

## CO-FIRING AND MICROWAVE PRE-TREATMENT OF LIGNOCELLULOSIC PELLETS FOR CONTROL OF THERMOCHEMICAL CONVERSION OF BIOMASS MIXTURES AND SUSTAINABLE ENERGY PRODUCTION

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**Abstract.** Original experimental device with heat output up to 20 kW was developed and tested with the aim to provide wider use of the locally available renewable energy resources - agriculture residues (wheat straw) for sustainable energy production and reduced effect of energy production on climate changes. To provide efficient control of thermochemical conversion of straw pellets, mixtures of straw pellets with microwave (mw) pre-treated straw or wood pellets were used, providing selective pre-treatment of the mixture components at frequency 2.45 GHz with temperatures of pre-treatment 473 K and 548 K. The effect of selective microwave pre-treatment of the mixture components on kinetics of thermochemical conversion was estimated providing complex on-line measurements of the flame temperature, produced heat and composition of the products at different stages of the mixture's thermochemical conversion. The results of complex measurements reveal that selective microwave pre-treatment of mixture components can be used as a tool to provide control of ignition and burnout of mixtures and composition of the products. The most pronounced effect during thermochemical conversion of selectively activated mixtures was observed for the mixture of raw straw with additives of pre-treated wood pellets with mass fraction 30%, when the total amount of produced heat can be increased about 9%, produced heat energy per mass of burned mixture by more than 5%, the volume fraction of carbon-neutral CO<sub>2</sub> emission in the products relative to that for raw straw pellets by 7% with decrease of the mass fraction of polluting NO<sub>x</sub> emissions in the products by 18% confirming cleaner sustainable heat energy production and improved heat production efficiency.

**Keywords:** straw thermochemical conversion, straw mixtures with renewable fuels, selective microwave pre-treatment of mixtures, pellet combustion

### Introduction

With impending Europe's energy crisis and climate changes, European energy producers are looking for more effective use of sustainable energy sources for energy production intensifying the use of widely available naturally replenished energy resources- wind, solar, hydro- power or geothermal with minimal risk of running out. Sustainable energy, such as wind and solar energy, creates zero carbon emissions that can harm the atmosphere and contribute to global warming [1-3]. However, when evaluating the use of these sustainable energy sources, it should be considered that the amount of energy produced and its quality are highly affected by changes in local weather conditions, when sunny days are replaced by rainy days or snow falls, the formation of intense wind or storm, by no wind conditions. Considering the intermittent behavior of solar, wind, and hydro power, possibilities of balancing it with electricity from gasification and combustion of corn cobs has been studied and proved [4], as well as positive effects of this technology through LCA estimated. To limit the impact of the local changes in weather conditions on stability and quality of the produced sustainable energy, the energy producers recommend to use different origin solid renewable energy resources – lignocellulosic harvesting residues (wood waste), agricultural residues (rice or wheat straw) [5; 6], corn cob, corn grains, etc. [7; 8], which have different elemental and chemical composition of the components [9] responsible for different rates of their thermochemical conversion. Because of relatively high heating values of agriculture residues, such as wheat or rice straw biomass pellets, they can be used as alternatives to wood residues for energy production partially replacing wood waste by co-firing wood waste with straw [10]. Additives of straw in the mixture with wood residues promote a decrease of the yield of greenhouse CO<sub>2</sub> emissions because the thermochemical conversion of straw additives promotes faster returning of CO<sub>2</sub> into atmosphere, which is absorbed during the plant growth thus enhancing sustainable energy production by thermochemical conversion of the mixtures. In addition, ash from burning straw pellets with high levels of mineral contents can be used as a mineral fertilizer [6]. Preliminary research of co-firing wood waste with straw suggests that thermochemical conversion of the mixtures of wood with straw is highly influenced by the thermal and chemical interaction between the components, which can be modified by varying the mixture composition and main characteristics of the components [10]. Microwave (mw) pre-treatment of biomass pellets is suggested as an effective tool for modification and control of the thermochemical conversion of biomass mixtures, which can cause changes in their

structure and chemical composition [11; 12]. Applicability of mw pre-treatment of pellets as a tool for control of thermochemical conversion of biomass mixtures is confirmed providing detailed experimental research and numerical simulation of thermal decomposition and combustion characteristics of selectively activated mixtures using a small-batch-size scale pilot device with heating power up to 5kW [13]. The main aim of the current study is to provide research of the processes developing during cofiring selectively activated mixtures of wood and wheat straw in a device using a biomass burner with continuous supply of the selectively activated mixture of biomass mixtures and heat output up to 20 kW with estimation of the main factors responsible for their ignition and thermochemical conversion.

### Materials and methods

The experimental unit with a heat capacity of up to 20 kW is in line with the boilers used for domestic heating, using the selectively activated mixtures of wood or wheat straw pellets with average mass fraction 30% of pre-treated pellets in the mixture with raw pellets as fuel. The device is composed of a combustion chamber (1) and two heat exchanger units (2, 3). For supply of the biomass mixtures into the combustion chamber Pelltech PV-20a burner is used ensuring the average supply of the pellet mixtures up to  $0.9 \text{ g}\cdot\text{s}^{-1}$ . The device is equipped with special openings to provide kinetic study of the main combustion characteristics during thermochemical conversion of selectively activated mixtures. A kinetic study of the effect of selective microwave pre-treatment of wheat straw and wood pellets on gas temperature was provided using K-type thermocouples and data online registration with Pico TC-08 logger. Kinetics of produced heat for each section of the device was studied using calorimetric measurements of cooling water flow and providing online data registration by using the Quick DAQ program. Kinetics of products composition - volume fraction of  $\text{CO}_2$  and mass fractions of  $\text{CO}$  and  $\text{NO}_x$  in the products was controlled using a gas analyser Testo 350. MW pre-treatment of pellets was carried out using the originally developed mw reactor [14] at two different temperatures of microwave pre-treatment – 473 K and 548 K.

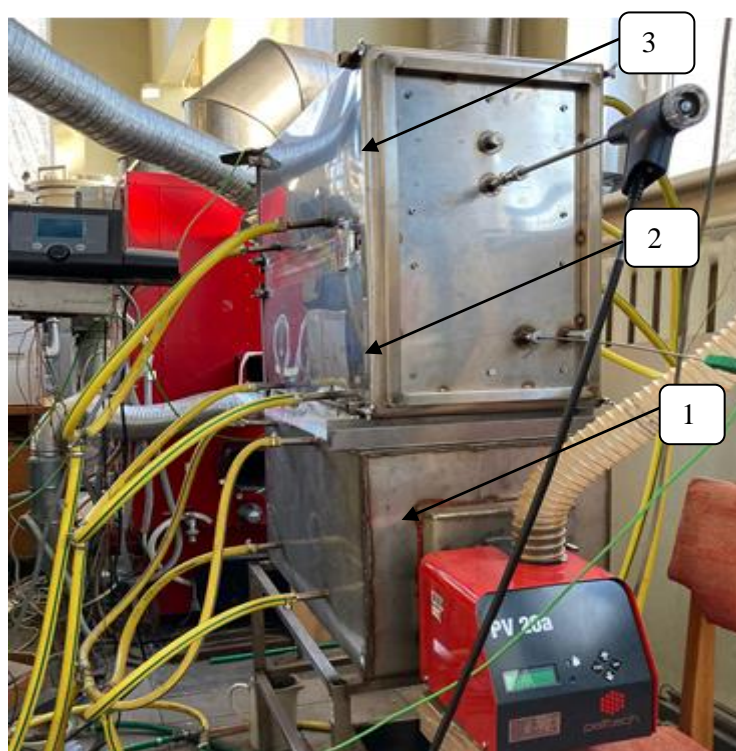


Fig. 1. Image of the experimental device: 1 – combustion chamber; 2, 3 – heat exchangers

### Results and discussion

In accordance with the data of the preliminary experimental research mw pre-treatment of lignocellulosic pellets (wood, wheat straw) starts with drying of pellets and follows by the enhanced thermal decomposition of the main constituents of lignocellulosic pellets (hemicelluloses, cellulose, and

lignin) increasing the yield of combustible volatiles ( $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2$ ), enhancing carbonization and the increasing heating value of pre-treated pellets ( $\text{HHV}$ ,  $\text{MJ}\cdot\text{kg}^{-1}$ ), which depend on the pre-treatment temperature of pellets [15]. Mw-induced drying of lignocellulosic pellets with enhanced release of moisture and combustible volatiles correlate with structural changes of pre-treated pellets, increasing specific surface area, porosity, and reactivity of pre-treated pellets with gradual transition from the gas-phase to surface reactions as it was confirmed by the research results presented in [15; 16]. Similar effects of mw pre-treatment on the main characteristics of pre-treated pellets follow from a review of the mw-induced effects on the main characteristics and thermochemical conversion of lignocellulosic biomass [14]. In accordance with the data presented in [14; 17], microwave-induced carbonization of lignocellulosic pellets enhances development of self-gasification of char increasing the yields of  $\text{H}_2$  and  $\text{CO}$ , whereas decreasing the yields of  $\text{CO}_2$  emission. Besides, increasing the yields of moisture and  $\text{H}_2$  can result in the enhanced development of endothermic water gas reaction on the surface of carbonized pellets responsible for an additional increase of the yields of  $\text{CO}$  and  $\text{H}_2$  [17]. Mw-induced changes of the main characteristics and thermochemical conversion of pre-treated pellets suggest that additives of mw pre-treated pellets can be used to provide control of thermal and chemical interaction between raw and pre-treated pellets and thermochemical conversion of biomass mixtures. Such a conclusion follows from studies of thermal decomposition and combustion of selectively activated mixtures, which were carried out using a batch-size pilot device [13]. The results of these studies confirm that selective mw pre-treatment of the mixture components activates thermal decomposition of the mixture constituents resulting in faster and enhanced thermochemical conversion of the mixtures [13]. Therefore, results of the preliminary research suggest that selective pre-treatment of the components of biomass mixtures can be used for control of heat energy production and composition of products in heating devices with higher heat energy output. To test this suggestion, experimental studies were conducted using the originally developed experimental device (Fig. 1) and providing detailed test research of the effects of co-firing and selective mw pre-treatment of lignocellulosic pellets on thermochemical conversion of the mixtures of raw wheat straw and wood pellets as well mixtures of microwave pre-treated and raw wheat straw or wood pellets. The results of kinetic study of thermochemical conversion of raw or selectively pre-treated mixtures of biomass pellets have shown that for equal mass fractions of raw or pre-treated pellets in the mixtures (30%) their thermal decomposition is influenced by difference in elemental composition and HHV of mixture components and temperature of selective mw pre-treatment of wood or wheat straw pellets (Fig.2, Table 1). Kinetic study of thermochemical conversion of the mixture of raw wood pellets with raw wheat straw pellets confirms that higher contents of hemicellulose in wheat straw pellets [12] activates the thermochemical conversion of the mixture resulting in faster rise of the volume and mass fraction of the main products and combustion efficiency up to the maximum value (Fig. 2). Besides, lower carbon content in wheat straw pellets with lower HHV of these pellets causes a decrease of heat production efficiency ( $Q/\text{HHV}$ ) if compared with raw wood pellets (Table 1). Faster thermochemical conversion of this mixture is observed providing selective mw pre-treatment of wheat straw pellets and increasing the pre-treatment temperature of wheat straw pellets (Fig. 2). Besides, increasing the average values of carbon and nitrogen content in pre-treated wheat straw pellets and HHV of pellets [14] results in an increase of carbon and nitrogen contents in selectively pre-treated mixture relative to that in raw wood respectively by 1.19% and 96.07%, increasing HHV of the mixture by 1.35% (Table 1). The mw-induced changes of carbon content and HHV of selectively pre-treated mixture correlate with increase of the produced heat power by 2.5% and produced heat energy by 5.9%, increasing efficiency of energy production ( $Q/\text{HHV}$ ) during thermochemical conversion of selectively pre-treated mixture by 4.42%. Increasing efficiency of heat energy production correlates with a slight decrease of the temperature at the outlet of the combustion chamber (by 0.67%), decreasing the volume fraction of  $\text{CO}_2$  in the products by 2.45%, while increasing the mass fraction of polluting  $\text{CO}$  by 109%, which suggests that selective mw pre-treatment of wheat straw pellets enhanced development of endothermic water-gas reactions by varying a balance between development of the competitive exothermic and endothermic surface reactions promoting instability of  $\text{CO}$  and  $\text{NO}_x$  production (Fig. 2, c-f).

The most pronounced mw-induced changes of kinetics of the main combustion characteristics and composition of products are observed during thermochemical conversion of the mixture of pre-treated wood pellets with raw straw pellets (Fig.2) when higher carbon content and HHV of pre-treated wood relative to raw wheat straw pellets activates thermochemical conversion of selectively activated mixture

increasing heat power of device by 11.35%, produced heat energy per mass of burned pellets by 5.5% and efficiency of heat energy production ( $Q/HHV$ ) by 0.76% (Table 1).

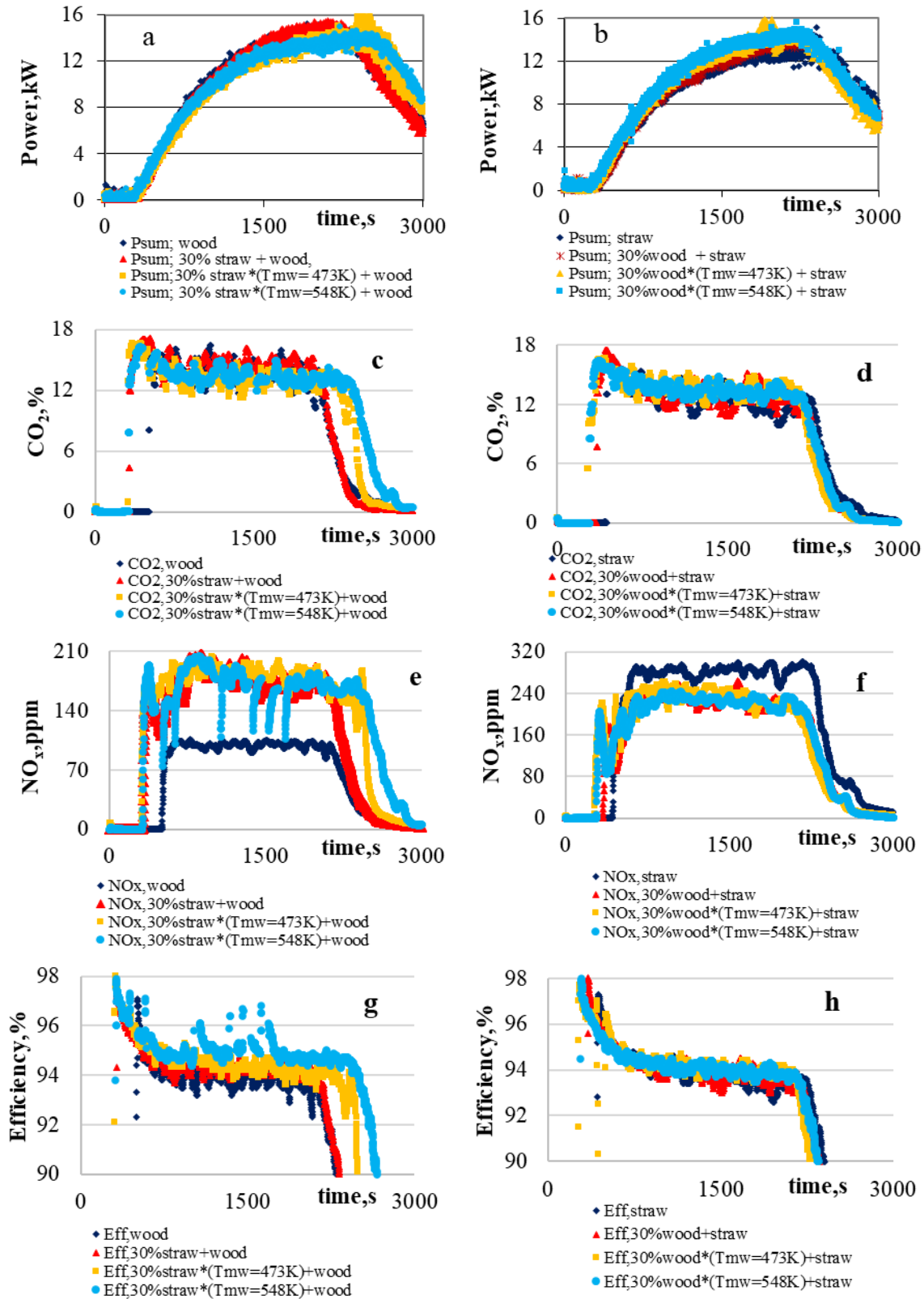


Fig. 2. Effect of selective microwave pretreatment of the components of biomass mixtures on kinetics of: produced heat power (a, b), volume fraction of CO<sub>2</sub> in the products (c, d), mass fraction of NO<sub>x</sub> emission in the products (e, f) and combustion efficiency (from Testo) (g, h)

Besides, the average volume fraction of CO<sub>2</sub> increases by 2.5%, and the average mass fraction of CO in the products if compared with changes of the yield of CO emissions during thermochemical conversion of the mixtures of raw wood with mw-pre-treated wheat straw pellets increases (by 15%). The mass fraction of NO<sub>x</sub> emission in the products decreases by 4.34%, and 18.55% against raw straw (Table1), which can be related to a decrease of nitrogen content in selectively activated mixture by 24.5%. A slight decrease of the average flame temperature at the outlet of the combustion chamber (by 3.09%) correlates with an increase of the produced heat power of the device, confirming development of the enhanced processes of heat transfer in the device and mw-induced transition from gas-phase to surface reactions. Co-firing raw and pre-treated wheat straw pellets noticeable thermal effect while cleaner heat energy production is observed during combustion. The main characteristics and product composition revealed that the average value of the produced heat power during thermochemical conversion of mw activated mixture relative to that of raw straw increases by 4.39% and the produced heat energy by 12.65%, increasing efficiency of the heat energy production by 8.07% with a correlating decrease of the average flame temperature at the outlet of the combustion chamber by 3.96%, volume fraction of CO<sub>2</sub> in the products by 5.36%, mass fraction of CO by 20.22% and mass fraction of NO<sub>x</sub> emissions by 1.39% (Table 1).

Table 1

**Mw-induced changes of the main characteristics of pre-treated pellets, produced heat and product composition during thermochemical conversion of selectively pre-treated mixtures**

Type and pre-treatment temperature of the pellets and composition of mixtures	C, %	HHV, MJ·kg <sup>-1</sup>	P <sub>sum</sub> , kW	Q, MJ·kg <sup>-1</sup>	Q/HHV	T, K	CO <sub>2</sub> , %	NO <sub>x</sub> , ppm	Eff., %
Wood pellets mw = 0	50.59	19.94	10.00	18.04	0.905	594	13.87	99.04	94.0
30%; straw (mw = 0) + wood	49.2	19.43	10.23	17.55	0.903	559	14.68	174.41	94.53
30%; straw* (T <sub>mw</sub> = 473K) + wood	49.47	19.52	9.9	18.39	0.942	565	13.41	178.57	94.65
30%; straw* (T <sub>mw</sub> = 548K) + wood	51.19	20.21	10.25	19.11	0.945	590	13.53	172.86	95.09
Wheat straw pellets mw = 0	46.43	18.41	9.33	15.73	0.854	581	12.68	258.32	93.71
30%; straw* (T <sub>mw</sub> = 473K) + straw	46.7	18.5	9.76	16.86	0.911	587	12.31	260.22	-
30%; straw* (T <sub>mw</sub> = 548K) + straw	57.43	19.19	9.74	17.72	0.923	558	12.0	254.72	94.25
30%; wood + straw	47.82	18.92	9.16	17.35	0.917	581	13.24	219.84	94.19
30%; wood* (T <sub>mw</sub> = 473K) + straw	47.87	19.01	10.39	17.40	0.915	587	13.50	222.13	94.42
30%; wood* (T <sub>mw</sub> = 548K) + straw	55.92	19.82	10.20	18.31	0.924	563	13.57	210.40	94.02

### Conclusions

In the paper the effects of co-firing and selective MW pre-treatment of renewable fuels - lignocellulosic wood or wheat straw pellets on the main combustion characteristics and composition of the products during thermochemical conversion of their mixtures in a device with heat output up to 18 kW were studied and analyzed with account of complex variations of the elemental composition of mixture components.

The results of the experimental research and analysis suggest that main combustion characteristics and product composition are highly influenced by the difference of elemental composition and heating value of the mixture components and their changes during selective MW pre-treatment of the mixture components, which can be used to provide control of the thermochemical conversion of biomass mixtures.

The most pronounced changes of the main combustion characteristics and composition of the products with increased energy efficiency (Q/HHV by 8.15% and power by 11,42%) can be obtained during thermochemical conversion of selectively pre-treated mixture of wood with raw straw pellets, when mw pre-treatment of wood pellets causes increase of carbon content in the mixture and its heating value, less pronounced differences of combustion characteristics with limited increase of energy efficiency (by Q/HHV 4.45% and power 2.5% accordingly) can be obtained during thermochemical conversion of selectively pre-treated mixture of wheat straw with wood pellets. Noticeable effects of control on thermochemical conversion are observed for the mixture of pre-treated and raw wheat straw pellets (Q/HHV by 8.1% and power by 4.43%).

The analysis of the effect of wood and wheat straw cofiring and selective pre-treatment of components of heat energy production and composition of products suggests that replacing a part of wood with straw allows to control thermochemical conversion of the mixtures with control of sustainable development of heat energy production, because of faster returning of CO<sub>2</sub> into atmosphere, which is absorbed during the wheat straw growth.

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### Author contributions

Conceptualization, M.Z. AND R. V.; methodology, M.Z. and R.V.; validation, M.Z. and R.V.; formal analysis, M.Z. and R.V.; experimental work, V.Š. and R.V.; data curation, M.Z., V.Š. and R.V.; writing – original draft preparation, M.Z.; writing – review and editing, M.Z. and R.V.; visualization, M.Z. and R.V.; All authors have read and agreed to the published version of the manuscript.

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