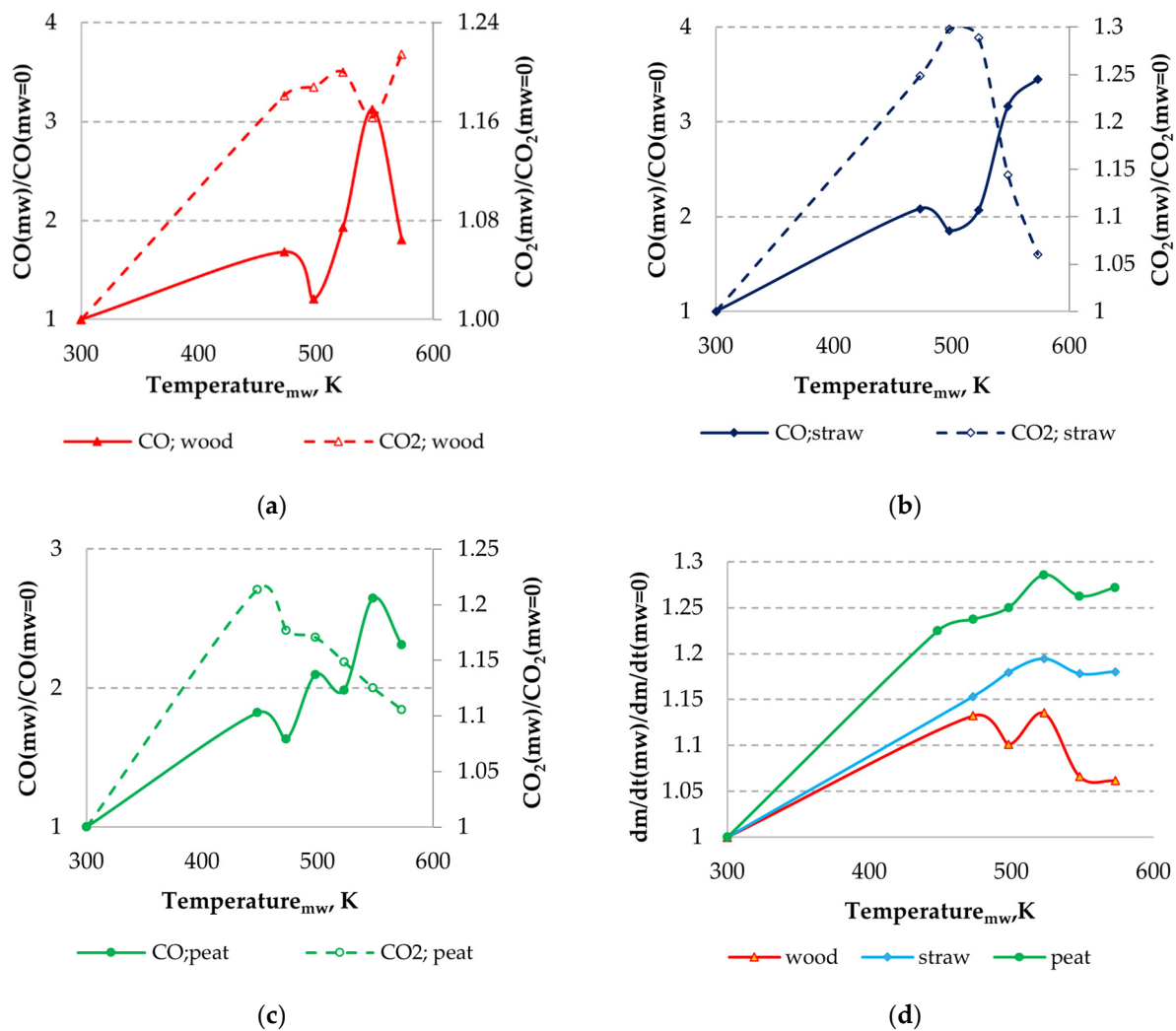
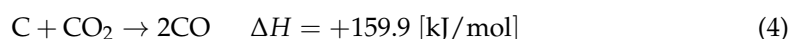
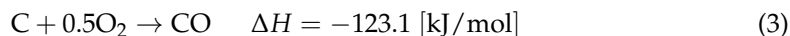


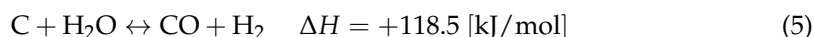
Figure 7. Effect of increasing the pretreatment temperature on the average values of the yield of volatiles: CO, CO₂ during the thermal decomposition of pretreated wood (a), wheat straw (b) and peat pellets (c) and on the relative variations of the weight loss rate of pretreated pellets (d).

Considering the effect of mw pretreatment of lignocellulosic pellets on the yields of volatiles, it should be noted that there are several factors that can cause changes in the average yield of energy enriched volatiles during thermal decomposition of pellets if the pretreatment temperature of the pellets is increased. As was shown, the mw treatment promoted simultaneously the degradation and secondary condensation reactions of major biomass components by removing from volatiles a portion of water that varied in the range of 68–99%. The yield of volatiles was increased with increasing of mw treatment temperature (Figure 4). Therefore, the relative portion of water in products of pretreated biomass gasification was decreased, thus increasing the content of energy-enriched volatiles. In addition, the enhanced yield of volatiles could be related to the partial thermal destruction of hemicellulose, cellulose and lignin; as the temperature of mw pretreatment was raised, the enhanced porosity and reactivity of pellets (Table 1) elevated the yield of volatiles and the weight loss of pellets during the thermal decomposition of pretreated pellets (Figures 5 and 6). Next, as follows from Figure 3a, increasing the temperature of mw pretreatment could cause carbonization of lignocellulosic pellets. Correspondingly, as follows from Figures 6a–f and 7a–c, the enhanced carbonization of pellets, caused by increasing

the mw pretreatment temperature, could produce considerable variations in the yield of CO and CO₂ during the thermal decomposition of pretreated pellets, which for the limited sub-stoichiometric primary air supply in the device, could be attributed to the development of the exothermic partial oxidation of carbonized pellets (3) and competitive development of endothermic Boudouard's reaction (4), increasing the yield of CO, while gradually decreasing the yield of CO₂ [19]:



In addition, the higher yields of CO and H₂ during thermal decomposition of carbonized pellets can be produced due to the development of the endothermic water-gas reaction:



As a result of the competing processes developed during thermal decomposition of pretreated pellets, increasing the pretreatment temperature significantly affected the thermal decomposition of activated pellets and the formation of volatile compounds, causing a rapid increase in the yield of CO and H₂ when the mw pretreatment temperature of pellets was increased above 470–500 K (Figure 7). However, the yield of CO₂ increased to its maximum value with a subsequent decrease if the pretreatment temperature exceeded 470–500 K (Figure 7a–c). A particularly pronounced decrease in the yield of CO₂ during thermal decomposition of pretreated pellets with a subsequent increase of the yield of CO and H₂ was observed for pretreated straw and peat pellets for which an increase in mw pretreatment temperature provided a more rapid increase in the carbon content of pretreated pellets (Figure 3a).

3.3. The Effect of MW Pre-Treatment of Lignocellulosic Pellets on the Combustion Characteristics

The formation of the combustion zone for the given configuration of the pilot device (Figure 1) was determined by mixing of the axial flow of combustible volatiles (CO, H₂) with the secondary swirling air, which was fed to the base of the combustor. The ignition and combustion of volatiles resulted in the formation of the reaction zone, with a marked increase in temperature and axial velocity up to their peak values, which were observed close to the flame axis, where the average flame temperature tended to increase to 1000–1200 K, whereas the axial and tangential velocities increased to 1.3–1.4 m/s. Microwave pretreatment of lignocellulosic pellets, with the enhanced weight loss in pellets and the yield of volatiles during the thermal decomposition of pretreated pellets, significantly affected the combustion conditions at the flame base, gradually decreasing the air excess ratio at the flame base from $\alpha \approx 1.2$ –1.35 during thermochemical conversion of raw pellets to $\alpha \approx 0.97$ –1.17, increasing the temperature of mw pretreatment and thus improving the main combustion characteristics. In addition, the variations in the surface area, porosity and elemental composition of pellets contributed to faster ignition and burnout of volatiles. This was confirmed by measurements of the flame temperature and heat output kinetics for the different pretreatment temperatures of the pellets. Kinetic study of the flame temperature showed that increasing the temperature of mw pretreatment resulted in the faster ignition of volatiles, faster formation of flaming combustion and faster transition to after-flame smoldering stage, decreasing the duration of the burnout of pretreated pellets (Figure 8a–c). Kinetic study of the flame temperature and the weight loss of pellets for the different temperatures of mw pretreatment confirmed that the decrease in the duration of the burnout of the pretreated pellets correlated with the decrease in the duration of their thermal decomposition and the weight loss of pretreated pellets (Figure 5d). In addition, the most pronounced decrease in the duration of the burnout by increasing the temperature of mw pretreatment was observed for wheat straw pellets (Figure 8d), which had the largest increase in the weight loss of pellets, the yield of volatiles, surface area and porosity during the mw pretreatment (Table 1), thus promoting an increase in their reactivity, as it follows

from the kinetic study of the weight loss rates (Figure 5a–d) and the flame temperature (Figure 8a–d).

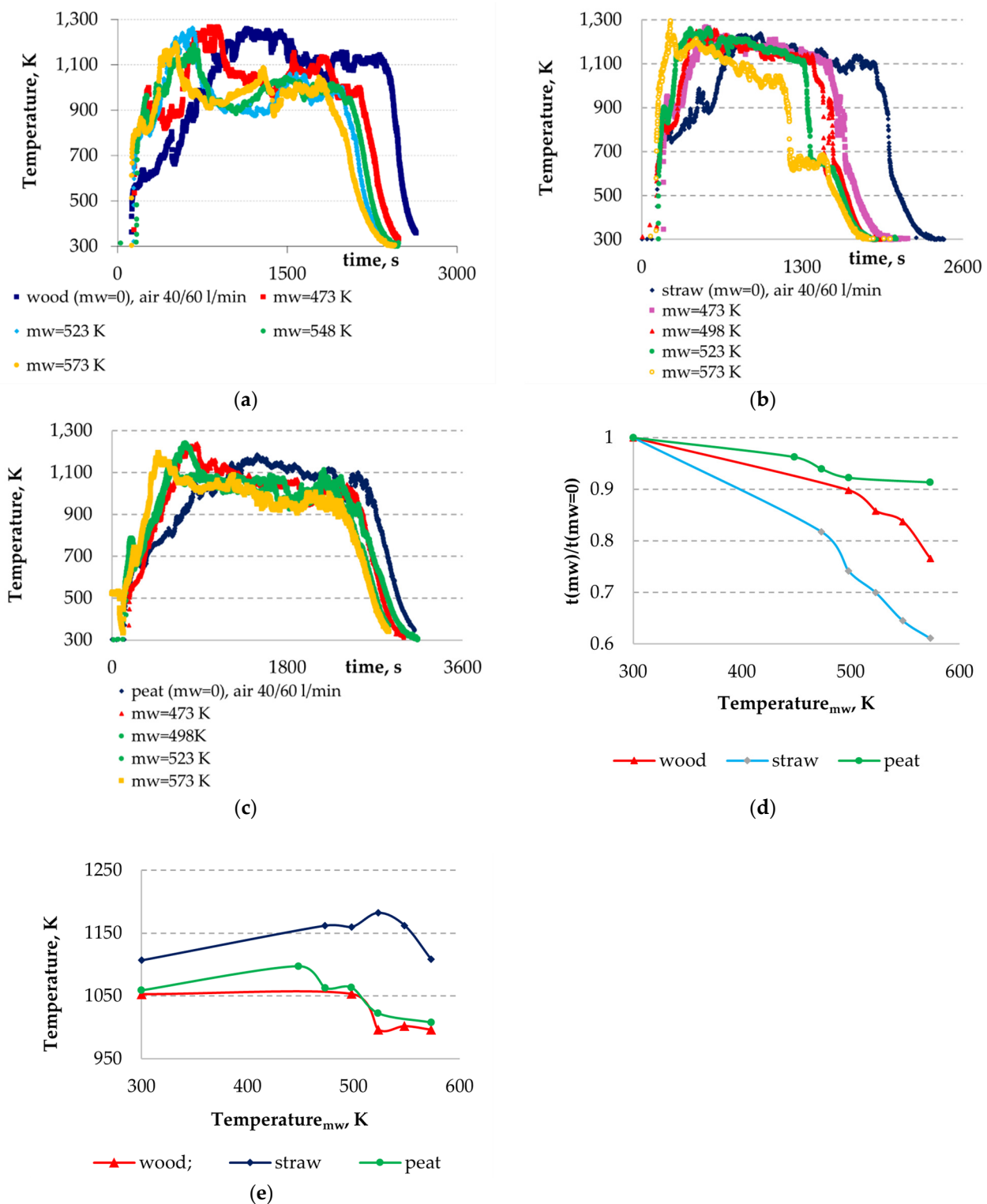


Figure 8. The effect of variations of the mw pretreatment temperature on the kinetics of the flame temperature during the burnout of wood (a), wheat straw (b) and peat pellets (c), on the relative duration of the burnout of pretreated pellets (d) and on the average values of the flame temperature (e).

It should be noted that the increase of the temperature of mw pretreatment also affected the average value of the flame temperature (Figure 8e), which could be related to

variations in the yield of volatiles during the thermal decomposition of pretreated pellets. Thus, the new balance between the competitive processes of the enhanced thermal decomposition of the main constituents (hemicellulose, cellulose and lignin) in lignocellulosic pellets after mw pretreatment promoted the ignition and burnout of combustible volatiles (CO , H_2) and the development of surface reactions (3)–(5). Increasing the pretreatment temperature of pellets correlated with an increase of the flame temperature up to the maximum value, which tended to decrease under the conditions when carbonization of the pellets enhanced the development of endothermic reactions (4) and (5).

The variations of the mw pretreatment regime substantially affected not only the thermal decomposition of lignocellulosic pellets and the flame temperature but also the heat capacity and produced heat energy per mass of burned pellets. By analogy with the effect of the pretreatment temperature on the kinetics of the weight loss of pellets and the flame temperature, increasing the pretreatment temperature of pellets provided faster and more intensive heat release, decreasing its duration (Figure 9a–c).

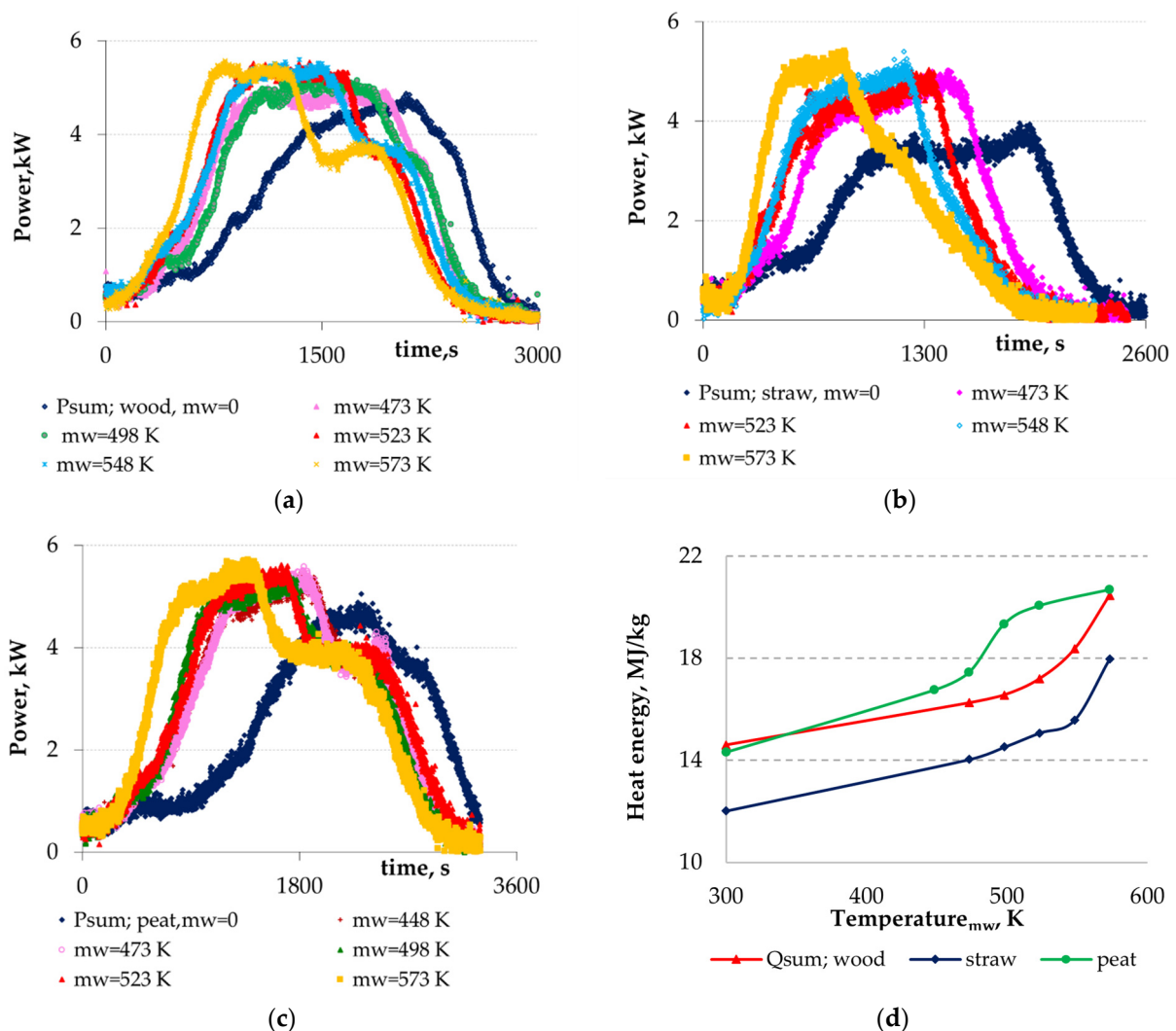


Figure 9. The effect of the mw pretreatment temperature on the kinetics of the heat power output (a–c) and produced heat energy per mass of pretreated pellets (d) during the burnout of wood (a), wheat straw (b) and peat pellets (c).

The time-dependent variations of produced heat energy for different regimes of mw pretreatment confirmed that the burnout of pretreated pellets was developing as a two-stage process, with a primary stage of flaming combustion of volatiles and the subsequent stage of the burnout of carbonized pellets. In addition, increasing the temperature of mw

pretreatment decreased the duration of the flaming combustion but increased the duration of the burnout of carbonized pellets (Figure 9a–c). Comparing the effect of mw pretreatment on the main characteristics of pretreated pellets (Figure 3a–f) and produced heat energy (Figure 9d), it can be concluded that the increase in the produced heat energy per mass of pretreated pellets can be related to the increase in calorific value of pretreated pellets.

3.4. The Effect of MW Pre-Treatment of Lignocellulosic Pellets on the Combustion Efficiency and Composition of the Products

Considering the effect of mw pretreatment of lignocellulosic pellets on their thermal decomposition, flame temperature and heat capacity, it can be concluded that mw pretreatment of pellets can produce variations in the product's composition and combustion efficiency. Kinetic study of the formation of the main product—CO₂—confirms that, by analogy with kinetics of the temperature and heat output from the device, mw pretreatment of pellets, by producing an increase of porosity and reactivity of pellets, enhances the formation of CO₂ downstream the flame reaction zone, completing the burnout of volatiles and correlating to an increase of the peak and average values of the volume fraction of CO₂ in the products (Figure 10a).

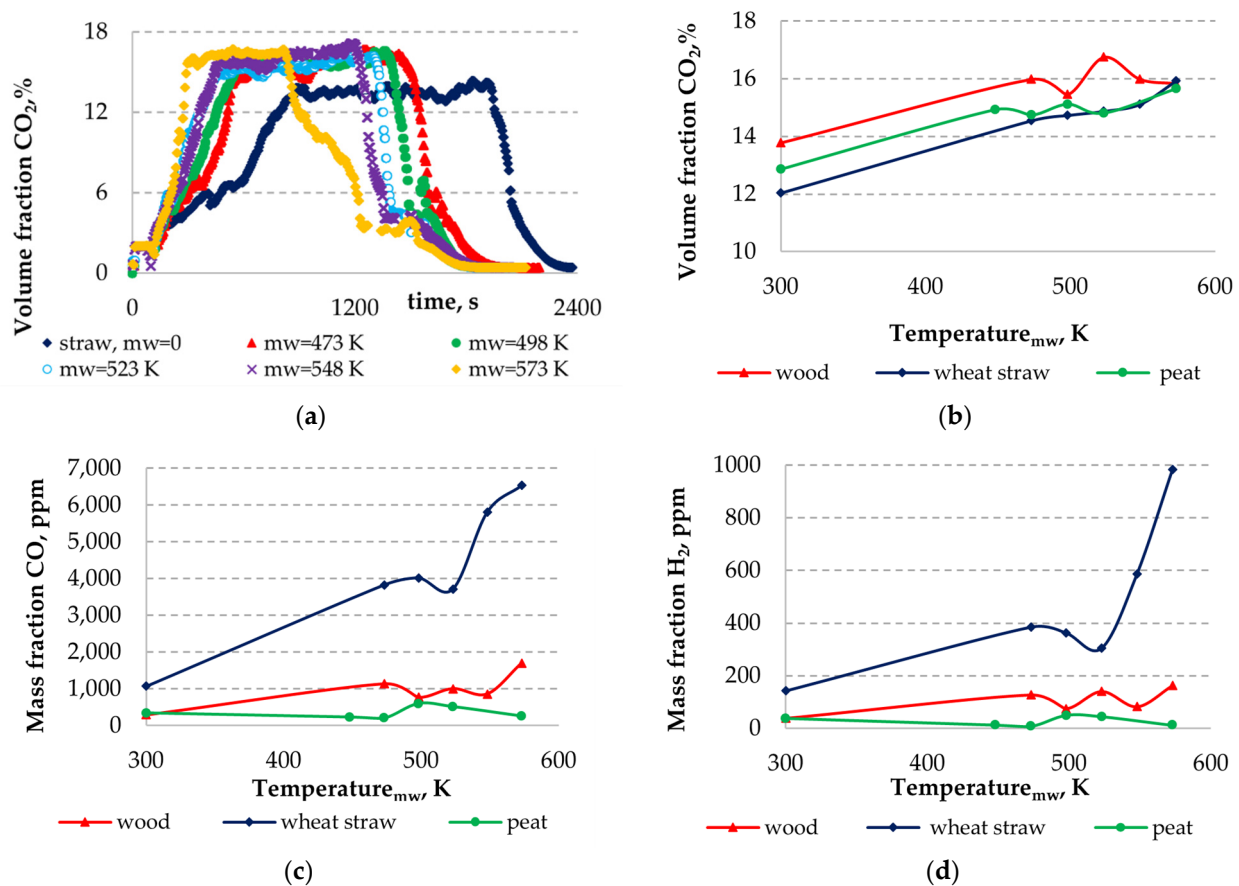


Figure 10. The effect of mw pretreatment on kinetics of the formation of CO₂ emission (a) and the average values of CO₂ (b), CO (c) and H₂ (d) in the products.

In addition, the higher weight loss of wheat straw pellets during their mw pretreatment, increasing the surface area, porosity and reactivity of pellets, resulted in a faster and more complete burnout of volatiles, with faster transition from flaming combustion to the surface reactions (3)–(5) and a pronounced decrease of the volume fraction of CO₂ emissions. At the same time, if the temperature of mw pretreatment was raised, an increase of the mass fraction of CO and H₂ in the products (Figure 10c,d) confirmed the development of endothermic surface reactions (4) and (5). For the pellets pretreated at a

higher temperature, the enhanced burnout of volatiles correlated with a decrease of the air excess ratio in the products (Figure 11a), increasing combustion efficiency (Figure 11b). In addition, as follows from Figure 11c, increasing the temperature of mw pretreatment resulted in a decrease of the NO_x emissions in the products, which could be related to the decrease of the flame temperature (Figure 8e), when carbonization of pellets contributes to the development of endothermic surface reactions (4) and (5) (Figure 11c).

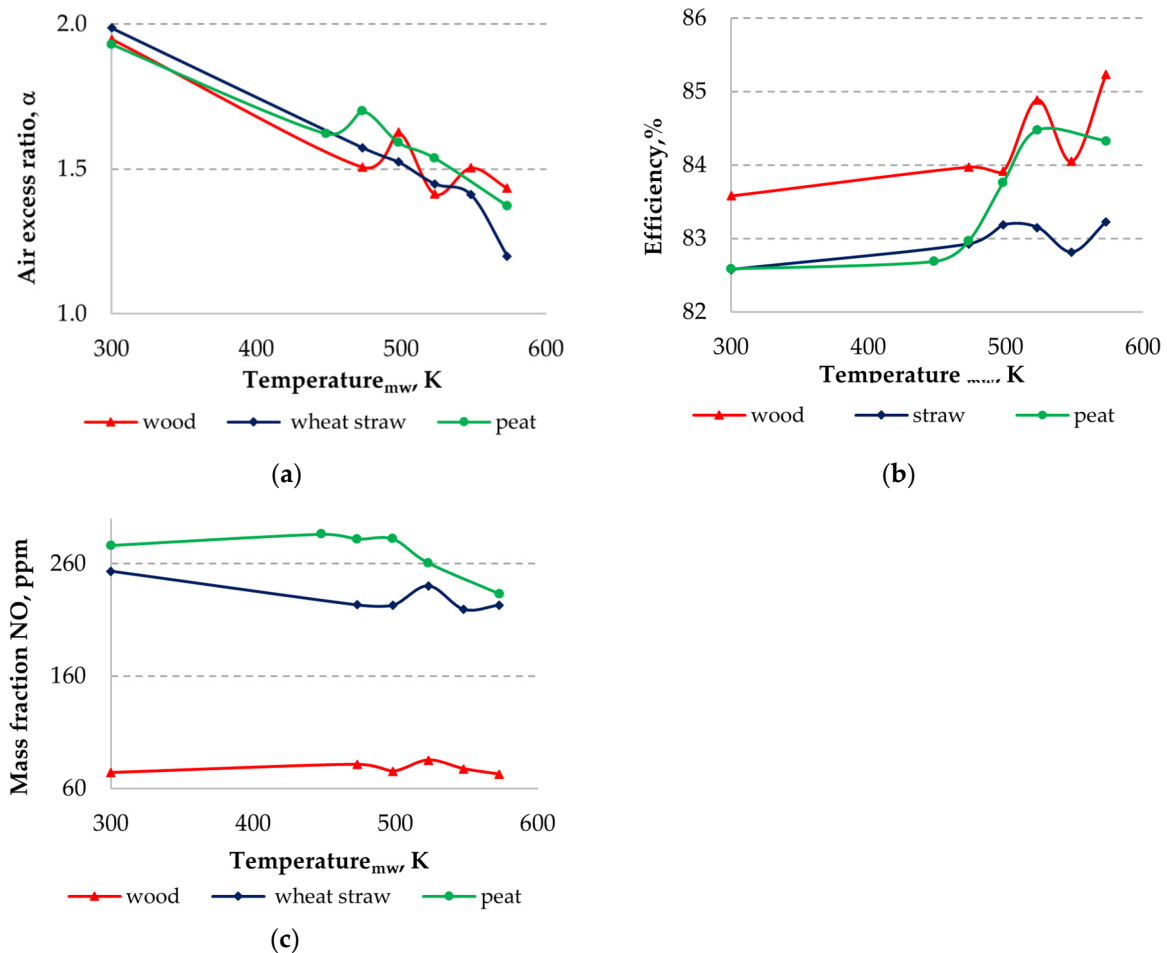


Figure 11. The effect of mw pretreatment on the average values of air excess ratio (a), combustion efficiency (b) and mass fraction of NO_x emissions (c).

4. Conclusions

From the experimental study of the effects of mw pretreatment of straw, wood and peat pellets by varying the temperature of mw pretreatment, the following conclusions can be made.

First, the mw pretreatment of pellets causes the thermal degradation of the main constituents (hemicelluloses, cellulose and lignin) of lignocellulosic pellets, increasing the weight loss of pellets, which depends on their elemental and chemical composition and can be expressed in the following order: straw > wood > peat. The weight loss of pellets causes a decrease in their mass density, with complex structural changes of the pellets, increasing the surface area, porosity, and reactivity of pellets, depending on the temperature of mw pretreatment. In addition, increasing the temperature of mw pretreatment causes variation of the elemental and chemical composition and heating value of pretreated pellets, enhancing their carbonization.

Second, the increased porosity and reactivity of mw pretreated pellets enhances their thermal decomposition during gasification of the pretreated pellets, increasing their weight

loss rate, with a faster yield of volatiles, and decreasing the duration of the thermal decomposition, with the highest weight loss for wheat straw (by about 53%), which has the highest content of hemicellulose in biomass. When increasing the temperature of mw pretreatment, the weight loss rate of pre-treated pellets and the yield of volatiles during thermal decomposition of pre-treated pellets depend on the development of competitive processes of partial thermal destruction of the main constituents of lignocellulosic pellets (hemicelluloses, cellulose and lignin) and the processes of their condensation, thus promoting the carbonization of pellets. As a result of these competitive processes, increasing the pretreatment temperature promotes an increase of the weight loss of pellets and the yield of CO₂ up to the peak values; these start to decrease at $T > 470\text{--}500\text{ K}$, when the carbonization of pretreated pellets enhances the development of endothermic reactions on the surface of carbonized pellets.

Third, the structural conversion of pretreated pellets, creating an increased reactivity, promotes faster ignition and burnout of volatiles, with a faster rise of the flame temperature and heat output from the device, up to their peak values, and a faster transition from the flaming combustion to the char conversion stage, with most pronounced decrease of duration of the thermochemical conversion being for wheat straw pellets. By analogy with the changes of the average values of the weight loss rate and the yield of volatiles, the average values of the flame temperature and heat capacity are influenced by transition from flaming combustion to development of endothermic reactions on the surface of carbonized pellets.

Finally, the mw pretreatment, producing structural changes and increased reactivity of pre-treated pellets, causes faster and more complete combustion of volatiles downstream the flame reaction zone, increasing the volume fraction of CO₂ in the products, and decreasing the air excess ratio in the products while increasing the combustion efficiency of pretreated pellets. An observed decrease in the flame temperature with an increase of the mass fraction CO and H₂ indicates the carbonization of pellets with development of endothermic surface reactions. In addition, a decrease in the flame temperature is responsible for a decrease in the mass fraction of NO_x emission. Hence, mw pretreatment of pellets can be used as an effective tool to control and improve the composition of combustion products.

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Abbreviations

E''	dielectric loss
E	EM field intensity, V/m
dm/dt	weight loss rate, g/s
dm/m_0	normalized weight loss
m_0	initial mass, g
m	current mass, g
m_f	final mass, g
α	degree of conversion
A	frequency factor, s^{-1}
E_a	activation energy, kJ/mol
R	gas constant, 8.3145 J/K mol
n	reaction order
$C(mw)/C(mw = 0)$	normalized carbon content
$H(mw)/H(mw = 0)$	normalized hydrogen content
$O(mw)/O(mw = 0)$	normalized oxygen content
$N(mw)/N(mw = 0)$	normalized nitrogen content
$Ash(mw)/Ash(mw = 0)$	normalized ash content
$HHV(mw)/HHV(mw = 0)$	normalized heating value
Temperature _{mw}	temperature mw pretreatment, K
Specific surface area	BET, m^2/g
Total pore values	mm^3/g
P	heat power, kW
Q	heat energy, MJ/kg
α	air excess ratio
T/T_0	normalized temperature

References

- Climate & Energy Framework. Available online: https://ec.europa.eu/clima/policies/strategies/2030_en (accessed on 1 October 2020).
- Huang, Y.-F.; Chiueh, P.-T.; Lo, S.-L. A review on microwave pyrolysis of lignocellulosic biomass. *Sustain. Environ. Res.* **2016**, *26*, 103–109. [[CrossRef](#)]
- Mitani, T. Recent Progress on Microwave Processing of Biomass for Bioenergy Production. *J. Jpn. Pet. Inst.* **2018**, *61*, 113–120. [[CrossRef](#)]
- Keshwani, D.R. Microwave Pretreatment of Switchgrass for Bioethanol Production. Ph.D. Thesis, North Carolina State University, Raleigh, NC, USA, February 2009.
- Lanigan, B. Microwave Processing of Lignocellulosic Biomass for Production of Fuels. Ph.D. Thesis, University of York, York, UK, 2010.
- Lanigan, B.; Budarin, V.; Clark, J.; Deswarte, F.; Shuttleworth, P.; Wilson, A. Microwave processing as a green and energy efficient technology of energy and chemicals from biomass and energy crops. *Asp. Appl. Biol.* **2008**, *90*, 277–282.
- Barmina, I.; Lickrastina, A.; Valdmanis, J.; Zake, M.; Arshanitsa, A.; Telysheva, G.; Solodovnik, V.; Valdmanis, R. Effect of Microwave Pre-Processing of Pelletized Biomass on its Gasification and Combustion/Mikroviļņu Priekšapstrādes Ietekme Uz Granulētas Biomasas Gazifikācijas Un Degšanas Procesiem. *Latv. J. Phys. Tech. Sci.* **2013**, *50*, 34–47. [[CrossRef](#)]
- Barmina, I.; Valdmanis, R.; Zake, M.; Arshanitsa, A.; Akishin, Y.; Telysheva, G. Combustion characteristics of modified plant biomass pellets. *Chem. Eng. Trans.* **2016**, *52*, 1111–1116.
- Li, H.; Qu, Y.; Yang, Y.; Chang, S.; Xu, J. Microwave irradiation—A green and efficient way to pretreat biomass. *Bioresour. Technol.* **2016**, *199*, 34–41. [[CrossRef](#)] [[PubMed](#)]
- Ethaib, S.; Omar, R.; Kamal, S.M.M.; Biak, D.R.A. Microwave-assisted pretreatment of lignocellulosic biomass: A review. *J. Eng. Sci. Technol.* **2015**, *10*, 97–109.
- Aguilar-Reynosa, A.; Romani, A.; Rodríguez-Jasso, R.M.; Aguilar, C.N.; Garrote, G.; Ruiz, H.A. Microwave heating processing as alternative of pretreatment in second-generation biorefinery: An overview. *Energy Convers. Manag.* **2017**, *136*, 50–65. [[CrossRef](#)]
- Ma, H.; Liu, W.-W.; Chen, X.; Wu, Y.-J.; Yu, Z.-L. Enhanced enzymatic saccharification of rice straw by microwave pretreatment. *Bioresour. Technol.* **2009**, *100*, 1279–1284. [[CrossRef](#)] [[PubMed](#)]
- Xu, J.; Chen, H.; Kádár, Z.; Thomsen, A.B.; Schmidt, J.E.; Peng, H. Optimization of microwave pretreatment on wheat straw for ethanol production. *Biomass Bioenergy* **2011**, *35*, 3859–3864. [[CrossRef](#)]
- Lu, X.; Xi, B.; Zhang, Y.; Angelidaki, I. Microwave pretreatment of rape straw for bioethanol production: Focus on energy efficiency. *Bioresour. Technol.* **2011**, *102*, 7937–7940. [[CrossRef](#)]

15. Pang, F.; Xue, S.; Yu, S.; Zhang, C.; Li, B.; Kang, Y. Effects of microwave power and microwave irradiation time on pretreatment efficiency and characteristics of corn stover using combination of steam explosion and microwave irradiation (SE–MI) pretreatment. *Bioresour. Technol.* **2012**, *118*, 111–119. [[CrossRef](#)]
16. Barmina, I.; Kolmickovs, A.; Valdmanis, R.; Vostrikovs, S.; Zake, M. Thermo-Chemical Conversion of Microwave Activated Biomass Mixtures. *IOP Conf. Ser. Mater. Sci. Eng.* **2018**, *355*, 012018. [[CrossRef](#)]
17. Arshanitsa, A.; Akishin, Y.; Zile, E.; Dizhbite, T.; Solodovnik, V.; Telysheva, G. Microwave treatment combined with conventional heating of plant biomass pellets in a rotated reactor as a high rate process for solid biofuel manufacture. *Renew. Energy* **2016**, *91*, 386–396. [[CrossRef](#)]
18. Barmina, I.; Kolmickovs, A.; Valdmanis, R.; Zake, M.; Vostrikovs, S.; Kalis, H.; Strautins, U. Electric Field Effect on the Thermal Decomposition and Co-combustion of Straw with Solid Fuel Pellets. *Energies* **2019**, *12*, 1522. [[CrossRef](#)]
19. Larina, O.M.; Sinelshchikov, V.A.; Sytchev, G.A. Comparison of thermal conversion methods of different biomass types into gaseous fuel. *J. Phys. Conf. Ser.* **2016**, *774*, 012137. [[CrossRef](#)]
20. Yang, H.; Yan, R.; Chen, H.; Lee, D.H.; Zheng, C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* **2007**, *86*, 1781–1788. [[CrossRef](#)]
21. Robus, C.L.; Gottumukkala, L.D.; Van Rensburg, E.; Görgens, J.F. Feasible process development and techno-economic evaluation of paper sludge to bioethanol conversion: South African paper mills scenario. *Renew. Energy* **2016**, *92*, 333–345. [[CrossRef](#)]
22. Deineko, I.P. The chemical conversion of cellulose by pyrolysis. *Forest J.* **2004**, *4*, 97–112. (In Russian)
23. Diblasi, C. Modeling chemical and physical processes of wood and biomass pyrolysis. *Prog. Energy Combust. Sci.* **2008**, *34*, 47–90. [[CrossRef](#)]
24. Sutton, R.; Sposito, G. Molecular Structure in Soil Humic Substances: The New View. *Environ. Sci. Technol.* **2005**, *39*, 9009–9015. [[CrossRef](#)]