

ACTIVATED THERMAL DECOMPOSITION OF BIOMASS MIXTURES BY MICROWAVE PRETREATMENT OF COMPONENTS

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Abstract. Joint research has been conducted, evaluating methods that provide opportunities for wider and improved use of local renewable energy resources (agricultural and forestry waste) for energy production. Opportunities for creating biomass mixtures of different origins have been evaluated, optimizing the composition of these mixtures and performing selective thermal decomposition activation of these mixtures using microwave pretreatment of mixture components to ensure an increase in the quality and efficiency of the energy produced. The research has used originally created experimental equipment for microwave processing of biomass pellets, thermal decomposition and combustion of microwave-activated mixtures, evaluating the correlations between microwave-induced modification in the elemental, chemical composition and structure of the mixture components, development of the mixture's thermal decomposition and combustion processes and composition of emissions. It was found that selective microwave pre-treatment of the mixture components enhances synergistic interaction between the components by improving thermal decomposition of mixture and yields of combustible volatiles (CO , H_2 , C_xH_y), by activating ignition, completing combustion of volatiles and increasing heat output from the device, which depend on microwave pretreatment temperature. The most pronounced increase of the heat output from the device and produced heat energy is observed for the mixtures of pre-treated wheat straw or wood pellets with raw peat, when increasing the MW pre-treatment temperature to 548K the heat output can be increased by more than 10%. Completing combustion of volatiles by increasing mass fraction of MW pretreated additives in the mixtures results in an increase of CO_2 emissions in the products for all types of mixtures, while the formation of NO_x emissions can be decreased when cofiring pre-treated wheat straw or wood with raw peat.

Keywords: thermochemical conversion, biomass mixtures, selective microwave pre-treatment of mixtures, pellet combustion.

Introduction

Because of gradually increasing climate changes EU supports research and innovation related to more efficient and sustainable bioenergy production by converting different types of available regional biomass feedstocks, such as agricultural and forest residues, organic municipal waste and energy crops into useful biofuels (liquid biofuels, biogas, chips, biochar, pellets, briquettes, etc), which can be used for efficient production of renewable bioenergy at local and industrial scale [1-3]. All these biomass types are accepted as sustainable, renewable and carbon-neutral energy resources with the potential for replacing fossil fuels in energy-intensive sectors with biofuels while their efficient use for energy production requires thermochemical transformation of biomass (pyrolysis, gasification, carbonization, torrefaction, etc.) to improve their physicochemical characteristics [4-6]. Detailed analysis of the methods of biomass thermochemical transformation suggests that two stage pyrolysis of biomass feedstocks can be used to achieve a high degree of biomass conversion into gaseous fuel to produce a high calorific value ($10\text{-}12 \text{ MJ}\cdot\text{m}^{-1}$) synthesis gas with the ratio between the volume content of hydrogen and carbon monoxide in a range from 1 to 2, depending on the biomass type [7]. Among the methods of biomass pretreatment improving the process of biomass conversion into biofuels microwave-based pretreatment technologies have been developed in recent years, which are important for sustainable biofuel production with efficient control of biomass structure, porosity, reactivity, elemental composition and heating values [8,9]. Previous experimental studies with evaluation of the effect of MW pretreatment on the thermal decomposition of biomass pellets, which are produced from forestry and agriculture residues confirm that the microwave induced oscillations produce variations in the biomass structure, elemental and chemical composition, and their heating value. It results in a decrease of the mass density of pre-treated biomass, faster thermal decomposition, faster yield, ignition, and burnout of combustible volatiles, improving main characteristics of biomass pellets, increasing the energy output and average values of carbon-neutral CO_2 emissions in the products [10]. In this study MW induced improvement of biomass characteristics motivates applicability of pretreated biomass pellets as additives to different types of regionally available biomass feedstocks to produce selectively MW activated biomass blends with improved and controllable combustion characteristics, assessing the main factors responsible for improvement of their thermochemical conversion. Evaluation the influence

of the changes in pre-treatment regimes of pretreated additives, composition of selectively MW-activated biomass blends and synergistic effects on the thermochemical conversion of selectively activated blends will offer opportunities for wider use of different origin biomass feedstocks with efficient and sustainable energy production.

Materials and methods

Commercially available biomass – softwood, wheat straw and peat pellets, which are produced using regionally available forestry and agriculture residues, as well peat, are used in this study. To produce the selectively MW-activated blends, biomass pellets were pretreated using pretreatment temperatures 473K and 548K by mixing pretreated pellets in different proportions (0, 15%, 30%, 45%, 60%, 100%) with non-pretreated pellets to produce selectively activated biomass blends: straw* + straw, straw* + wood, straw* + peat, wood* + straw, wood* + peat (where “*” refers to “MW pre-treated” pellets). To provide pretreatment of biomass pellets an originally developed MW reactor and pretreatment methodology were used [11]. To provide research of thermochemical conversion of selectively activated biomass mixtures an originally developed batch-size device and methodology were used (Fig. 1) [10].

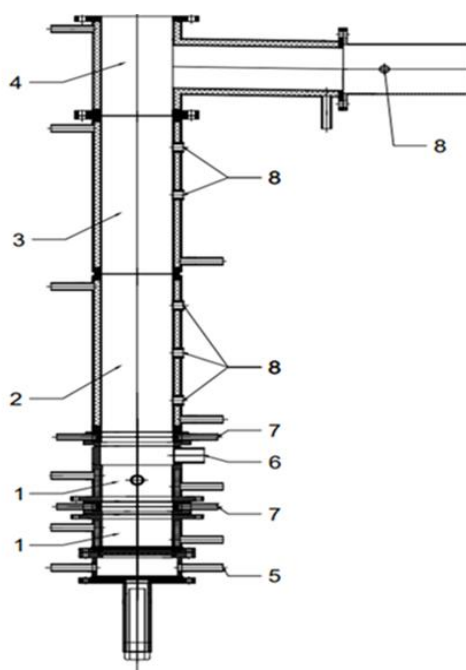


Fig. 1. **Sketch of the experimental device:** 1 – gasifier; 2, 3, 4 – water-cooled sections of the combustor; 5 – primary air supply nozzle; 6 – propane flame supply nozzle; 7 – secondary swirling air supply nozzle; 8 – orifices for the diagnostic tools [10]

The device is composed of a water-cooled gasifier (1), which is charged with a biomass mixture of different origin biomass pellets and sections of a combustor (2-4) downstream of which the swirl-enhanced mixing of the axial flow of volatiles with air swirl promotes the thermochemical conversion of combustible volatiles (CO , H_2) produced during thermal decomposition of mixtures. The originally developed device is used for measurement of weight loss of mixtures during their gasification. PT/PT-Rh thermocouple is used for measurements of the flame temperature at the flame axis ($R = 0$) and distance 30 mm from the bottom of the combustor. Calorimetric measurements of water-cooled sections are used to estimate the heat output from the gasifier (P_{gas}), sections of the combustor (P_1 , P_2 , P_3) and the heat output from the device. Gas-analyser Testo 350 is used for measurement of the composition of the products [10]. All measurements are carried out once per second with average duration of the process in a range from 2000 to 3000s.

Results and discussion

When MW-pretreatment of biomass pellets is used to produce selectively activated biomass mixtures, MW-induced thermal destruction of the main components of lignocellulosic pellets results in

enhanced yield of combustible volatiles and changes of the main characteristics (elemental and chemical composition, heating value, activation energy, porosity and reactivity, etc.) of pretreated pellets [10; 12]. Consequently, MW pretreatment of lignocellulosic pellets significantly influences the development of the processes of thermal destruction and thermochemical conversion of the mixtures, development of gas-phase reactions and char conversion, heat output from the device and the formation of main products. Development of these processes depends on the mixture composition, mass fraction of pretreated additives in the mixture and the temperature of their pretreatment by microwaves with correlations between the MW-induced changes in average values of the mixture weight loss rate during its gasification, flame temperature, heat output from the device and volume fraction of carbon (CO_2) emission during thermochemical conversion of different origin selectively activated blends (Fig. 2).

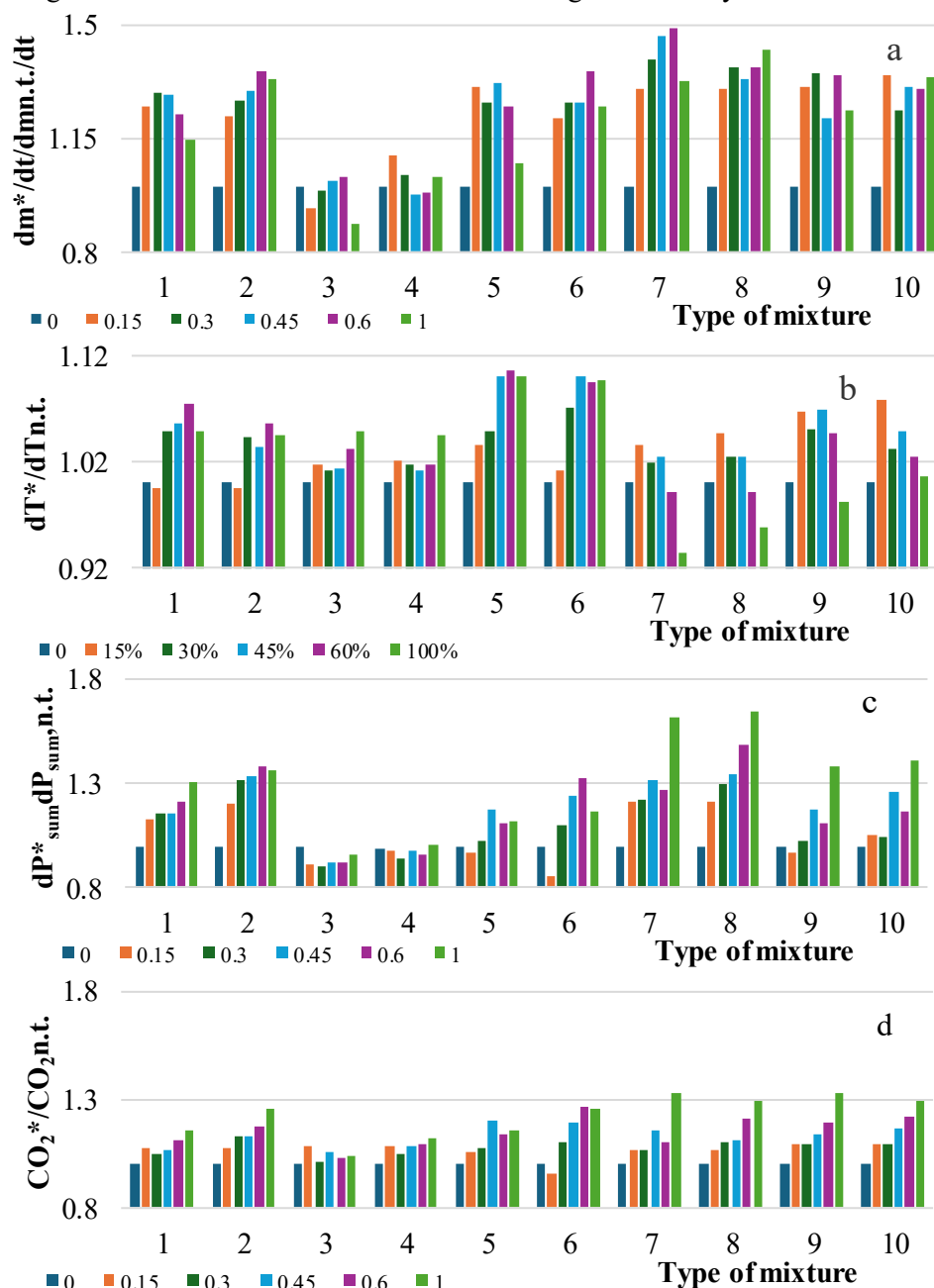


Fig. 2. Microwave induced relative changes of the weight loss of mixtures, temperature of the reaction zone, heat output and the yield of CO_2 in products during thermochemical conversion of selectively activated mixtures by varying mass fraction and pretreatment temperature of additives: 1 – $s^* + s$, $T_{mw} = 473\text{K}$; 2 – $s^* + s$, $T_{mw} = 548\text{K}$; 3 – $s^* + w$, $T_{mw} = 473\text{K}$; 4 – $s^* + w$, $T_{mw} = 548\text{K}$; 5 – $s^* + p$, $T_{mw} = 473\text{K}$; 6 – $s^* + p$, $T_{mw} = 548\text{K}$; 7 – $w^* + s$, $T_{mw} = 473\text{K}$; 8 – $w^* + s$, $T_{mw} = 548\text{K}$; 9 – $w^* + p$, $T_{mw} = 473\text{K}$; 10 – $w^* + p$, $T_{mw} = 548\text{K}$

Besides, for all types of selectively activated mixtures increasing the mass fraction of pretreated additives in mixtures and MW pretreatment temperature reveals non-linear changes in the relative weight loss rates of the mixtures during their gasification, which follow by non-linear changes in flame temperature, heat output and yield of the main product (CO₂).

The deviation from linearity in the weight loss rate with increasing mass fraction of pretreated additives is observed for all types of selectively activated mixtures during the gasification stage (Fig. 2a). This behavior suggests the influence of synergistic effects resulting from thermal and chemical interactions between pretreated and non-pretreated pellets during the process development [13]. The synergistic effects of thermal interaction between the components are strongly influenced by microwave (MW)-induced carbonization of the pretreated additives, which results in relative changes in their higher heating values (HHV*/HHV_n) depending on the temperature of MW pretreatment [10] (Table 1). As shown in Table 1, increasing the pretreatment temperature of straw or wood pellets to T = 548 K leads to an average increase in HHV of approximately 12–13%. In general, the synergistic effect of thermal interaction between pretreated and non-pretreated pellets is positive when the HHV of the pretreated pellets exceeds that of the non-pretreated pellets (HHV* > HHV_n), and negative when the HHV of the pretreated pellets is lower than that of the non-pretreated pellets (HHV* < HHV_n). In the present study, the most pronounced positive synergistic effect on the mixture weight loss rate is observed for the w* + s mixture, where the HHV of pretreated wood pellets exceeds that of non-pretreated straw. The addition of pretreated wood to straw increases the relative weight loss rate of the mixture from 1 to 1.5 (Fig. 2a-7,8). A less effective thermal interaction is observed when pretreated straw is added to wood. In this case, the HHV of the pretreated straw pellets remains lower than that of wood pellets, resulting in a negative synergistic effect and a slight decrease in the weight loss rate.

Table 1

MW-induced relative changes of carbon content and HHV for different origin lignocellulosic pellets during their MW pretreatment

Pellets	C*/C _{n.t.} , %-straw	C*/C _{n.t.} , %-wood	C*/C _{n.t.} , %-peat	HHV*/HHV _n .t.-straw, MJ·kg ⁻¹	HHV*/HHV _n .t.-wood, MJ·kg ⁻¹	HHV*/HHV _n .t.-peat, MJ·kg ⁻¹
Non-treated pellets	1	1	1	1	1	1
T _{mw} = 473K	1.017	1.003	1.05	1.015	1.014	1.053
T _{mw} = 548K	1.128	1.11	1.236	1.127	1.135	1.268

The MW-enhanced weight loss of the mixture during the gasification stage correlates with an increased yield of combustible volatiles (CO and H₂) formed during gasification and their subsequent thermochemical conversion downstream of the reaction zone. These processes influence the flame temperature (Fig. 2b), the heat output from the device (Fig. 2c), and the volume fraction of CO₂ in the products (Fig. 2d), which tends to increase with increasing mass fraction of pretreated additives. In contrast, measurements of MW-induced changes in product composition reveal that the mass fraction of NO_x emissions in the products tends to decrease. This reduction can be attributed to the decrease in nitrogen content in the pellets during MW pretreatment [10]. These results demonstrate that selectively MW-activated mixtures enable improved process control, increasing heat production while enhancing the conversion of volatiles and char and improving product composition. For all types of selectively activated mixtures, the influence of MW pretreatment on the development of gas-phase reactions and char conversion is reflected in the varying relationship between the heat output from the gas-phase reaction zone (P₂) and that from the gasifier, where char conversion reactions dominate. The ratio between these processes (P₂/P_{gas}) is sensitive to changes in pretreatment temperature and mixture composition and affects the total heat production (Fig. 3a–e), which tends to increase with increasing mass fraction of carbonized pellets in the mixture and the corresponding relative increase in their heating values (Table 1). In addition, the relative increase in the heating value of selectively activated mixtures (Q*/Q_{n.t.}) slightly exceeds the relative changes in HHV*/HHV_{n.t.}. This suggests that the produced heat energy of selectively activated mixtures is influenced not only by changes in the HHV of pretreated

pellets but also by modifications in their porosity, reactivity, and the pathways of their thermochemical conversion [10].

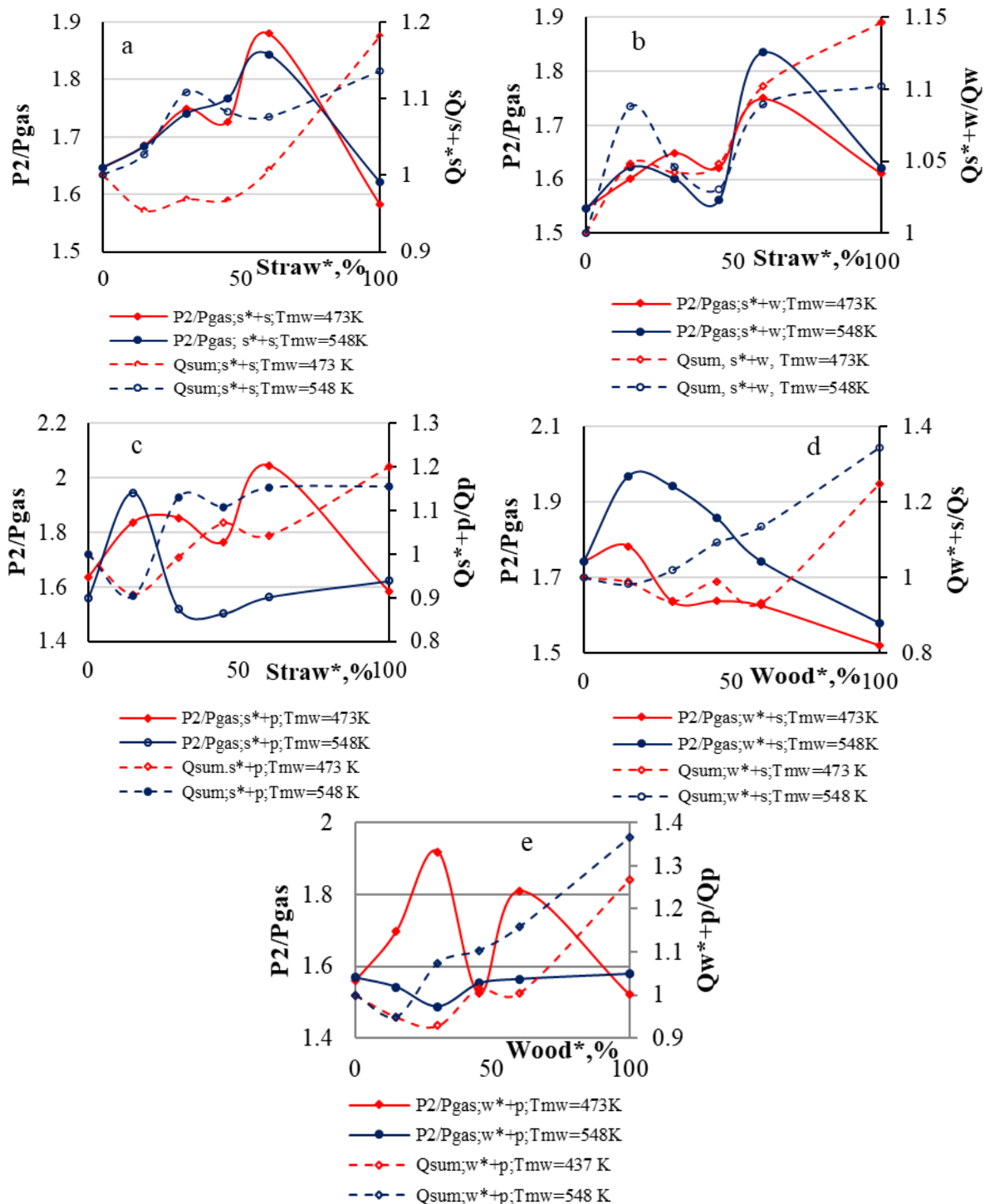


Fig. 3. Effect of changes in mass fraction of MW pretreated additives and pretreatment temperature on relation between the heat output from flame reaction and gasification zones and the produced heat energy during thermochemical conversion of selectively pretreated mixtures

Conclusions

1. The results demonstrate that MW pretreatment of biomass pellets from different origins enhances the thermal decomposition and thermochemical conversion of selectively activated mixtures, leading to increased weight loss, higher flame temperature, greater heat output, and improved product composition due to synergistic thermal and chemical interactions between the components.

- MW-induced carbonization of pretreated pellets affects the development of the gas-phase and surface reactions in selectively activated mixtures. This carbonization modifies the relative contribution of gas-phase reactions and char conversion, leading to increased heat production. The most significant enhancement is observed for mixtures of pretreated wood with straw or peat.

Acknowledgements

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

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 R.V.; data curation, M.Z. and R.V.; writing – original draft preparation, M.Z.; writing – review and editing, M.Z. and R.V.; visualization, M.Z. and R.V.; Both authors have read and agreed to the published version of the manuscript.

References

- Bioenergy. [online] [11.02.2026] Available at: https://research-and-innovation.ec.europa.eu/research-area/energy/bioenergy_en
- Gupta K., Potumarthi R., O'Donovan A., Kubicek C. P., Gauri Dutt Sharma G. D., Tuohy M., G. Bioenergy Research: An Overview on Technological Developments and Bioresources, *Bioenergy research: Advances and Applications* 2014, pp. 23-47.
- Włodarczyk B., Firoiu D., Ionescu G.H., Ghiocel F., Szturo M., Markowski L. Assessing the Sustainable Development and Renewable Energy Sources Relationship in EU Countries. *Energies* 2021, 14, 2323.
- Straume I., Dubrovskis V., Plume I. Co-digestion of cattle manure with paper dust briquettes, *Engineering for Rural Development*, 2025, pp. 58-64, DOI: 10.22616/ERDev.2025.24.TF013
- Arshanitsa A., Ponomarenko J., Andersone A., Telysheva G., Zaķe M., Characteristics of the Main- and side-streams products of microwave assisted torrefaction of lignocellulosic biomass of different origination, *Energies* 2022, 15(5), 1857; DOI: 10.3390/en15051857
- Kumar B., Bhardwaj N., Agrawal K., Chaturvedi V., Verma P. Current perspective on pretreatment technologies using lignocellulosic biomass: An emerging biorefinery concept. *Fuel Process. Technol.* 2020, 199, 106244.
- 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.
- 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, pp. 97-109.
- Huang Y. F., Chiueh P. T., Lo S.L. A review of microwave pyrolysis of lignocellulosic biomass. *Sustainable Environmental Research*, 2016, 26, 103-109.
- Goldšteins L., Valdmanis R., Zaķe M., Arshanitsa A. and Andersone A., Thermal Decomposition and Combustion of Microwave Pre-treated Biomass Pellets, *Processes*, 2021, 9, 429. DOI: 10.3390/pr9030492
- 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, *Renewable Energy*, 2016, vol. 91, pp. 386-396, DOI: 10.1016/j.renene.2016.01.080
- Arshanitsa A., Andersone A., Telysheva G. Non-isothermal thermal analysis of different originated lignocellulosic biomass, non-treated and torrefied by microwave treatment, *Engineering for Rural Development*, 2021, pp. 424-430, DOI: 10.22616/ERDev.2021.20.TF090
- Xue J., Ceylan S., Goldfarb L. Synergism among biomass building blocks? Evolved gas and kinetics analysis of starch and cellulose pyrolysis, *Thermochemical Acta*, 2015, 618, pp. 36-47. DOI: 10.1016/j.tca.2015.09.002