KINETIC STUDY ON MICROWAVE PRE-TREATED BIOMASS COMBUSTION, HEAT PRODUCTION AND EMISSION COMPOSITION

Raimonds Valdmanis, Maija Zake
Institute of Physics, University of Latvia, Latvia
raimonds.valdmanis@lu.lv

Abstract. To promote more efficient use of local renewable energy resources for heat production, an original pilot device has been created with a maximum heat power of 20 kW for combustion of different origin biomass pellets (forestry and agriculture residues). For the improvement of the processes developing downstream of the device, the preliminary heating of biomass pellets by microwaves (MW) was carried out using the batch-size MW (2, 45 GHz) reactor. From the results of preliminary studies, it follows that MW pretreatment of biomass pellets enhances biomass drying and thermal decomposition and structural changes of biomass pellets, increasing their reactivity, porosity, and heating values, which depend on biomass pretreatment temperature with direct influence on combustion dynamics and kinetics of heat production. The MW-induced changes of combustion kinetics influence kinetics of the formation of emissions, which is provided using the gas analyzer Testo 350. The results of kinetic study show that the developed pilot device ensures efficient burnout of raw and pretreated wood and wheat straw pellets reaching the combustion efficiency 93.7-94.34. It was observed that the heat amount produced by development of gas-phase reactions decreases, while the heat amount produced by development of surface reactions increases. The kinetic study of main combustion characteristics suggests that development of surface reactions is influenced by MW-induced increase of the heating value of pre-treated pellets and development of a scope of exothermal and endothermic surface reactions. As a result, transition from the gas-phase to surface reactions promotes more lasting burnout of pretreated pellets, while increasing the total amount of produced heat by about 18.74% for wood pellets and by about 24.4% for wheat straw pellets, slightly reducing the average values of CO_2 and NO_x emissions in the products, which can be related to MW-induced changes of the elemental composition of pre-treated pellets.

Keywords: microwave pretreatment, biomass combustion, thermochemical conversion, wood pellets, straw pellets.

Introduction

The main goal of the proposed research and development complies with the objectives of the European Commission's foreseeing to develop methods for efficient energy production, climate, and energy regulation, which envisages at least a 40% reduction in greenhouse gas emissions (compared to 1990 levels), increasing renewable energy production at least by 32% and its efficiency by 2030 and gradually replacing fossil fuels with renewable energy sources to achieve zero greenhouse carbon emissions till 2050 [1]. While developing the new technologies for energy production, more interest is being paid to assess possibilities of using microwaves (2.45 GHz) for low-carbon biomass pretreatment, which is expected as an efficient and energy-cost-saving method for improvement of biomass characteristics and conversion into biofuel with increased energy production efficiency [2-4]. The review and analysis of preliminary research using the batch-size biomass MW heating system [5] for improvement of characteristics of different origin biomass pellets confirms that MW heating causes MW-induced structural changes of pellets, changes of their elemental and chemical composition, heating values and reactivity [6-8], which depend on duration and power of MW irradiation and can be attributed to MW-induced thermal destruction of the main constituents of lignocellulosic biomass. In accordance with the data [9; 10], hemicellulose decomposes at temperatures 220-315 ºC, cellulose -at temperatures 315-400 ºC and lignin in a wide temperature range from 160 to 900 ºC. MW-activated thermal destruction of the main biomass constituents enhances the yields of CO_2, CO, CH_4 and H_2 and can produce microwave-activated liquid and solid biofuels [9; 10]. Relative changes in the yields of gaseous, liquid, and solid products depend on MW power and duration of biomass heating. Increasing the power and duration of MW heating activates the yield of gas products and char conversion. Overall, the results of preliminary research confirm that there are a lot of factors responsible for low-carbon biomass MW heating, its thermal decomposition and thermochemical conversion. To ensure more stable, sustainable, and flexible thermochemical conversion of MW-activated biomass, when different origin biomass pellets are used as fuels for energy production, the pilot-scale device was developed, to assess the most important factors that influence the processes developing during thermochemical

DOI: 10.22616/ERDev.2024.23.TF039

conversion of MW-activated biomass pellets and to ensure complete thermochemical conversion of pre-treated pellets.

It should be noticed that MW-induced improvement of biomass characteristics promotes wider use of low-quality biomass (agriculture and forestry residues) for energy production, increasing sustainability of renewable energy production with faster circulation of biomass feedstocks, thus reducing the dependence of regional energy producers on fuel imports.

Materials and methods

The original pilot-scale boiler with a heat capacity up to 20 kW (TRL 5 readiness level) is designed for domestic heating using MW-activated different origin biomass (wood and wheat straw) pellets (in experiment batch of 1800 g) as fuel (Fig. 1). The pilot-scale unit consists of three separate sections, including a combustion chamber with a Pelltech PV20 pellet burner, and two heat exchanger units.

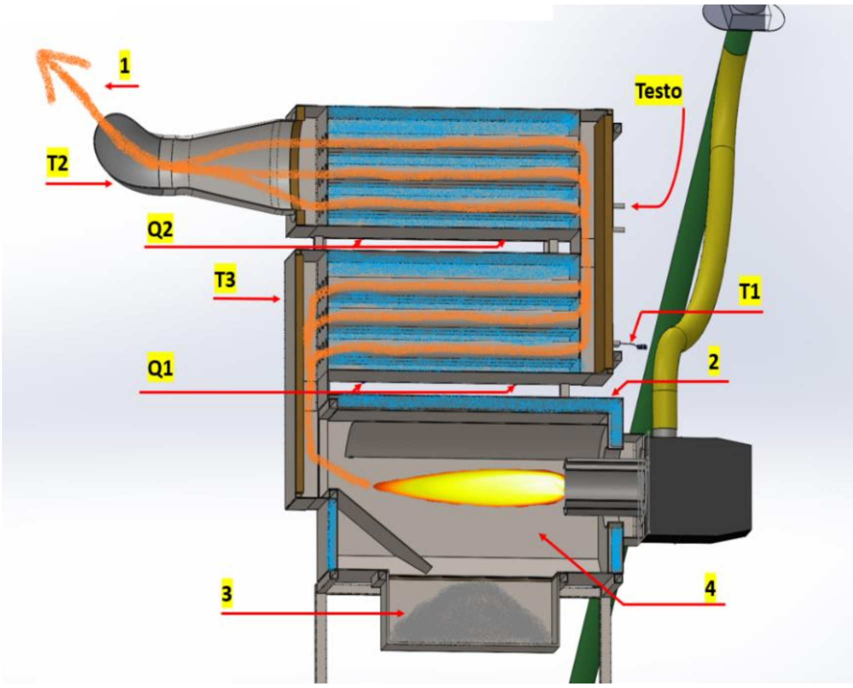

Fig. 1. **Schematic sketch of a boiler (TRL-5) with flow-type biomass supply:** 1 – flue gases; 2 – water jacket of combustion chamber; 3 – ash tank; 4 – combustion chamber with PV20 pellets burner; Q1 and Q2 – separate water supply to heat exchanger sections for calorimetric measurements; T1, T2, T3 – places of gas flow temperature measurements; Testo – place of flue gas composition measurements

The device is equipped with special openings for the local measurements of gas flow temperature (T_1, T_2, T_3) using K-type thermocouples and data online registration with a Pico logger. The gas analyzer Testo 350 XL is used for local measurements of flue gas composition (CO_2%, CO ppm, H_2, ppm, NO_x, ppm), temperature and combustion efficiency. Besides, calorimetric measurements of cooling water flow were provided using the Quick DAQ program with data online registration. A combined kinetic study of temperature, heat production and composition of combustion products was performed to evaluate the effect of MW pretreatment of pellets on the development of their thermochemical conversion. Microwave pretreatment of wood and straw pellets was performed at two microwave pretreatment temperatures (T_{mw} = 473 K and T_{mw} = 548 K) with a pretreatment duration of 20 min using the previously developed MW reactor [5]. Changes in biomass elemental composition during MW pretreatment were evaluated providing measurements of the elemental composition of raw and activated pellets at these different pretreatment temperatures. Using data of these measurements, changes in LHV and HHV of MW activated pellets were evaluated [5]. Differential thermogravimetric (DTG) analysis data were used to evaluate the effect of MW pretreatment on thermochemical conversion of lignocellulosic pellets [7].

Results and discussion

From the results of preliminary experimental research [7; 11], it follows that MW induced thermal decomposition of lignocellulosic pellets is a temperature-sensitive process, which depends on the temperature and duration of MW heating and significantly influences elemental composition of biomass feedstocks. Increasing the temperature of biomass MW heating, carbonization of MW-pretreated wood and wheat straw pellets is observed, increasing the carbon content (Fig. 2 – a) in pellets, which is estimated as average values of repeated three measurements, while decreasing oxygen and hydrogen contents in pretreated pellets [11]. Carbonization of pretreated pellets correlates with an increase of their heating values, increasing LHV and HHV of pre-treated pellets (Fig. 2- b). In addition, MW-induced partial thermal decomposition of hemicellulose, cellulose, and lignin enhances the yield of non-condensable fractions, predominately volatile compounds (CO_2, CO, H_2, CH_4), depending on the biomass temperature. In accordance with the data of DTG analysis [7], increasing the yield of volatiles by increasing the temperature of lignocellulosic pellets correlates with an increase of the weight loss of pellets (Fig. 2 – c) by changing their porosity and reactivity. Furthermore, MW pre-treatment of pellets influences reactivity of pellets by varying the activation energy (E_a, kJ·mol^{-1}) during combustion of volatiles and char conversion stages [7] (Fig. 2 – d). Comparing the effect of MW heating on changes in weight loss of wheat straw and wood pellets (Fig. 2 – c), suggests faster weight loss of wheat straw pellets if compared with wood pellets, it can be related to higher content of thermolabile hemicellulose and amorphous structure of cellulose in wheat straw. The less content of hemicelluloses and more ordered structure of cellulose in wood pellets requires increasing temperature of MW heating up to 595 K to achieve the peak value of the weight loss with the highest yield of volatiles.

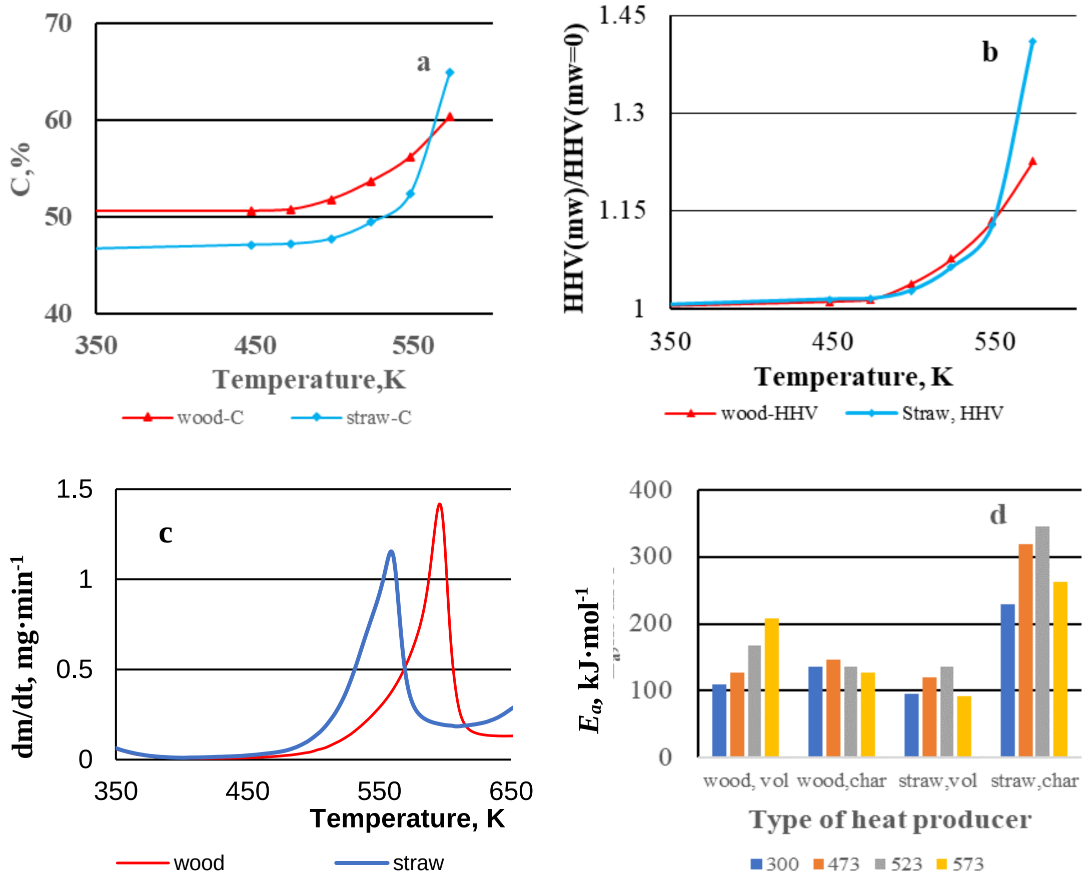

Fig. 2. **Effect of MW-induced changes of biomass pretreatment temperature on carbon content (a), relative changes of the heating value (b), DTG profiles (c), and activation energy for volatilization and char combustion stages of wood and wheat straw pellets (d)**

The MW-induced changes of the main characteristics of biomass pellets influence the development of thermochemical conversion of pre-treated pellets in the pilot-scale boiler, which is confirmed by the kinetics study of heat power production, flue gas temperature and composition of the products.

Considering the main factors that influence kinetics of thermochemical conversion of MW-pretreated pellets, it should be noticed that MW pretreatment enhances the thermal destruction of hemicellulose, cellulose and lignin, which activates the formation and ignition of combustible volatiles during thermochemical conversion of pretreated pellets with faster increase of the flame temperature to the maximum value (Fig. 3 – a, b). Next, the weight loss of pellets during MW pretreatment of pellets (Fig. 2 – c) confirms the MW-enhanced yield of combustible volatiles, promoting a partial loss of combustible volatiles in pretreated pellets with partial loss of produced heat and slight decrease of the temperature. Another factor that causes differences in burning duration of the equal mass of pellets is that the algorithm built in the burner feeding system is based on the pellet volume density, which changes significantly with the pretreatment, especially for 548 K temperature for straw pellets (it becomes significantly lower). A good picture of changes in the volume density is given if we look at one pellet and imagine that with pretreatment it loses certain percent of mass, but the size and structure of the pellet remains the same, only water vapor and part of low calorific volatiles have been released, losing a part of its mass. As a result, the burner feeding system feeds the same volume of pellets, but their mass is accordingly lower. And finally, the MW-induced changes in activation energy of volatilization and char combustion are responsible for a decrease of the weight loss rate of pretreated pellets [5] by increasing duration of the thermochemical conversion of pretreated pellets (Fig. 3, a-d).

Table 1

Effect of MW heating on Q, HHV and combustion efficiency

Pretreatment conditions	Wood			Straw		
	Q, MJ·kg^{-1}	HHV, MJ·kg^{-1}	Average Efficiency, %	Q, MJ·kg^{-1}	HHV, MJ·kg^{-1}	Average Efficiency, %
300 (no MW)	18.04	19.74	94	15.72	18.43	93.66
473	19.66	20.22	94	17.99	18.69	93.68
548	21.42	22.63	94.3	19.56	20.75	93.7

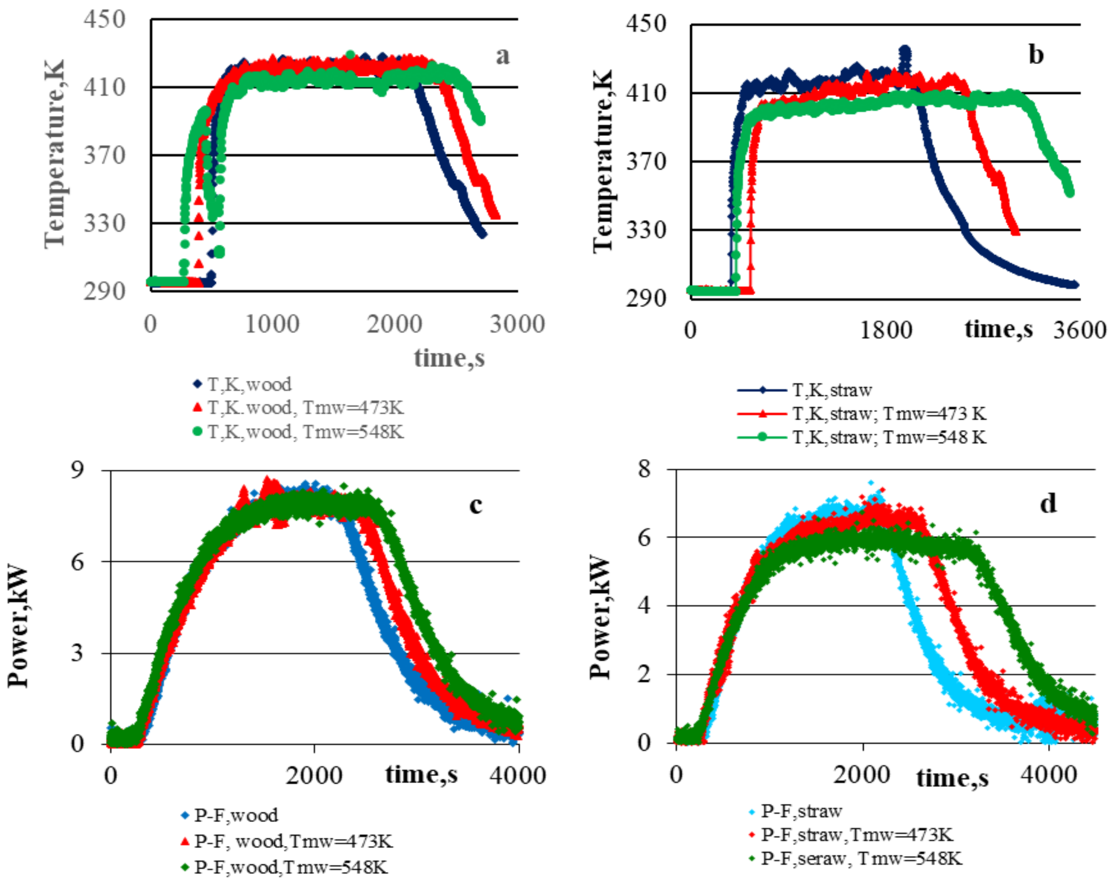

Fig. 3. **Effect of MW-heating temperature on kinetics of the flue gas temperature and heat power of the furnace during burnout of wood and wheat straw pellets**

More lasting thermochemical conversion is observed for pre-treated wheat straw pellets which have higher weight loss rate and yields of combustible volatiles during MW pre-treatment and higher activation energy of pre-treated pellets both for volatilization and char conversion stages (Fig 2 – c, d).

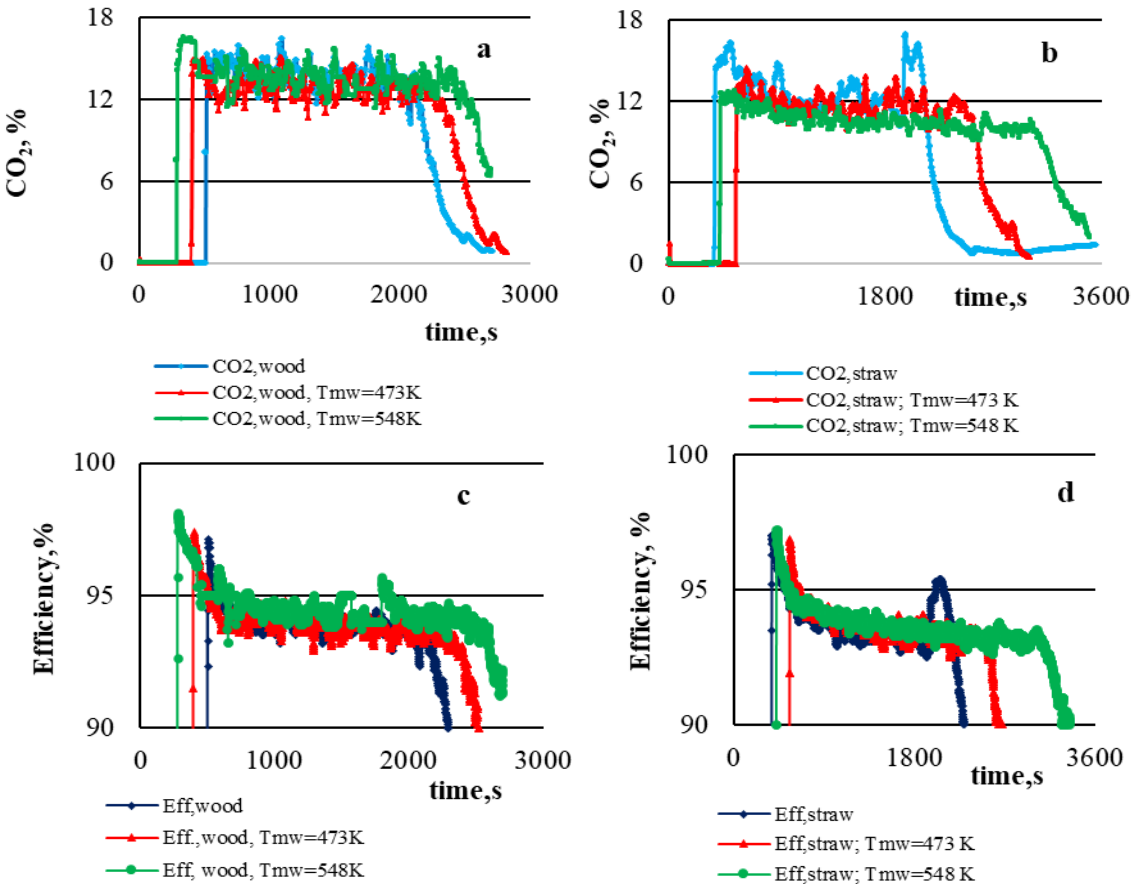

Fig. 4. **Effect of MW-heating temperature on kinetics of formation of CO_2 emissions and the combustion efficiency during burnout of wood and wheat straw pellets**

However, estimation of the produced heat during burnout of pretreated pellets confirms that MW pretreatment promotes an increase of produced heat per mass of pretreated pellets (Q, MJ·kg^{-1}) (Table 1), which can be related to carbonization of pretreated pellets with correlating increase of the heating value of pretreated pellets (Fig. 2-a, b). Such correlation suggests that MW pre-treatment of biomass pellets can be used to improve the heat energy production.

Faster ignition of volatiles with lasting burnout of volatiles during thermochemical conversion of pretreated pellets is also confirmed by the kinetic study of formation of the products (CO_2) (Fig. 4 – a, b). Increasing the temperature of MW pretreatment causes faster rise of the volume fraction of carbon-neutral CO_2 emissions and combustion efficiency (Fig. 4 – c, d) up to the peak value. With pretreatment of wood pellets at temperature 573 K the mass fraction of CO emissions decreases in average from 120 ppm to about 113 ppm, while for straw- from and to 558 ppm to 192 ppm.

Conclusions

1. The results of the experimental research and analysis suggest that the main combustion characteristics of pre-treated pellets and product composition are highly influenced by lot of the factors, such as MW-induced thermal destruction of hemicelluloses, cellulose and lignin, by varying the chemical and elemental composition of pre-treated pellets, their porosity and reactivity, changes in the volume density, weight loss of pellets and the yield of combustible volatiles, which depend on the temperature of MW pre-treatment of pellets.
2. MW pretreatment of biomass activates the formation and ignition of volatile compounds during burnout of pretreated pellets and causes faster formation of the reaction zone with correlating increase of combustion efficiency during the primary stage of volatile burnout. Pretreatment at 548

K increases the total amount of produced heat by 18.7% for wood pellets and by 24,4% for wheat straw pellets.
3. Increasing the temperature of MW pretreatment the volume density of the pellets changes significantly and the changes allowed in the program of Pelltech PV 20 burner do not allow to change it sufficiently. For better comparison the algorithm of the burner feeding system has to be modified.
4. The analysis of the effect of MW pretreatment on wood and wheat straw thermochemical conversion suggests that MW-induced changes of the main characteristics of wood with straw pellets can be used to provide control of their thermochemical conversion with more efficient and sustainable heat energy production when agriculture or forestry residues are used as fuel with faster circulation of CO_2.

Acknowledgements

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

Author contributions

Conceptualization, M.Z.; methodology, M.Z. and R.V.; validation, R.V.; formal analysis, investigation, M.Z. and 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.; project administration, M. Z.; funding acquisition, G.R. All authors have read and agreed to the published version of the manuscript.

References

[1] Climate & Energy Framework. [online] [11.02.2024] Available at: https://ec.europa.eu/clima/policies/strategies/2030_en
[2] Mitani T. Recent Progress on Microwave Processing of Biomass for Bioenergy Production, Journal of the Japan Petroleum Institute, 2018, 61, [online] [11.02.2024] Available at: https://www.jstage.jst.go.jp/article/jpi/61/2/61_113/_article/-char/ja/ doi.org/10.162//jpi.61-113
[3] AMT advanced microwave technologies. [online] [11.02.2024] Available at: https://www.advancedmicrowavetechnologies.com/
[4] SAIREM microwave and radio frequency. [online] [11.02.2024] Available at: https://www.sairem.com/
[5] Andersone A., Arshanitsa A., Akishin Y., Semenischev A., Telysheva G., Microwave assisted torrefaction of plant biomass of different origin with focus on the solid products valorizations for energy and beyond, Chemical Engineering Transactions, 2021, vol.86, pp. 109-116. [online] [11.02.2024] Available at: http://www.cetjournal.it/cet/21/86/019.pdf
[6] Ethaib S, Omar R, Kamal SMM, Biak DRA (2015) Microwave-assisted pretreatment of lignocellulosic biomass: a review [J Eng Sci Technol] Vol.10 P.97, [online] [11.02.2024] Available at: https://www.researchgate.net/publication/281789098_Microwave-assisted_pretreatment_of_lignocellulosic_biomass_A_review
[7] Arshanitsa A. Andersone A., Telysheva G., Non-isothermal thermal analysis of different originated lignocellulosic biomass, non-treated and torrefied by microwave treatment, Proceedings of 20th International Scientific Conference “Engineering for Rural Development”, 2021, pp. 424-430.
[8] Huang YF, Chiueh PT, Lo SL. Review on microwave pyrolysis of lignocellulosic biomass. Sustainable Environment Research 2016, 26, pp. 103-109.
[9] Yang H., Yan R., Chen H., Lee D.H., Zheng Ch., Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel, 2007, 86 (12-13), pp. 1781-1788, DOI: 10.1016/j.fuel.2006.12.01310.1016/
[10] Lanigan B. Microwave Processing of Lignocellulosic Biomass for Production of Fuels. Ph.D. Thesis, University of York, York, UK, 2010. [online] [11.02.2024] Available at: https://etheses.whiterose.ac.uk/1237/1/B_Lanigan.pdf
[11] Goldšteins L., Valdmanis R., Zaķe M., Arshanitsa A. and Andersone A., Thermal Decomposition and Combustion of Microwave Pre-treated Biomass Pellets, 2021, 9, 492. [online] [11.02.2024] Available at: https://www.mdpi.com/2227-9717/9/3/492/pdf