CHEMICAL ENGINEERING TRANSACTIONS

VOL. 86, 2021

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Sauro Pierucci, Jiří Jaromír Klemeš

ISBN 978-88-95608-84-6; **ISSN** 2283-9216

DOI: 10.3303/CET2186247

Thermochemical Conversion of Microwave Pre-treated Biomass Pellets: Combustion of Activated Pellets

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Studies were carried out to evaluate the influence of microwave (MW) pre-treatment of different lignocellulosic biomass pellets (wood, wheat straw and peat) on the development of combustion characteristics of pre-treated pellets. Biomass pellets were MW pretreated using a 700 W power microwave oven by varying the MW irradiation time of biomass pellets along with estimation of the effect of MW pre-treatment on the development of flow dynamics, flame temperature, produced heat energy and composition of emissions. Experimental studies were conducted using a laboratory-scale setup with 5 kW power, which combines a biomass gasifier and a combustor. Results of the complex research show that the MW pre-pretreatment of biomass pellets activates the formation of combustible volatiles intensifying their ignition and combustion, increasing thus the generated heat power and the produced heat energy per mass of activated pellets. A noteworthy result is that the combustion efficiency and the composition of emissions are improved.

1. Introduction

In accordance with the EU long-term strategy in the field of energy and environmental protection, which sets a target to develop climate-neutral economy by 2050 with net-zero greenhouse gas emissions, the energy must be produced by increasing the use of renewable energy sources and energy efficiency by at least 20-27 % while reducing domestic GHG by 25 % in 2020, by 40 % in 2030 and by 60 % in 2040 with reference to 1990 levels. To develop climate-neutral economy, many lignocellulosic feedstocks, such as agricultural and forest residues and waste biomass are available to produce heat or electricity. Recently, the most widely used source of bioenergy for residential heating is woody biomass, whereas the rapidly increasing demand for wood pellets causes a significant shortage of raw materials. Therefore, an alternative raw biomass feedstock for pellet production, such as wheat straw (Jandačka et al., 2012) and peat biomass (Olsson, 2011) is of great interest. At the same time, it must be admitted that the use of these alternative lignocellulosic biomass feedstocks for energy production is limited because of the difference in their calorific value, moisture, nitrogen and ash content in raw biomass (Vasilev et al., 2010), resulting in the formation of harmful emissions during combustion. Besides, the efficient use of this feedstock for energy production is also limited because of the dissimilarity in the structure, content of hemicelluloses, cellulose and lignin in raw biomass determining different rates of thermal decomposition (Gani et al., 2007) and different yield of volatile substances by varying the balance between endothermic and exothermic effects during the thermal decomposition of the lignocellulosic biomass (Yang et al., 2007) leading to an unstable and unpredictable combustion process. To stabilize the processes of biomass combustion and heat production, biomass is briquetted or granulated and torrefied to produce biofuels with greater energy density and calorific value. In addition, to ensure the development of a more stable and cleaner combustion process by expanding the possibilities of using alternative biomass feedstock for heat production, co-firing of biomass pellets with crushed coal (Larina et al., 2020) and co-firing of straw pellets with wood or peat pellets (Barmina et al., 2018) was proposed. Torrefaction as a way of biomass treatment is known (Brachi et al. 2018) but to additionally control the process and improve the combustion characteristics, when different types of biomass pellets as fuels are used, microwave (2.45 GHz) pre-treatment of pellets is recommended (Barmina et al., 2013), which activates the thermal decomposition of hemicellulose, cellulose and lignin (Lanigan, 2010) and allows to control and

Paper Received: 27 August 2020; Revised: 28 February 2021; Accepted: 4 April 2021
Please cite this article as: Barmina I., Valdmanis R., Zake M., 2021, Thermochemical Conversion of Microwave Pre-treated Biomass Pellets: Combustion of Activated Pellets, Chemical Engineering Transactions, 86, 1477-1482 DOI:10.3303/CET2186247

stabilize the combustion conditions and the composition of emissions which depend on the MW pre-treatment regime of pellets, i.e. the duration and the temperature of MW pre-treatment. Thus, the discussed experimental study is aimed at assessing the main factors influencing the development of the main characteristics of combustion and the composition of emissions when using mw pre-treatment of pellets to ensure effective control of the process.

2. Experimental equipment and measurement methodology

The effects of MW pre-processing of different biomass pellets (straw, wood, peat) on the development of combustion dynamics and on the composition of emission were studied using an experimental setup which combines a batch-size gasifier and combustor. The fixed bed gasifier is filled with 340-560 g pre-treated pellets and ensures their thermal decomposition, the formation of combustible volatiles (CO, H_2) and supply of volatile compounds into the combustor, whereas the combustor provides complete combustion of the volatile compounds. Thermo-chemical conversion of the activated pellets was initiated providing additional heat supply by a propane flame to the top layer of the pellets with the average heat input 1 kW during 400 s. To support the thermal decomposition of the activated pellets, primary air was supplied below the layer of the MW pre-treated pellets at the average rate 0.6 g/s, determining so the development of the fuel-rich condition during the pellets' gasification. Secondary swirling air was supplied to the flame base at the average rate 0.8 g/s, determining the average air excess ratio (α) in the flame reaction zone ranging from $\alpha \approx 1$ to $\alpha \approx 1.6$. Straw pellets were MW pre-processed in a conventional 700 W microwave power oven by varying the duration of MW-pre-processing in the 0 – 300 s range.

The experimental study includes time-dependent measurements of the following parameters: flame temperature (T), heat output from the setup (P, kW), produced heat energy per mass of burned pellets (Q, MJ/kg), composition of emissions and combustion efficiency; all data were recorded once per second.

The composition of the products (the mass fraction of CO, H_2, NO, NO_x with an accuracy of ± 0.5 % and the volume fraction of O_2 and CO_2 with an accuracy of ± 1 %), the combustion efficiency and the air excess ratio were measured online using a gas sampling probe and a Testo 350 gas analyzer.

The calorimetric measurements of the heat output involve the joint measurements of the cooling water mass flow for each water-cooled section of the setup measured with the accuracy ± 2.5 % and of the temperature at the inlet and outlet of the water-cooled sections with the accuracy ± 1 % by AD 590 thermo sensors, along with online data recording by the Data Translation DT9805 data acquisition module and Quick DAQ program.

3. Results and discussion

3.1. The effect of MW pre-treatment of pellets on the dynamics of the flame temperature.

To evaluate the effect of MW pre-treatment on the thermo-chemical conversion of biomass pellets of different origin, the flame temperature dynamics was studied by varying the MW pre-treatment duration (Figure 1a-d). The studies have confirmed that the MW pre-treatment of biomass pellets changes their structure and elemental composition, increasing thus the reactivity and HHV of the MW pre-treated pellets and activating the process of thermal decomposition along with a faster and enhanced yield of volatile compounds. As a result, the air-to-fuel ratio at the flame base decreases improving so the combustion conditions with a faster ignition and a more complete burnout of volatiles. When evaluating the effect of the MW pre-treatment duration on the temperature dynamics for different biomass pellets, the most pronounced changes in temperature dynamics was found for straw pellets which have the highest content of hemicelluloses (≈ 28 %) in biomass (Barmina et al., 2013) and the highest weight loss of pellets during MW pre-treatment (≈ 26 %), which increased the reactivity of the pre-treated pellets and activated their thermal decomposition. The flame temperature changes during the thermo-chemical conversion of pre-treated pellets showed that increasing the irradiation time of wheat straw pellets led to a decrease of the duration of the burnout of pre-treated pellets by ~ 40 %, whereas the peak (~ 13.8 %) and average values (~ 10.5 %) of the flame temperature (Figure 1b, d) increased. Less pronounced changes in temperature kinetics were observed for peat pellets with the lowest hemicellulose content (Olsson, 2011) in biomass (~ 13-22%) along with smaller changes in the weight loss during the MW pre-treatment of pellets (by ~ 11 %). The duration of the burnout of pre-treated peat pellets decreases by ~ 4 %, whereas the peak (~ 12.5 %) and average values (~ 8 %) of the temperature increased (Figure 1c). As it follows from Figure 1d, with increasing duration of MW pre-treatment, the average values of the temperature gradually increase up to the peak values and then start to decrease when the irradiation time of pellets exceeds 160-190 s. The behavior of the flame temperature demonstrates that the average value of the flame temperature is affected by a gradual transition from flaming combustion of volatiles to after-flame low temperature smoldering of carbonized residues which develops on the surface of carbonized residues.

The transition from the flaming combustion to the smoldering stage results in a decrease of the flame length and that of the average temperature to about 700 K determining the formation of an after-flame low temperature shoulder (Figure 1a-c) which depends on the development of a sequence of exothermic and endothermic reactions on the surface of pre-treated pellets:

$C + ½ O_2 \rightarrow CO$ $\Delta H = -123.1$ kJ/mol (1)

$C + O_2 \rightarrow CO_2$ $\Delta H = -393.5$ kJ/mol (2)

$C + CO_2 \rightarrow 2CO$ $\Delta H = +159.9$ kJ/mol (3)

$C + H_2O \leftrightarrow CO + H_2$ $\Delta H = +118.5$ kJ/mol (4)

As it follows from Figure 1a-c, when increasing the irradiation time of pellets, a faster transition from flaming combustion to low-temperature surface reactions is observed for the MW pre-treated peat pellets which have the lowest content of volatiles (64.1 %) and the highest content of fixed carbon in biomass (55.7 %). The longer lasting flaming combustion of volatiles with a higher average value of the temperature in the flame reaction zone is observed for wood pellets with a higher content of volatiles (83.6 %) and a lower content of fixed carbon (50.3 %) in biomass if compared with peat (Larina, 2016).

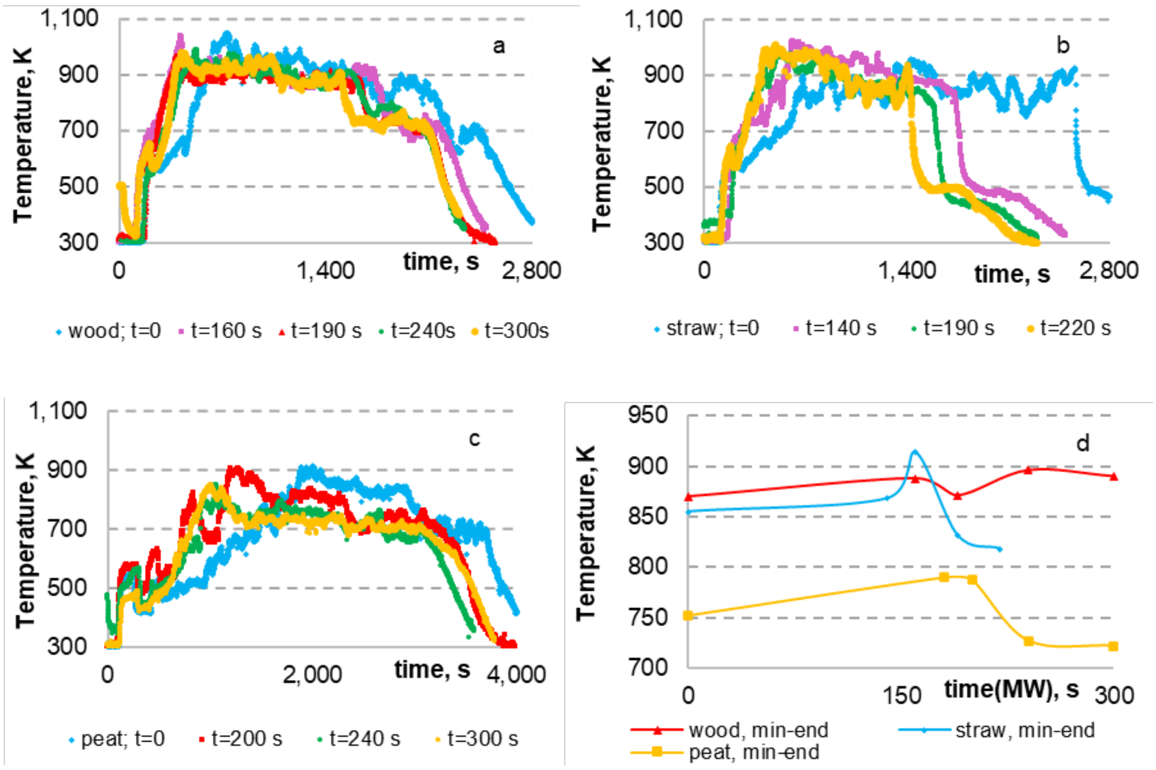

Figure 1: The effect of MW irradiation time of wood (a), straw (b) and peat (c) pellets on dynamics and average values of the flame temperature (d).

3.2. The effect of MW pre-treatment of pellets on the heat output and produced heat energy

Structural modifications of biomass pellets and increase of the carbon content and heating value (HHV) of pellets during their MW pre-treatment also affect the kinetics and the average values of the heat output from the setup. The increased reactivity of the pellets promotes faster heat output from the setup (P_{sum}) as the pellets' irradiation time increases (Figure 2a-c). Besides, the increased carbon content (C) and heating value of the pellets (HHV) after their MW pre-treatment are responsible for the increase of the peak and average values of the heat output from the setup (Figure 2a-d) and the total amount of the heat produced per mass of burned pellets (Q_{sum}). The variations of the carbon content, HHV of the pellets, Q_{sum} and P_{sum} for the fixed duration of MW pellets' irradiation when the temperature of the pellets during pre-treatment reaches 500 K, are summarized in Table 1.

Table 1: Variations of the carbon content, HHV, Q_{sum} and P_{sum} for the fixed temperature of MW pre-treatment

Biomass	*C, %*	*HHV, MJ/kg*	*Q_{sum}, MJ/kg*	*P_{sum}, kW*
Wood pellets				
T = 300 K (raw pellets)	*50.59*	*19.94*	*12.77*	*3.08*
T_{mw} = 500 K	*51.78*	*20.7*	*13.01*	*4.35*
Wheat straw pellets				
T = 300 K (raw pellets)	*46.43*	*18.41*	*11.96*	*2.38*
T_{mw} = 500K	*47.7*	*18.92*	*12.76*	*3.27*
Peat pellets				
T = 300 K (raw pellets)	*52.81*	*20.86*	*10.32*	*2.42*
T_{mw} = 500 K	*61.5*	*24.7*	*12.21*	*3.14*

By analogy with the variations of the flame temperature, the heat output from the setup is influenced by the content of volatiles in biomass. The highest content of volatiles in woody biomass (83.6 %), if compared with wheat straw (79.4 %) or peat pellets (64.1 %) (Larina et al., 2016), determines the enhanced flaming combustion of volatiles during the burnout of wood pellets, increasing the flame length and the highest heat output (up to 5.2 kW) downstream the combustor (Figure 2a).

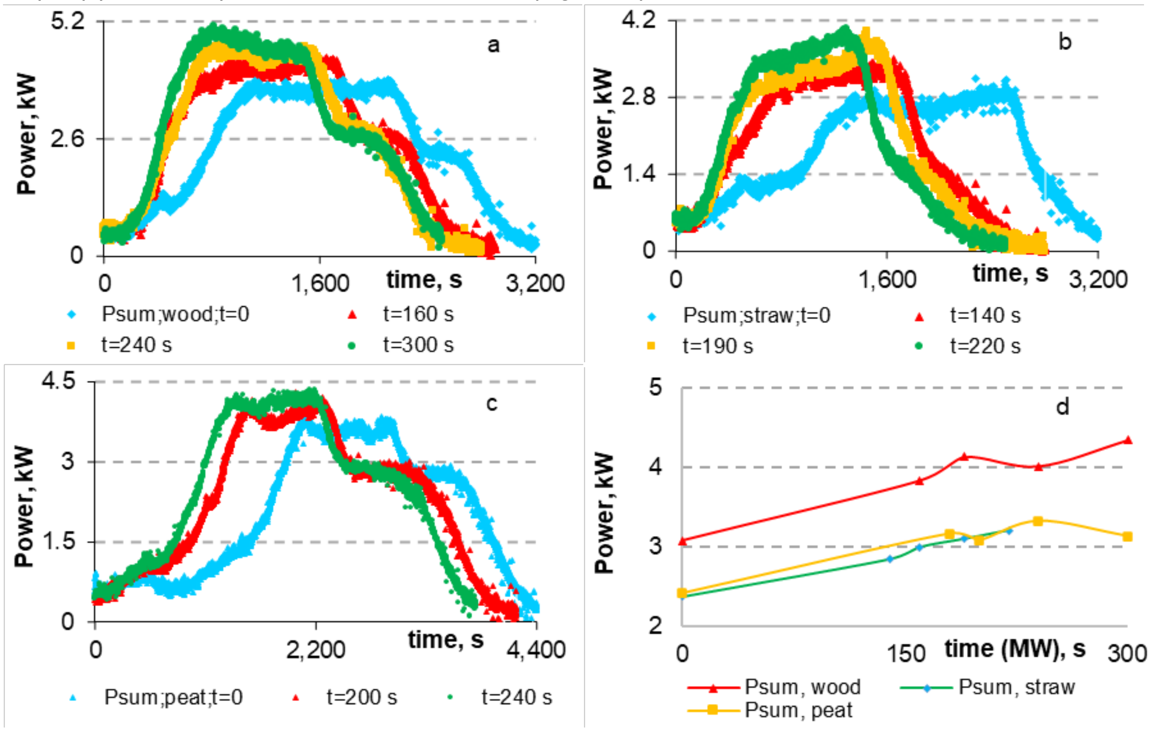

Figure 2: The effect of MW pre-treatment time of wood, straw, and peat pellets on kinetics of the heat output (a-c) and average values of the heat output from the setup in the flame reaction zone (d).

The lower volatile substance for peat pellets limits the flaming combustion of volatiles decreasing the flame length and the heat output from the reaction zone to 4.5 kW with a faster transition to the low-temperature char conversion stage (Figure 2c). Besides, the duration of the smoldering stage of carbonized peat if compared with the smoldering of carbonized wood pellets increases by about 400 s. Therefore, the enhanced carbonization of peat pellets after MW pre-treatment with the enhanced transition from the flaming combustion to the char conversion stage is a main factor which decreases the average values of the flame temperature and the heat output during the burnout of MW pre-treated pellets as the duration of MW pre-treatment increases (Figure 2d). As it follows from Figure 2d, the lower average values of the temperature (Figure 1d) and heat output from the flame reaction zone, if compared with wood pellets, are observed for straw pellets which have lower content of volatiles and lower heating value of the pellets. Besides, the higher weight loss accompanied by the enhanced release of volatiles at MW pre-treatment of wheat straw pellets limits the yield of combustible volatiles during thermal decomposition of pellets, decreasing so the calorific value of the flame reaction zone during the flaming combustion of volatiles and the average value of the heat output during the burnout of pre-treated straw pellets.

3.3. Effect of MW pretreatment of pellets on the products composition

Structural modifications of biomass pellets after their MW pre-treatment along with variations of their weight loss, elemental and chemical composition and reactivity strongly affect the behavior and the average values of the main products during the burnout of the MW pre-treated pellets by enhancing the burnout of the pre-treated pellets with a faster transition from the flaming combustion of volatiles to the char conversion stage. The dynamic study of the formation of the main product (CO_2) suggests that the MW pre-treatment of biomass pellets activates ignition and combustion of volatiles with faster formation of CO_2. Besides, as it follows from Figure 3a-c the duration of the flaming combustion decreases, whereas the duration of the char conversion stage gradually increases, when the formation of CO_2 emissions can be related to the developing reactions on the surface of carbonized pellets Eq(1-4). The most pronounced decrease of the flaming combustion duration and that of CO_2 formation (by 1300 s) was observed for straw pellets with the highest weight loss of pellets (26 %) after their MW pre-treatment. The less pronounced variations of the flaming combustion time were found for peat with the lowest content of the volatile substances in peat biomass (Larina at al., 2016) and with the lowest weight loss after the pellets' MW pre-treatment. As follows from Table 1, the MW pre-treatment of wood and straw pellets resulted in an increase of the carbon content in pretreated pellets by about 1.2-1.3 %, promoting the correlating increase of the peak and average values of CO_2 emissions during the flaming combustion of volatiles with a slight increase of the duration of the char conversion stage. As follows from Figure 3a, b, during the transition from flaming combustion to surface reactions, the peak values of CO_2 emissions in the products decrease from 19 % to about 12 % for wood pellets and from 16 % to 13 % for straw pellets with the correlating decrease of the flame temperature during the char conversion stage (Figure 1b). This is confirmed by the enhanced release of CO emissions as the MW pre-treatment duration of wheat straw pellets increases.

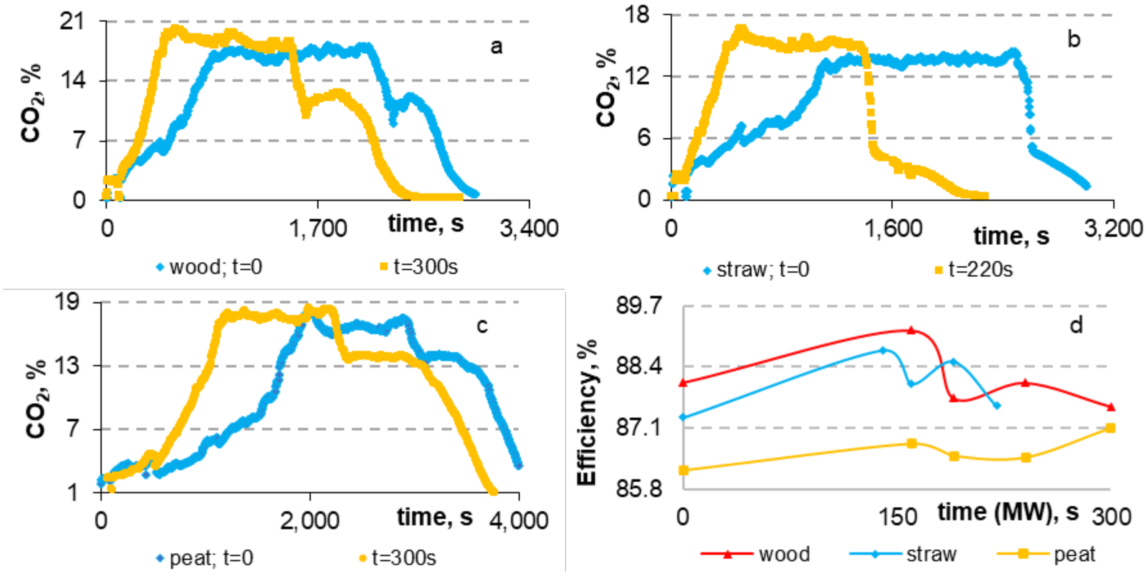

Figure 3: The effect of MW pretreatment time on the formation of CO_2 emission for wood (a), straw (b) and peat (c) pellets and the average value of combustion efficiency (d).

More pronounced increase of the carbon content (by ~ 8.7 %) after MW pre-treatment was observed for peat pellets determining a slight increase of CO_2 emissions (0.6 %) during the flaming combustion of the pre-treated pellets, with the enhanced formation of CO_2 emissions during the char conversion stage (Figure 3c). The transition from flaming combustion to char conversion affects the combustion efficiency of pre-treated pellets, increasing the combustion efficiency up to the peak value during the flaming combustion of volatiles and gradually decreasing during the transition from flaming combustion of volatiles to char conversion stage (Figure 3d). With the constant air supply rates in the setup, the enhanced yield of combustible volatiles during the thermal decomposition of pre-treated pellets promotes a decrease of the air-to-fuel supply ratio in the combustor, which improves the combustion conditions in the flame reaction zone and decreases the air excess ratio in the products by about 9-15 % with the correlating linear increase of CO_2 emissions in the products by about 8-25 %. Finally, it should be emphasized that the pre-treatment of wood and peat pellets does not affect the NO_x formation by Zeldovich mechanisms, which requires a relatively high temperature (T > 1,000 K) in the reaction zone. A decrease of the mass fraction of NO_x in the products by about 35 % was observed during the thermo-chemical conversion of the pretreated wheat straw pellets. Because MW pre-treatment of straw pellets at temperature about 500K promotes a relatively slight decrease of nitrogen content in pellets from 0.59% for raw pellets to about 0.58%, a decrease of NO_x at thermo-chemical conversion of pretreated straw pellets can be related to the decrease of the flame temperature (Figure 1b).

4. Conclusions

The performed experimental study of the effects of MW pre-treatment of straw, wood and peat pellets on the combustion characteristics with varying MW irradiation time of pellets allow the following conclusions.

The dynamic study of the influence of MW pre-treatment of lignocellulosic pellets on the variations of the combustion characteristics showed that MW pretreatment enhances the weight loss of pellets increasing so their reactivity and resulting in a faster and enhanced burnout of combustible volatiles, the intensity of which depends on the initial chemical composition of pellets and on the content of volatiles in biomass, with the most pronounced variations of flaming combustion during the combustion of MW pre-treated wheat straw pellets.

The enhanced flaming combustion of volatiles after MW pre-treatment of pellets determines the increase of the flame temperature, heat output from the setup and combustion efficiency up to peak values as the irradiation time of pellets increases to 160-190 s and the pre-treatment temperature increases to 450-500 K.

The development of the competitive process of carbonization of lignocellulosic pellets after their MW pre-processing results in a gradual transition from the flaming combustion of volatiles to the smołdering combustion of carbonized pellets, resulting in the decrease of the flame length and average values of the flame temperature, heat output from the device and combustion efficiency as the irradiation time of pellets increases more than 160-190 s and the temperature of MW pre-treatment exceeds 450-500 K.

Therefore, considering the development of the competitive processes of flaming combustion and smołdering of carbonized residues, it is necessary to take into account the optimal conditions for the pre-treatment of lignocellulosic pellets to ensure effective control of the combustion characteristics of lignocellulosic pellets.

Acknowledgments

The authors would like to acknowledge the financial support from the European Regional funding of the project Nr. 1.1.1.1/19/A/010.

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