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The Effect of Microwave Pre-processing of Straw Pellets on the Thermal Decomposition of Biomass Mixtures

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Thermal decomposition of biomass mixtures has been experimentally studied to assess the potential for more intensive use of local bioenergy resources (straw) in heat production by co-firing straw with wood or peat pellets and for process control using microwave (MW) pre-treatment of straw pellets. It was found that microwave pre-treatment of straw pellets provides modification of their structure, elemental and chemical composition, increases the porosity of pellets and the heating values of the pellets with partial decomposition of the main components of lignocellulosic pellets, i.e., hemicelluloses, cellulose and lignin. Besides, microwave pre-treatment of straw pellets activates the thermal interaction between the activated pellets of straw and unpre-treated pellets of the mixture that results in faster thermal decomposition and faster release of combustible volatiles (CO, H_2, C_xH_y). The time required for thermal decomposition of biomass mixtures decreases by about 300 s, the average weight loss rate of activated mixtures increases by about 17-20 %, increasing the yield of combustible volatiles by about 24 %.

1. Introduction

The experimental studies summarized in the article have been performed in accordance with EU green energy strategy, which sets a target to develop climate-neutral economy by 2050 with net-zero greenhouse gas emissions. The energy must be produced by limiting the use of fossil fuel (natural gas, oil, coal) for energy production, with increasing use of renewable energy sources and energy efficiency by at least 20-27 % and reducing domestic GHG by 25 % in 2020, by 40 % in 2030 and by 60 % in 2040 with reference to 1990 levels. To meet these goals, the use of different types of lignocellulosic biomass (harvesting and agriculture residues) as an alternative to fossil fuels for transport and energy production must be increased in the coming years. The rapidly growing consumption of harvesting residues for residential heating is driving a growing demand for a wider use of alternative biofuels, i.e. agriculture residues (wheat straw or rape straw pellets) which are problematic fuels for energy producers because of the lower heating value and higher nitrogen and ash contents if compared with wood pellets which have a negative impact on the environment and make it difficult to maintain heat devices, which limits the use of straw for energy production. Besides, the different elemental and chemical composition of wood and straw (Vassilev et al., 2010) determines different rates of their thermal decomposition (Burhenne et al., 2013) and different yield of combustible volatiles (Yang et al., 2007). Therefore, it is necessary to take additional actions to ensure the wider applicability of straw as a fuel for energy production. One of the most effective ways to reduce the negative impact of straw on heat production is to advance combustion and heat production processes by co-firing of straw with solid fuels of different origin (Nussbaumer, 2003), such as coal (Larina et al., 2020) or wood (Barmina et al., 2016), when the thermal interaction between the components results in an enhanced thermal decomposition of mixtures. To additionally improve and control the thermal decomposition of biofuel mixtures, microwave (mw) treatment of straw pellets is suggested which can cause changes of the chemical composition of lignocellulosic biomass (Lanigan, 2010), of the structure and elemental composition of pellets (Arshanitsa et al., 2016). As a result, mw pre-processing of lignocellulosic biomass can boost the char reactivity of pre-treated biomass pellets enhancing the rate of reactions (Mitani, 2018) and providing a higher yield of volatiles (H_2, CO, CH_4, CO_2) during thermal decomposition of the mixtures (Huang et al., 2016). The reactivity of straw pellets after mw pre-treatment is dependent on mw pre-processing conditions, such as the irradiation time and the temperature of

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mw pre-treatment with direct influence on the thermal decomposition of biomass mixtures, which can be varied by varying the mass load of activated straw in the mixture and which is strongly influenced by the elemental and chemical composition of raw pellets. Therefore, to effectively improve and control the thermal decomposition of biomass mixtures, the optimal pre-treatment regimes, and optimal mass load of microwave pre-treated straw in a mixture should be estimated for different types of raw pellets. In this regard, the main goal of this research is a comprehensive experimental study of the processes developing during co-firing microwave pre-treated straw with raw straw, wood or peat pellets, in order to assess optimal mw pre-treatment regimes and optimal composition of activated mixtures to ensure effective control of the thermal decomposition.

2. Experimental

The influence of microwave pre-treatment of straw pellets on the thermal decomposition of mixtures of microwave (MW) pre-treated straw with raw pellets (straw, wood or peat) was studied using a device combining a batch-size biomass gasification reactor and a combustor. The gasification reactor was filled with a mixture of biomass pellets, with the mass load of the MW pre-treated straw in the mixtures varied from 0 up to 100 %. The thermal decomposition of the mixture in the reactor was initiated by a propane flame flow with the average heat input 1 kW and 400 s duration. The straw pellets were mw pre-treated using a microwave oven with the 700 W mw-power by varying the duration of MW pre-treatment in the 60-220 s range and the temperature of pellets in the 300- 540 K range. The thermal decomposition of the mixtures was studied experimentally at the average air excess ratio in the reactor α = 0.4-0.5. The experimental study of the effect of mw pre-processing of straw pellets on the thermal decomposition of mixtures involved measurements of the mixture weight loss rate (dm/dt) and yield of volatiles (CO, H_2, CO_2) by varying the pre-treatment regimes for straw pellets and the mass load of pre-treated straw in the mixture using the methodology described in (Barmina et al., 2016). Changes in the temperature of wheat straw pellets during MW pre-treatment were measured using ScanTemp pyrometer. The effect of mw pre-treatment on the elemental composition of wheat straw pellets was measured using a Vario MACRO elemental analyzer with estimation of HHV of wheat straw pellets using a regression equation and the data of elemental composition (Arshanitsa et al., 2016).

3. Results and discussion

The experimental studies of the effect of mw pre-treatment of wheat straw pellets on the thermal decomposition of mixtures of MW pre-treated wheat straw with raw biomass pellets of different origins (wheat straw, wood, peat) included the primary stage of MW pre-treatment of straw pellets under different pellet MW pre-treatment regimes. As a result of MW pre-treatment, a partial thermal decomposition of lignocellulosic straw pellets occurred, which intensified the release of moisture and volatile compounds with subsequent changes in the chemical composition, structure and reactivity (R_{ws}, s^{-1}) of the pre-treated wheat straw pellets, which can be expressed in terms of the conversion rate dm/dt per remaining mass m_t (Di Blasi et al., 2006):

$$R_{ws} = \frac{1}{m_t} * \frac{dm}{dt} = \frac{1}{m_t} * (k_0 * exp^{-E_a/RT_{ws}}) * \frac{(m_t - m_{ash})}{(m_0 - m_{ash})} \quad (1)$$

where k_0 is the pre-exponential factor (s^{-1}), E_a is the activation energy (kJ/mol) of the thermal destruction of wheat straw pellets, (T_{ws}, K) is the temperature of pellets, R = 8.314 $JK^{-1}mol^{-1}$ is the universal gas constant, m_t is the biomass weight measured as a function of the time, m_0 is the initial weight of wheat straw pellets, m_{ash} is the weight of ash residues.

Test experiments on the wheat straw thermal decomposition after microwave pre-treatment were carried out for portions of 120 g with increase in the duration of pellets mw irradiation from 60 s up to 220 s and increasing temperature of the pellets to about 530-540 K. Under the given conditions of mw pre-treatment, wheat straw pellets underwent complex structural changes, which increased the surface volume (Huang et al., 2016) and porosity (Fatehi, 2014) of the pellets and changed their elemental and chemical composition (Lanigan, 2010), with the partial thermal decomposition of hemicellulose, cellulose and lignin. In accordance with analysis of the literature data (Yang et al., 2007) hemicellulose and cellulose decomposed at about 500–590 K and 590-670 K, respectively, with a maximum mass loss rate at about 540 K and 630 K, whereas the thermal decomposition of lignin occurred in a wide temperature range from 440 K to 1170 K. Measurements of weight loss of wheat straw pellets by increasing the duration of MW pre-treatment allow conclude that the general trend of the mw treatment of wheat straw pellets was an increase of the weight loss (dm, g), which decreased the mass density of the pellets by 20-24 %, while increasing the reactivity (R = 1/m*dm/dt, ms^{-1}) of the processed pellets (Figure 1a). Besides, the carbon content in the wheat straw pellets during their mw pre-processing can be increased from 46.43 % for raw pellets to about 50 % for MW pre-treated pellets with the correlating increase of the heating value (HHV) from 18.4 MJ/kg to about 20 MJ/kg (Figure 1a).

The next stage of the experimental study was the evaluation of the influence of mw pre-treatment of wheat straw pellets on the weight loss rates and on the yield of volatile compounds (CO, H_2, CO_2) during the thermal decomposition of the MW pre-treated mixtures containing MW pre-treated and raw wheat straw, wood, or peat pellets. Considering the effect of MW pre-treatment on the reactivity and heating value of wheat straw pellets it was assumed that the increase of the reactivity and heating value of wheat straw pellets could be used to enhance the thermal decomposition of mixtures and the yield of volatile compounds. To verify this assumption, kinetics studies of the thermal decomposition and yield of volatiles were performed, in order to compare the development of these processes for raw wheat straw pellets and for mixtures of MW pre-treated straw pellets (25 % by weight) with raw straw pellets. The test experiments showed that the increased reactivity and heating value of wheat straw pellets determined by their mw pre-treatment assured a faster yield of volatiles along with a decrease in the duration of the mixture thermal decomposition (Figure 1b-d).

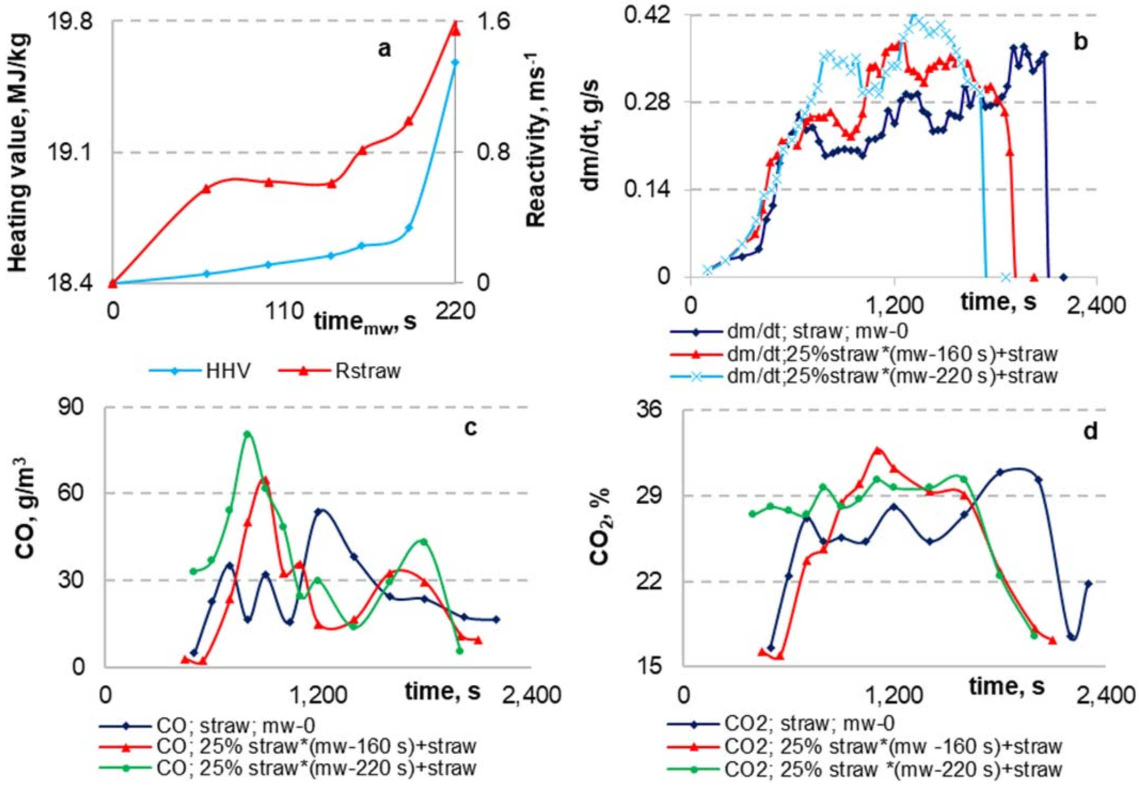

Figure 1: Effect of the duration of wheat straw pellets mw irradiation on (a) the heating value and reactivity of straw pellets; (b) on the weight loss rate, and (c, d) on the yield of volatiles during thermal decomposition of a mixture of MW pre-treated and raw straw pellets

By increasing the irradiation time of the wheat straw pellets MW pre-treatment up to 220 s, the weight loss rate during the thermal decomposition of a mixture of MW pre-treated and raw wheat straw pellets (25 % straw*+straw) can be increased from 0.248 g/s for raw straw pellets to 0.282 g/s (by about 14 %), decreasing so the duration of the thermal decomposition by about 430 s. The average value of the CO yield under the given conditions of thermal decomposition can be increased from 25 g/m^3 to 41 g/m^3, the CO_2 yield increases from 25 to 28 %, whereas the yield of H_2 increases from 0.45 g/m^3 to 1.22 g/m^3.

A kinetic study of the thermal decomposition of raw straw pellets has shown that, up to 1,000 s, the increase in the weight loss rate correlates with the increase in the yield of volatile compounds (Figure 1b-c), determining the formation of individual peaks of the time-dependent variations of the weight loss rate and yield of volatiles (Figure 1b, c), which in accordance with data (Yang et al., 2007) can be related to the thermal decomposition of hemicelluloses, cellulose and lignin. A kinetic study of the activated mixture (25 % straw*+straw) allows to conclude that the thermal decomposition of the mixture and the yield of volatiles are influenced by the variations of the irradiation time and temperature of pre-treated wheat straw pellets (Figure 1b-d). Increasing the mw irradiation time of wheat straw pellets up to 220 s and temperature of pellets up to 530-540 K results in a faster and enhanced thermal decomposition of the mixture with a faster and intense formation of volatiles

(CO, H_2, CO_2), which increases the peak values of the yield of combustible volatiles (CO, H_2) by overlapping individual peaks in the kinetics of the volatiles' formation and determines the formation of a single peak at t ≈ 800-900 s. It should be noted that the enhanced yield of combustible volatiles at the primary stage of the thermal decomposition of the mixture of MW pre-treated and raw pellets can be predominately related to the increase of the heating value and reactivity of the MW pre-treated wheat straw pellets, which enhances the thermal interaction between the mixture components and increases the rate of their thermal decomposition (Yang et al., 2007). As follows from Figure 1c, d, the enhanced release of CO at the primary stage of thermal decomposition during the gasification of the mixture correlates with the much slower rise of the CO_2 yield. This confirms that the fuel-rich conditions at the primary stage of gasification restrict the thermochemical conversion of combustible volatiles and the yield of CO_2 and can be related to the thermal decomposition of hemicelluloses (Yang et al., 2007). In addition, the weight loss rate of the activated straw mixture is influenced by the variations of the mixture composition, i.e., increasing the mass fraction of MW pre-treated wheat straw pellets in the mixture up to 80 % results in an increase of the heating value of the mixture and improves the thermal interaction between the MW pre-treated and the raw straw pellets. As a result, the average weight loss rate of the mixture increases along with the dominant increase of dm/dt (from 0.11 to 0.19 g/s) during the primary stage of the thermal decomposition (t < 1,000 s) when hemicellulose, cellulose and lignin decompose with the correlating increase of the yield of combustible volatiles (CO, H_2). The yield of CO increases from 19.5 g/cm^3 to 27.8 g/cm^3, the yield of H_2 increases from 0.31 to 0.5 g/cm^3, whereas the yield of CO_2 increases from 25.5 % to 27.14 %.

As follows from Figure 1c, the yield of CO_2 starts to decrease during the next stage of the thermal decomposition of the activated mixture (t > 1,100 s) when the carbonization of wheat straw pellets (Barmina et al., 2013) advances the endothermic char gasification reactions ($C + CO_2 \rightarrow 2CO$) which control the rate of the thermal decomposition of the mixture and the yield of volatiles. As a result, the yield of CO_2 decreases, whereas the yield of CO and H_2 slightly increases with the formation of a secondary peak at t ≈ 1,600 s. Finally, the fast decrease of the weight loss rate of the mixture with the correlating decrease of the yield of volatiles at t > 1,800 s determines the end stage of the mixture gasification.

Changes in the heating value and reactivity after MW pre-treatment of wheat straw pellets also affect the weight loss rate and the yield of volatiles during the thermal decomposition of the mixture of pre-treated wheat straw with wood pellets (straw*+wood). Wood pellets have a higher heating value (19.71 MJ/kg) (Barmina et al., 2013) and a higher volume fraction of combustible volatiles (CO - 0.28 %, H_2 - 0.26 %, CH_x - 16 %) (Larina et al., 2016) if compared with straw pellets (CO - 0.23 %, H_2 - 0.19 %, CH_x - 13 %). The preliminary study of the effect of wheat straw co-firing with wood pellets on the mixture thermal decomposition allows to conclude (Barmina et al, 2016) that co-firing of raw wheat straw pellets with wood pellets leads to a slight increase of the weight loss of the mixture up to the peak value if the mass fraction of straw pellets is about 25-30 %, and it starts to decrease, when the mass fraction of straw pellets is above 30 % with a correlating decrease of the mixture heating value. The pronounced increase of the weight loss rate and yield of volatiles during the thermal decomposition of the mixture of MW pre-treated wheat straw with raw wood pellets (25 % straw*+wood) was found when increasing the irradiation time for straw pellets up to 220 s (Figure 2a, b), when the temperature of wheat straw pellets reached 530 – 540 K. In this case, the heating value of the pre-treated wheat straw pellets increased to about 19-20 MJ/kg, which becomes comparable with the HHV of raw wood pellets (19.71 MJ/kg). Hence, the MW pre-treatment of straw pellets makes it possible to minimize the negative effect of straw pellets on the heating value of the mixture as it was observed when co-firing raw straw and wood pellets. Moreover, the enhanced reactivity of straw pellets results in a faster formation of volatiles, which decreases the duration of the thermal decomposition of the mixture by about 500 s. By analogy with the thermal decomposition of the mixtures of MW pre-treated and raw pellets (straw*+straw), the dominant increase of the weight loss rate from 0.22 g/s to 0.29 g/s, the yield of CO from 16 g/cm^3 to 30 g/cm^3 and that of H_2 from 0.3 g/cm^3 to 0.52 g/cm^3 was observed at the primary stage of thermal decomposition (t < 1000 s). During this stage of the thermal decomposition of the mixture (25 % straw*+wood), MW pre-treatment of straw pellets enhanced the thermal interaction between the components along with the accelerated decomposition of hemicellulose, cellulose and lignin responsible for the formation of two individual peaks in the yield of CO, H_2 and CO_2 at about 600 s and 900 s. The enhanced and lasting yield of CO (Figure 2b), along with the reduced yield of CO_2, was observed at the next stage of the mixture thermal decomposition (1200 s -1600 s), which indicated much slower variations of the CO_2 yield. This suggests a faster decomposition of hemicelluloses at the primary stage of thermal decomposition with a longer thermal decomposition of cellulose.

The enhanced thermal decomposition of the mixture (straw*+wood pellets) was observed increasing the mass fraction of the pre-treated straw pellets in the mixture up to 80% when the average weight loss rate of the mixture increased from 0.29 g/s to 0.36 g/s (by about 24 %), the average CO yield increased from 14.7 g/cm^3 to 30.3 g/cm^3, the yield of H_2 from 0.2 g/cm^3 to 0.6 g/cm^3 and the yield of CO_2 decreased from 25 % to 21 %.

In addition, the peak value of the CO yield with the 45 % mass fraction of pre-treated wheat straw pellets correlates with the minimum value of the weight loss rate, which suggests the enhanced endothermic decomposition of cellulose.

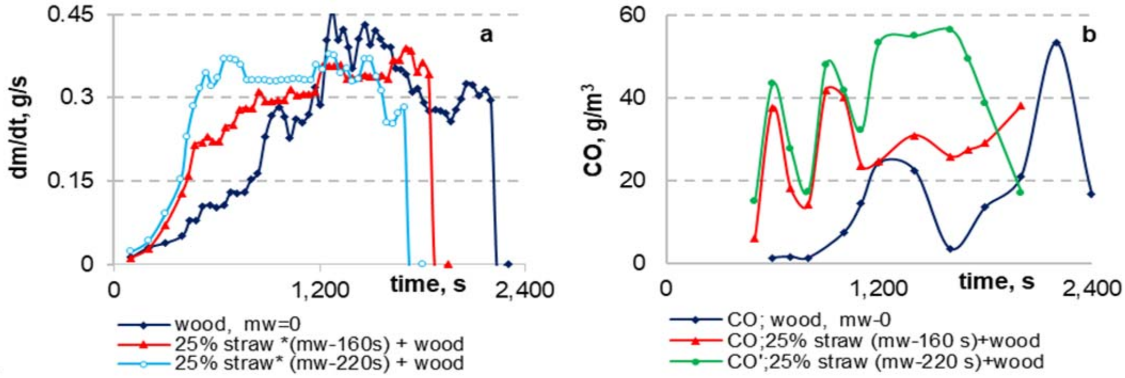

Figure 2: Effect of the increasing irradiation time for wheat straw pellets on the weight loss during the thermal decomposition of the 25 % straw (MW)+wood mixture (a) and on the yield of CO (b)*

The pronounced variations of the weight loss rate and yield of volatiles were observed also for the mixtures of MW pre-treated wheat straw mixtures with raw peat pellets (straw*+peat), when the increased duration of the straw pellet microwave pre-treatment resulted in a faster thermal decomposition of the mixture with a faster and enhanced yield of volatiles (Figure 3a, b).

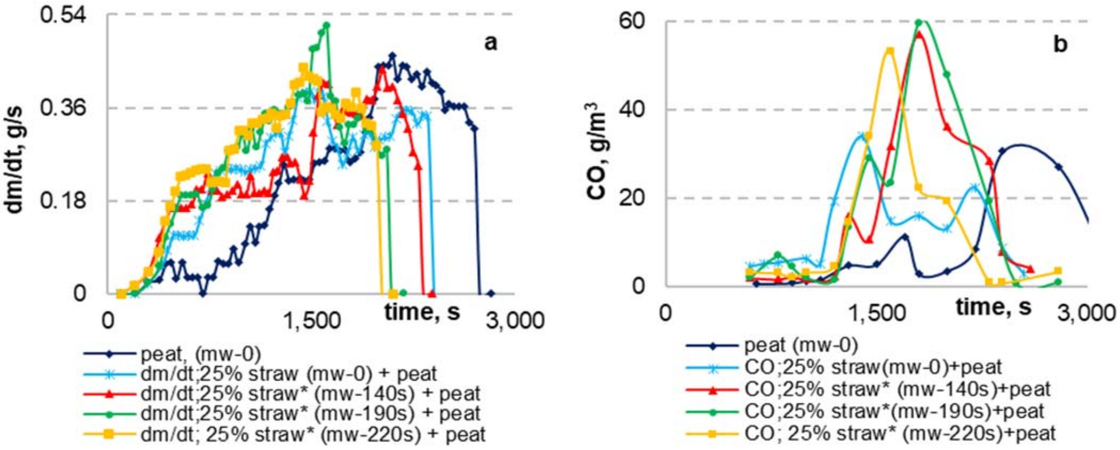

Figure 3: Effect of the increasing irradiation time for wheat straw pellets on the weight loss at the thermal decomposition of the 25% straw (MW)+peat mixture (a) and on the yield of CO (b)*

It should be noted that raw peat pellets have a higher heating value (HHV = 20.86 MJ/kg), a higher carbon content (C = 52.81 %), and lower contents of volatiles (VC = 64.1 %), if compared with wheat straw pellets which have HHV = 18.41 MJ/kg, C = 46.43 % and VC = 79.1 % (Larina et al., 2016). Therefore, to enhance the thermal decomposition of the straw*+peat mixture, the irradiation time for straw pellets must be increased up to 220 s (Figure 3a) when the temperature of pellets reaches 540 K, whereas the HHV of straw pellets reaches 20 MJ/kg. With the fixed mass fraction of pre-treated wheat straw pellets in the mixture (25 %), the longer mw pre-treatment of straw pellets up to 220 s results in an increase in the average value of the weight loss rate of the activated mixture from 0.265 g/s to 0.37 g/s (by about 39 %), the average yield of CO increases from 12.5 g/m^3 to 16.3 g/m^3 (by about 30 %), with a peak value of the CO yield at 140-190 s of straw pre-treatment; the yield of H_2 increases from 0.25 g/m^3 to 0.36 g/m^3 (by about 43 %), whereas the yield of CO_2 slightly (by about 0.8 %) decreases. Moreover, when increasing the irradiation time for wheat straw pellets up to 220 s, the duration of the thermal decomposition of the activated mixture decreases by about 700 s. When increasing the mass fraction of pre-treated wheat straw pellets in the mixture from 15 % to 80 %, the average weight loss rate of the mixture increases from 0.26 g/s to 0.36 g/s, which increases the CO yield from 15 g/m^3 to 19.76 g/m^3 and that of H_2 from 0.2 g/m^3 to 0.29 g/m^3. The yield of CO and H_2 for raw peat and for a mixture of raw straw pellets with peat pellets indicates the formation of two individual peaks at t ≈ 2,400 s and t

≈ 1,400 s, respectively. The enhanced thermal decomposition of hemicellulose accompanied by the formation of the peak value of the CO_2 yield was observed at the primary stage of the thermal decomposition of the activated mixture (t = 1,000 s) which starts to decrease during the next stage of thermal decomposition when the thermal decomposition of cellulose dominates increasing the yield of CO.

4. Conclusions

In the experimental study, it has been found that the MW pre-treatment of wheat straw pellets results in complex variations of their structure, elemental and chemical composition. As the irradiation time of pellets increases, the weight loss, the heating value and the reactivity of pellets also increase.

The enhanced reactivity of wheat straw pellets is responsible for faster thermal decomposition of activated mixtures which decreases the duration of the mixture thermal decomposition by about 400-700 s. When increasing the irradiation time of pellets up to 220 s, the weight loss of the mixtures can be increased by about 18-40 % with a correlating increase of the yield of combustible volatiles (CO, H_2) at the primary stage of thermal decomposition when the thermal decomposition of hemicelluloses, cellulose and lignin dominates. The increased heating value and reactivity of wheat straw pellets are responsible for the enhanced thermal decomposition of the mixtures of MW pre-treated wheat straw pellets with raw pellets of straw, wood, or peat, which increases the peak and average values of the yield of volatiles. In general, the MW pre-treated wheat straw pellets serve as a heat source, which enhances the thermal decomposition of the mixture.

Thus, the results of the experimental study show that MW pre-treatment of wheat straw pellets can be used as a tool to provide effective control of the thermal decomposition of mixtures with beneficial use of straw as a fuel for energy production.

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